



HAL
open science

ropriétés Diélectriques des *Matériaux Biosourcés*

Morgan Lecoublet

► **To cite this version:**

Morgan Lecoublet. *ropriétés Diélectriques des Matériaux Biosourcés*. Polymères. Normandie Université; Université du Québec à Abitibi-Témiscamingue, 2024. Français. NNT : 2024NORMR027 . tel-04698770

HAL Id: tel-04698770

<https://theses.hal.science/tel-04698770v1>

Submitted on 16 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



THÈSE

Pour obtenir le diplôme de doctorat

Spécialité **CHIMIE**

Préparée au sein de l'**Université de Rouen Normandie**

En cotutelle internationale avec l'**Université du Québec (Canada), CANADA**

Propriétés Diélectriques des Matériaux Biosourcés

Présentée et soutenue par
MORGAN LECOUBLET

Thèse soutenue le 04/06/2024
devant le jury composé de :

MME NATHALIE LEBLANC	Maître de Conférences HDR - Université de Rouen Normandie	Directeur de thèse
M. AHMED KOUBAA	Professeur des Universités - Université du Québec en Abitibi	Co-directeur de thèse
MME CARMEN MIHAELA NECULITA	Professeur des Universités - Université du Québec (Canada)	Président du jury
M. MOHAMED RAGOUBI	- UniLaSalle	Co-encadrant
MME FLAVIA BRAGHIROLI	Professeur des Universités - Université du Québec (Canada)	Membre du jury
M. SEBASTIEN ALIX	Professeur des Universités - UNIVERSITE REIMS CHAMPAGNE ARDENNE	Rapporteur du jury
M. SOFIANE GUESSASMA	Directeur de Recherche - Centre Régional de l'Inrae Angers-Nantes Pays de la Loire	Rapporteur du jury

Thèse dirigée par **NATHALIE LEBLANC** (TRANSFORMATIONS ET AGRO-RESSOURCES) et **AHMED KOUBAA** (Université du Québec en Abitibi)

Remerciements

Ce travail de thèse est le fruit de la collaboration entre l'Unité de Recherche Transformations et Agro-Ressources d'UniLaSalle et l'Université du Québec en Abitibi Témiscamingue. Je désire remercier d'une façon particulière mes directeurs de recherche Nathalie Leblanc et Ahmed Koubaa pour leur patience, leur encadrement et leurs conseils scientifiques pertinents. De plus, je voudrais remercier aussi mon tuteur Mohamed Ragoubi pour sa grande disponibilité et de sa motivation tout le long du projet.

Je voudrais également remercier l'Institut de Thermique, Mécanique, Matériaux (ITheMM, Charleville-Mézières, FRA) pour leur accueil chaleureux et pour m'avoir permis d'utiliser leurs machines de mise en œuvre, qui ont été essentielles pour mon projet de thèse.

Je suis aussi reconnaissant envers Jean-Baptiste Besnard, Marianne Rosa de l'équipe T&A, ainsi qu'Asma Khouaja et Zeineb Siala de l'UQAT, pour leurs connaissances et leur aide pour l'utilisation des machines des différents laboratoires. Je tiens également à remercier l'équipe de doctorants et d'étudiants m'ayant aidée et soutenue tout au long du projet : Léo, Maya, Désiré, Paul, Anouk, Élodie, Asma, Hamza, Thomas, Ana, Yuchen, Bilel, Khouloud, sans compter ceux que j'ai oubliés.

Je tiens également à remercier ma famille pour son soutien et ses encouragements permanents. Je voudrais adresser mes remerciements envers de nombreuses émissions de vulgarisation scientifique, comme *C'est pas Sorcier*, *E-Penser*, *La Tronche en Biais*, sans lesquelles je ne pense pas que j'aurais eu cette passion pour les sciences.

Une pensée spéciale pour deux personnes qui ont compté énormément pour moi, mes grands-pères. Ils ont éclairé avec bienveillance mon enfance, tels des phares, au milieu des tempêtes. L'un était Breton et l'autre Normand et si j'ai réussi à parvenir jusqu'ici, c'est aussi un peu grâce à eux. Leur lumière continuera à éclairer mon chemin à travers les écueils. Merci à eux.

« *Prends garde au temps, le sablier est insolent* »

Avant-propos

Dans le cadre des travaux de recherche accomplis durant cette thèse, l'ensemble des connaissances acquises a été valorisé ou est en cours de valorisation sous forme de publications dans des revues scientifiques avec comité de lecture, ainsi qu'au travers de présentations dans des conférences nationales et internationales.

Cette thèse se présente sous la forme de six articles scientifiques et d'une revue de la littérature. La revue de littérature est présentée en fin de **Chapitre 2**. Un article [A1] est présenté en **Chapitre 4**, trois articles [A2, A3, A4] sont présentés en **Chapitre 5** et deux articles [A5, A6] sont présentés en **Chapitre 6**. Le reste de la thèse est rédigé en français. Pour finir, un chapitre de livre est en cours de rédaction avec les données non utilisées du **Chapitre 6**.

Je suis le premier auteur des articles. Mes deux directeurs de thèse, Mme Nathalie Leblanc et Mr Ahmed Koubaa, ainsi que mon encadrant de thèse Mr Mohamed Ragoubi sont les coauteurs des articles. De plus, Mr Léonel Kenfack et Mr Raphaël Lack, ont aussi pu contribuer à la préparation de deux articles [A4, A5] dans le cadre de leur stage. L'ensemble de ces réalisations est détaillé ci-dessous.

Articles publiés et/ou acceptés et/ou soumis dans une revue avec comité de lecture

- [A1] **Lecoublet, M.**, Ragoubi, M., Leblanc, N. & Koubaa, A. Dielectric and rheological performances of cellulose acetate, polylactic acid and polyhydroxybutyrate-co-valerate biobased blends. *Polymer* 126358 (2023) DOI 10.1016/j.polymer.2023.126358.
- [A2] **Lecoublet, M.**, Ragoubi, M., Leblanc, N. & Koubaa, A. Dielectric and viscoelastic properties of 3D-printed biobased materials. *Indus. Crops and Prod.* 212 118354 (2024) DOI : 10.1016/j.indcrop.2024.118354.

- [A3] **Lecoublet, M.**, Ragoubi, M., Kenfack, L.B., Leblanc, N. & Koubaa, A. How Do 3D Printing Parameters Affect the Dielectric and Mechanical Performance of Polylactic Acid–Cellulose Acetate Polymer Blends? *J. Comp. Sci.* 7(12):492 (2023). DOI 10.3390/jcs7120492.
- [A4] **Lecoublet, M.**, Ragoubi, M., Leblanc, N. & Koubaa, A. Investigation of Thermomechanical and Dielectric Properties of PLA-CA 3D-Printed Biobased Materials. *J. Comp. Sci.* 8(6):197 (2024). DOI 10.3390/jcs8060197.

Articles en préparation

- [R1] **Lecoublet, M.**, Ragoubi, M., Lack, R., Leblanc, N. & Koubaa, A. Dielectric properties of biobased polymers – A review.
- [A5] **Lecoublet, M.**, Lack, R., Ragoubi, M., Leblanc, N. & Koubaa, A. Sustainable 3D printed cellulose based biocomposites and bionanocomposites: Evaluation of dielectric and viscoelastic performances.
- [A6] **Lecoublet, M.**, Ragoubi, M., Leblanc, N. & Koubaa, A. Optimizing the dielectric and mechanical performance of 3D-printed cellulose-based biocomposites and bionanocomposites through factorial design.

Présentations de conférences et séminaires

- 10/21 (Webinar) : Lecoublet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Dielectric performances of biobased materials. Présenté au 6th World Congress on Bio-Polymers and Polymer Chemistry.
- 05/22 (En ligne) : Lecoublet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Performances diélectriques des matériaux biosourcés. Présenté à l'ACFAS 2022, 210 - L'industrie de la transformation du bois à l'heure de la transition écologique et énergétique.

- 06/22 (La Sarre, QC, CAN) : Lecouplet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Applications des biopolymères dans le domaine diélectrique. Présenté à la 3^e édition du colloque annuel de la Chaire de recherche du Canada sur la valorisation, la caractérisation et la transformation du bois.
- 04/23 (Marrakesh, MAR) : Lecouplet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Dielectric performances of new 3D printed biobased materials. Présenté à Euromagh 2023 - Biobased materials for a sustainable future.
- 10/23 (Rome, ITA) : Lecouplet, M., Donfak, L., Ragoubi, M., Leblanc, N. & Koubaa, A. Dielectric performances of new 3D printed biobased materials. Présenté à l'International Conference on Polymer Science and Composite Materials.
- 11/23 (Rome, ITA) : Lecouplet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Dielectric Performance of new biobased materials produced by 3D printing. Présenté à l'European Congress on Biopolymers and Bioplastics.
- 12/23 (Hammamet, TUN) : Lecouplet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Dielectric analysis of 3D-printed cellulosic biocomposites for electrical insulation applications. Présenté au 10th International Congress on Design and Modelling of Mechanical Systems.
- 04/24 (Vaughan, ON, CAN) : Lecouplet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Cellulose-based 3D-printed materials for electrical insulation applications. Présenté à la CREATE Annual Conference 2024.
- 05/24 (La Sarre, QC, CAN) : Lecouplet, M., Ragoubi, M., Leblanc, N. & Koubaa, A. Applications des biopolymères dans le domaine diélectrique. Présenté à la 4^e édition du colloque annuel de la Chaire de recherche du Canada sur la valorisation, la caractérisation et la transformation du bois.

Table des Matières

Remerciements	i
Avant-propos	ii
Table des Matières	v
Table des Figures	x
Table des Tables	xv
Table des Annexes	xvii
Glossaire des sigles et des unités	xviii
Chapitre 1) Introduction générale	1
1.1. Mise en contexte	2
1.2. Problématique générale	3
1.3. Originalité du projet	3
1.4. Objectifs du projet	4
1.4.1. Objectif général	4
1.4.2. Objectifs spécifiques et hypothèses de recherche associées	4
1.5. Contenu de la thèse	5
1.6. Organisation de la thèse	7
Chapitre 2) Synthèse bibliographique	9
2.1. Notions diélectriques	10
2.1.1. Partie théorique	10
2.1.2. Grandeurs physiques dans le domaine diélectrique	13
2.1.2.a. <i>Permittivité complexe : constante diélectrique ϵ' et perte diélectrique ϵ''</i>	13
2.1.2.b. <i>Conductivité électrique σ_{AC} et σ_{DC}</i>	15
2.1.2.c. <i>Rigidité diélectrique E_{BR}</i>	16
2.2. Généralités sur les polymères biosourcés et/ou biodégradables	17
2.2.1.a. <i>Acide polylactique (PLA)</i>	17
2.2.1.b. <i>Polyhydroxyalcanoates (PHAs)</i>	19
2.2.1.c. <i>Poly(succinate de butyle) (PBS)</i>	20
2.2.1.d. <i>Polycaprolactone (PCL)</i>	21
2.2.1.e. <i>Acétate de cellulose (CA)</i>	22
2.2.1.f. <i>Autres polymères biosourcés</i>	23
2.2.2. Performances diélectriques des polymères biosourcés et/ou biodégradables ..	25

2.2.2.a.	<i>Constante diélectrique</i>	25
2.2.2.b.	<i>Perte diélectrique</i>	27
2.2.2.c.	<i>Conductivité électrique</i>	28
2.2.2.d.	<i>Rigidité diélectrique</i>	31
2.3.	Dielectric properties of biobased polymers – A review	33
2.3.1.	Abstract	33
2.3.2.	Résumé en français	33
2.3.3.	Introduction	34
2.3.4.	Biobased polymer improvements for dielectric applications.....	36
2.3.4.a.	<i>Influence of polymer blending strategy</i>	36
2.3.4.b.	<i>Influence of biobased composite strategy</i>	40
2.3.4.c.	<i>Influence of processing - Case of 3D printing process</i>	45
2.3.4.d.	<i>Printing temperature and speed</i>	51
2.3.5.	Biobased materials in the dielectric field application	51
2.3.5.a.	<i>Biobased polymers in electrical insulation and conduction</i>	51
2.3.5.b.	<i>Electronic device</i>	57
2.3.5.c.	<i>Electromagnetic interference shielding materials</i>	63
2.3.5.d.	<i>Other applications</i>	65
2.3.6.	Conclusion and perspectives.....	66
2.4.	Conclusion de la synthèse bibliographique	68
Chapitre 3)	Approches méthodologique et expérimentale	69
3.1.	Matières premières sélectionnées	70
3.2.	Détermination des plans d'expériences	71
3.3.	Préparation des fibres cellulosiques et du masterbatch	72
3.3.1.	Préparation des fibres cellulosiques.....	72
3.3.2.	Préparation du masterbatch de nanocristaux de cellulose (NCC).....	74
3.4.	Préparation des mélanges et mises en œuvre des matériaux	75
3.4.1.	Préparation des matériaux.....	75
3.4.2.	Procédé d'extrusion	77
3.4.3.	Procédé de thermocompression	78
3.4.4.	Procédé d'impression 3D	78
3.4.4.a.	<i>Obtention des filaments pour impression 3D</i>	79
3.4.4.b.	<i>Impression 3D</i>	79
3.5.	Caractérisations des matériaux	82
3.5.1.	Caractérisations physicochimiques	83
3.5.1.a.	<i>Analyse infrarouge à transformée de Fourier (FTIR)</i>	83
3.5.1.b.	<i>Calorimétrie différentielle à balayage (DSC)</i>	85
3.5.1.c.	<i>Analyse thermogravimétrique (ATG)</i>	87
3.5.1.d.	<i>Microscopie électronique à balayage (MEB)</i>	88
3.5.2.	Caractérisations dynamiques	88
3.5.2.a.	<i>Spectroscopie diélectrique à bande large (BDS)</i>	88
3.5.2.b.	<i>Analyse mécanique dynamique (DMA)</i>	90
3.5.2.c.	<i>Analyses rhéologiques</i>	91
3.5.3.	Caractérisations de mécanique statique	92

3.5.3.a.	<i>Tests de traction</i>	93
3.5.3.b.	<i>Tests de flexion</i>	94
3.5.3.c.	<i>Tests d'impact</i>	95
Chapitre 4)	Conception et caractérisation de mélanges polymériques à base de PLA, PHBV et de CA	97
4.1.	Introduction	98
4.2.	Dielectric and rheological performances of cellulose acetate, polylactic acid and polyhydroxybutyrate-co-valerate biobased blends *	100
4.2.1.	Abstract	100
4.2.2.	Résumé en français	100
4.2.3.	Introduction	101
4.2.4.	Materials & Methods	103
4.2.4.a.	<i>Raw materials and sample preparation</i>	103
4.2.4.b.	<i>Methods used</i>	105
4.2.5.	Results	106
4.2.5.a.	<i>Surface chemistry and morphology properties</i>	106
4.2.5.b.	<i>Dielectric properties</i>	110
4.2.5.c.	<i>Rheological properties</i>	113
4.2.6.	Conclusions	115
4.3.	Discussions et bilan du Chapitre 4	117
Chapitre 5)	Conception et caractérisation de mélanges polymériques PLA:CA pour impression 3D	119
5.1.	Introduction	120
5.2.	Dielectric and viscoelastic properties of 3D-printed biobased materials * ...	122
5.2.1.	Abstract	122
5.2.2.	Résumé en français	123
5.2.3.	Introduction	123
5.2.4.	Materials & Methods	125
5.2.4.a.	<i>Raw materials and sample preparation</i>	125
5.2.4.b.	<i>Methods used</i>	127
5.2.5.	Results and discussion	130
5.2.5.a.	<i>Microstructural properties</i>	130
5.2.5.b.	<i>Dielectric properties</i>	133
5.2.5.c.	<i>Relationship between porosity and permittivity</i>	137
5.2.5.d.	<i>Dynamic mechanical properties</i>	139
5.2.5.e.	<i>Glass transition determination by BDS and DMA analysis</i>	141
5.2.6.	Conclusion	143
5.3.	How can 3D printing parameters affect the dielectric and mechanical performance of PLA:CA polymer blends ? *	145
5.3.1.	Abstract	145
5.3.2.	Résumé en français	145
5.3.3.	Introduction	146
5.3.4.	Materials and methods	149
5.3.4.a.	<i>Raw materials and blend formulation</i>	149

5.3.4.b.	<i>Methods used</i>	150
5.3.4.c.	<i>Printing process optimization</i>	151
5.3.4.d.	<i>Architectural design</i>	151
5.3.5.	Results and discussion.....	152
5.3.5.a.	<i>Optimization of printing parameters</i>	152
5.3.5.b.	<i>Dielectric properties</i>	154
5.3.5.c.	<i>Electrical conductivity properties</i>	156
5.3.5.d.	<i>Dynamic mechanical properties</i>	158
5.3.6.	Conclusion.....	161
5.4.	What are the limitations of 3D-printed biobased materials for dielectric applications ?.....	163
5.4.1.	Abstract.....	163
5.4.2.	Résumé en français.....	163
5.4.3.	Introduction.....	164
5.4.4.	Material and methods.....	165
5.4.5.	Results and discussions.....	167
5.4.6.	Conclusion.....	172
5.5.	Discussions et bilan du Chapitre 5.....	173
Chapitre 6) Conception et caractérisation de biocomposites et bionanocomposites à base de cellulose pour impression 3D.....		175
6.1.	Introduction.....	176
6.2.	Sustainable 3D printed cellulose based biocomposites and bionanocomposites: Evaluation of dielectric and viscoelastic performances.....	178
6.2.1.	Abstract.....	178
6.2.2.	Résumé en français.....	179
6.2.3.	Introduction.....	179
6.2.4.	Materials & Methods.....	181
6.2.4.a.	<i>Raw materials</i>	181
6.2.4.b.	<i>Filler silanization and masterbatch processing</i>	182
6.2.4.c.	<i>Extrusion processing</i>	183
6.2.4.d.	<i>3D printing and hot-pressing processing</i>	183
6.2.4.e.	<i>Methods used</i>	185
6.2.5.	Results and discussion.....	187
6.2.5.a.	<i>Microstructural properties</i>	187
6.2.5.b.	<i>Thermal properties</i>	189
6.2.5.c.	<i>Dielectric properties</i>	193
6.2.5.d.	<i>Mechanical properties</i>	197
6.2.6.	Conclusion.....	199
6.3.	Optimizing the dielectric and mechanical performance of 3D-printed cellulose-based biocomposites and bionanocomposites through factorial design.....	201
6.3.1.	Abstract.....	201
6.3.2.	Résumé en français.....	201
6.3.3.	Introduction.....	202
6.3.4.	Materials and methods.....	204
6.3.4.a.	<i>Raw materials</i>	204
6.3.4.b.	<i>Filler silanization and masterbatch processing</i>	204

6.3.4.c.	<i>Extrusion processing</i>	205
6.3.4.d.	<i>3D-printing processing</i>	205
6.3.4.e.	<i>Application of factorial design</i>	206
6.3.4.f.	<i>Methods used</i>	208
6.3.5.	Results and discussions	209
6.3.5.a.	<i>Influence of infill ratio and printing temperature on 3D-printed PLA</i>	209
6.3.5.b.	<i>Dielectric properties</i>	212
6.3.5.c.	<i>Mechanical properties</i>	214
6.3.5.d.	<i>Discussions</i>	216
6.3.6.	Conclusion.....	217
6.4.	Discussions et bilan du Chapitre 6	219
	Conclusion Générale	223
	Annexes	228
	Références	253
	Résumé en français	285
	Abstract	287

Table des Figures

Figure 1.1 : Organisation de la thèse.....	7
Figure 2.1 : Variation théorique de la constante diélectrique (ϵ') et perte diélectrique (ϵ'') d'un matériau polaire, en fonction de la fréquence électrique appliquée (Psarras, 2018).....	10
Figure 2.2 : Classification des groupes chimiques par leur polarité	11
Figure 2.3 : a) Représentation schématique du spectromètre diélectrique et de la polarisation de l'échantillon soumis à un champ électrique, b) projection de la constante diélectrique et du facteur de perte dans le plan complexe (Adapté de (Hegde, 2017; Schönhals, 2010)).....	14
Figure 2.4 : Conductivité électrique de polymères et de divers matériaux (adapté de Solazzo et al. (2019))	16
Figure 2.5 : Synthèse par ouverture de cycles du PLA par différents isomères de lactides.....	18
Figure 2.6 : Synthèse de polyhydroxyalcanoate (PHA) et formulations chimiques de différents PHAs	19
Figure 2.7 : Structure chimique du PHBV	20
Figure 2.8 : Structures chimique du PBS et du PBSA	20
Figure 2.9 : Synthèse du PCL par ouverture de cycle du ϵ -caprolactone.....	22
Figure 2.10 : Synthèse de différents acétates de cellulose	23
Figure 2.11 : Chitine, chitosane et amidon.....	24
Figure 2.12 : Synthèse bibliographique de la constante diélectrique ϵ' de polymères biosourcés et/ou biodégradables, et de polymères conventionnels, mesurées à 100 Hz	26
Figure 2.13 : Synthèse bibliographique de la log (perte diélectrique ϵ'') de polymères biosourcés et/ou biodégradables, et de polymères conventionnels, mesurées à 100 Hz	28
Figure 2.14 : Synthèse bibliographique de la log (conductivité électrique) de polymères biosourcés et/ou biodégradables, et de polymères conventionnels, a) en mode AC σ_{AC} , b) en mode DC σ_{DC} . Les valeurs en mode AC sont mesurées à 100 Hz.....	30
Figure 2.15 : Synthèse bibliographique de la rigidité diélectrique E_{BR} de polymères biosourcés et/ou biodégradables, et de polymères conventionnels. Les valeurs en mode AC sont mesurées à 100 Hz	31
Figure 2.16 : a) Global production capacity of bioplastics and forecast for 2028, b) Distribution of bioplastics production in 2022 by applications fields (European Bioplastics, 2023a, 2023b).....	35
Figure 2.17 : Morphologies of immiscible binary blends in function of their ratio.....	36
Figure 2.18 : Mechanical, biological and electrical conductivity properties of PCL:PAI blends (Wibowo et al., 2020)	40

Figure 2.19 : Dielectric constant ϵ' of neat PLA and PLA:sisal biobased composite measured @ 20 °C and 100 Hz (Badia et al., 2017).....	41
Figure 2.20 : Log (electrical conductivity σ_{AC}) of plasticized PLA filled with nanosized biochar (Jasim and Ali, 2019).....	45
Figure 2.21 : a) Representation of an FFF-type 3D printer, b) Ishikawa diagram of critical process parameter of FFF 3d printing method (Horvath, 2014; Kundu and Mandal, 2022; Su and Al'Aref, 2018; Wohlers and Gornet, 2015).....	46
Figure 2.22 : Dielectric constant ϵ' versus the infill pattern of 3D-printed PLA samples (Kuzmanić et al., 2023).....	48
Figure 2.23 : Dielectric constant ϵ' VS infill ratio of 3D-printed PLA (Zhang et al., 2016).....	50
Figure 2.24 : Dielectric properties of 3D-printed PLA and ABS at room temperature. All tests minus electrical conductivity were performed at 50 Hz (Li et al., 2018). 54	54
Figure 2.25 : Dielectric constant ϵ' at 100 Hz of neat PLA and PLA-based nanocomposites (Spinelli et al., 2020).....	56
Figure 2.26 : Illustration of a theoretical organic FET (OFET).....	57
Figure 2.27 : Fatigue test of PLA-based sensor (Ma et al., 2022)	60
Figure 2.28 : Schematic diagram of a) Lithium-ion battery, b) supercapacitor.....	61
Figure 2.29 : Influence of ammonium iodine on DC conductivity σ_{DC} of CS:Dextran blends (Aziz et al., 2020b)	66
Figure 3.1 : Plan à trois facteurs et trois niveaux (3^3) en plan incomplet L9, a) plan de Taguchi, b) plan factoriel incomplet.....	72
Figure 3.2 : Silanisation des charges cellulosiques (dérivée de Gad et al. (2018))	74
Figure 3.3 : Préparation du masterbatch : a) mini-extrudeuse Haake Minilab II, b) système interne de double vis, c) extrusion du masterbatch, d) masterbatch refroidi	75
Figure 3.4 : Projection des mélanges de PLA, PHBV et CA confectionnés. La table inséré dans la figure indique les composants en proportion	76
Figure 3.5 : a) Imprimante 3D SIGMAX R19, b) éprouvettes diélectrique de PLA et PLA:CA à 40 % de CA (CA-40), c) Imprimante 3D CR-10 Max, d) éprouvettes diélectriques de PLA et biocomposites PLA:MCC à 5, 10 et 15 % de MCC (M5, M10, M15).....	80
Figure 3.6 : Programmes DSC utilisé pour : a) les mélanges PLA, PHBV et CA, b) les mélanges PLA:CA, c) les biocomposites à base de cellulose.....	86
Figure 3.7 : a) Keysight E4980A couplé au rhéomètre MCR 302, b) Keysight E4991A avec le cryostat.....	89
Figure 3.8 : Design des éprouvettes de mécaniques statiques	93
Figure 4.1 : Chemical structure of PLA, PHBV and CA.....	103
Figure 4.2 : Adapted mixture design used	104
Figure 4.3 : FTIR analysis of PLA, PHBV, and CA.....	106
Figure 4.4 : Zoomed FTIR a) PLA:CA blends at 3500 cm^{-1} , b) PLA:CA blends at 1750 cm^{-1} , c) PHBV:CA blends at 1750 cm^{-1} , d) PHBV:CA blends at 1750 cm^{-1}	107
Figure 4.5 : SEM pictures of neat biobased polymers and binary blends.....	108

Figure 4.6 : Dielectric constant ϵ' of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends @ 20 °C	110
Figure 4.7 : Dielectric constant ϵ' of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends versus temperature @ 100 Hz.....	111
Figure 4.8 : Log (dielectric loss ϵ'') of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends @ 20 °C	113
Figure 4.9 : Log (loss modulus G'') of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends versus frequency	114
Figure 4.10 : Log (complex viscosity η^* of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends versus frequency	114
Figure 4.11 : Graphique radar des performances diélectriques et mécaniques, la stabilité de ces dernières en température, la tenue à la température à 180 °C et de l'originalité scientifique du projet des mélanges caractérisés en Chapitre 4	118
Figure 5.1 : 3D-printed PLA and CA-40 samples. Disk-shaped specimens are used for BDS analysis and rectangular shaped specimens are used for DMA analysis.....	127
Figure 5.2 : SEM analysis of a) PLA, b) CA-10, c) CA-20, d) CA-30, e) CA-40 at x200	130
Figure 5.3 : a) Log (complex viscosity η^*) versus frequency of hot-pressed samples of PLA and CA:PLA blends, b) Zoom on high shear rate and their associated power law fit, c) log(complex viscosity η^*) versus CA content measured at 631 rad·s ⁻¹ and the associated first-order fit, d) Log (complex viscosity η^*) versus log (complex modulus G^*).....	131
Figure 5.4 : Dielectric constant ϵ' versus frequency of a) hot-pressed samples, b) 3D-printed samples. 3D-printed PLA and CA-20 curves are overlapping	133
Figure 5.5 : Log (dielectric loss ϵ'') versus frequency of a) hot-pressed samples, b) 3D-printed samples.....	134
Figure 5.6 : a) Dielectric constant VS CA content at 100 Hz. Error bars represent the standard deviation. b) log (DC conductivity) versus temperature and c) activation energy of electrical conductivity VS CA content. First-order fits are shown in all figures.....	136
Figure 5.7 : a) SEM analysis of a cross-section of 3D-printed PLA, b) Comparison of porosities of 3D-printed specimens with a 100 % infill density, determined by density and permittivity derived methods. Error bars represent the standard deviation.....	138
Figure 5.8 : Storage modulus E' versus temperature of a) hot-pressed samples, b) 3D-printed samples.....	139
Figure 5.9 : Loss modulus E'' versus temperature of a) hot-pressed samples, b) 3D-printed samples.....	139
Figure 5.10 : a) Cole-Cole plot E'' VS E'	141
Figure 5.11 : Glass transition temperature of PLA measured by DMA and BDS and their associate first-order fits.....	142
Figure 5.12 : PLA:CA 3D printed samples: rectangular samples with dimensions of 60*10*4 mm for dynamic mechanical analysis and circular samples of 25 mm diameter disks with a thickness of 4 mm for dielectric analysis	149
Figure 5.13 : Log (storage modulus E') versus temperature of PLA:CA 3D-printed blends	152

Figure 5.14 : SEM picture of PLA:CA blends at $W_{CA} = 40\%$, $T = 215\text{ °C}$ at a) $10\text{ mm}\cdot\text{s}^{-1}$, b) $20\text{ mm}\cdot\text{s}^{-1}$, c) $30\text{ mm}\cdot\text{s}^{-1}$	153
Figure 5.15 : Thermal stability of PLA:CA blends.....	154
Figure 5.16 : Dielectric constant ϵ' versus frequency. Condition 1 corresponds to a $W_{CA} = 20\%$, infill ratio = 40% , and layer thickness = $0,1\text{ mm}$. Condition 9, corresponds to a $W_{CA} = 40\%$, infill ratio = 80% , and layer thickness = $0,2\text{ mm}$	155
Figure 5.17 : Means dielectric constant ϵ' at room temperature and 100 Hz	155
Figure 5.18 : Log (electrical conductivity σ_{AC}) at room temperature versus frequency of condition 1 and 9.....	157
Figure 5.19 : Means for log (electrical conductivity σ_{AC}) at room temperature and 1 kHz	158
Figure 5.20 : Storage and loss modulus versus temperature of condition 3 and 8	159
Figure 5.21 : Means for storage modulus E' at 30 °C and 1 Hz	159
Figure 5.22 : Means for glass transition temperature measured by DMA analysis.....	161
Figure 5.23 : Fused filament fabrication (FFF) 3D printing process and produced samples.....	166
Figure 5.24 : Dielectric constant ϵ' and electrical conductivity σ_{AC} of PLA and CA-40 versus temperature, measured at 100 Hz	168
Figure 5.25 : Log (storage modulus E') and loss tangent $\tan \delta$ of PLA and CA-40 specimens versus temperature	170
Figure 5.26 : Dielectric constant, electrical conductivity, and storage modulus as a function of infill ratio measured on 4 mm – thick samples. Dielectric constant and electrical conductivity are measured at 100 Hz and 20 °C , and storage modulus is measured at 30 °C and 1 Hz	171
Figure 5.27 : Éprouvettes de CA-40 imprimé en 3D. Le filament a été étuvé à 60 °C durant 3 h pour l'éprouvette de gauche tandis que celle de droite n'a pas été étuvée	173
Figure 6.1 : Creality CR-10 Max 3D printer and used 3D printing parameters	184
Figure 6.2 : SEM pictures of biocomposites and bionanocomposites	187
Figure 6.3 : Complex viscosity η^* versus shear rate of biocomposites and bionanocomposites.....	188
Figure 6.4 : Storage modulus G' versus shear rate of biocomposites and bionanocomposites.....	188
Figure 6.5 : DSC curves for hot-pressed biocomposites and bionanocomposites.....	190
Figure 6.6 : TGA curves of biocomposites and bionanocomposites.	192
Figure 6.7 : Dielectric constant ϵ' of the tested materials. The plain lines correspond to the low frequency BDS analysis, and the dashed lines correspond to the high-frequency BDS analysis.....	194
Figure 6.8 : Log (dielectric loss ϵ'') and log (electrical conductivity σ_{AC}) of materials. The plain lines correspond to the low frequency BDS analysis, and the dashed lines correspond to the high-frequency BDS analysis.....	196
Figure 6.9 : Storage modulus E' versus temperature. NCC-3 and NCC-5 curves are overlapping	198
Figure 6.10 : Loss tangent $\tan \delta$ versus temperature.....	199
Figure 6.11 : Produced conditions for the flexural tests	207

Figure 6.12 : Influence of infill ratio and printing temperature on a) dielectric constant ϵ' , b) \log (electrical conductivity σ_{AC})	209
Figure 6.13 : Influence of infill ratio and printing temperature on a) tensile elastic modulus, b) tensile maximal stress, c) flexural elastic modulus, d) flexural maximal stress	210
Figure 6.14 : Influence of infill ratio and printing temperature on impact strength.....	211
Figure 6.15 : Dielectric properties versus frequency of biocomposites and biocomposites, a) dielectric constant ϵ' , b) \log (electrical conductivity σ_{AC}).....	212
Figure 6.16 : SEM picture of aggregates evidence in PLA at a $W_{NCC} = 5\%$	213
Figure 6.17 : Stress-strain curves of biocomposites and bionanocomposites in a) tensile mode, b) 3-point bending flexural mode.....	215

Table des Tables

Table 2.1 : Principales voies de synthèse du PLA (*).	18
Table 2.2 : Dielectric properties of Neat PCL and PCL:rice husks measured at 10 GHz (Yakubu et al., 2020)	42
Table 2.3 : Advantages and drawbacks of the main 3D printing technologies.	47
Table 2.4 : Dielectric properties of LDPE and PVC (Derived from Figure 2.12 , Figure 2.13 , Figure 2.14 , Figure 2.15 and (Khalaf, 2013; Nakatsuka, 2011; Omnexus, 2022).	52
Table 2.5 : Mechanical and dielectric properties of PLA, PLA:PBAT 80:20 %, LDPE and PVC (Shinyama, 2018)	53
Table 2.6 : Life cycle comparison of FR4-etched copper and PLA biobased composite-silver nanoparticle. The comparison was carried out on 1 m ² of four-layer PCB (Nassajfar et al., 2021)	55
Table 2.7 : EMI shielding performances of biobased materials.	64
Table 3.1 : Fiches techniques des polymères biosourcés sélectionnés durant le projet de thèse (informations provenant des documents techniques de Natureplast et Natureworks)	70
Table 3.2 : Proportions des différents mélanges de PLA:CA pour impression 3D	76
Table 3.3 : Proportions des constituants des différents biocomposites à base de cellulose pour impression 3D.	77
Table 3.4 : Paramètres utilisés pour la thermocompression des matériaux	78
Table 3.5 : Paramètres utilisés pour l'extrusion des filaments.	79
Table 3.6 : Paramètres utilisés pour l'étape d'impression 3D	80
Table 3.7 : Configuration du plan Taguchi proposé	81
Table 3.8 : Configuration du plan factoriel utilisé	82
Table 3.9 : Types de caractérisations réalisées sur les matériaux	83
Table 3.10 : Nombre d'onde d'absorption du spectre électromagnétique de quelques groupes chimiques (dérivé de ("18 Lecture Supplement: Infrared Spectroscopy," Compound Interest, 2015))	84
Table 4.1 : Different biobased polymeric blend formulations	104
Table 4.2 : Water angle contact of PLA, PHBV, and CA.	109
Table 5.1 : 3D printing parameters	126
Table 5.2 : Densities measured by pycnometer analysis for the hot-pressed samples.	130
Table 5.3 : Electrical conductivity σ_{AC} of hot-pressed and 3D-printed samples @ 20 °C	135
Table 5.4 : Dielectric and electrical variation between hot-pressing and 3D-printing processing @ 100 Hz	137

Table 5.5 : Calculated parameters for the VFT model. The Fragility Index m and activation energy of the α -relaxation E_a were added.....	143
Table 5.6 : Experimental 3D printing parameters	151
Table 5.7 : L9 (3^3) Taguchi experimental design.....	152
Table 5.8 : Variation of dielectric constant ϵ' in function of frequency at 20 °C	154
Table 5.9 : Log (electrical conductivity σ_{AC}) at room temperature and 1 kHz.....	156
Table 5.10 : Storage modulus E' @ 1 Hz and 30°C, and glass transition temperature measured by BDS analysis.....	158
Table 5.11 : Comparative analysis of the dielectric constant ϵ' and storage modulus E' for synthetic polymers.....	160
Table 5.12 : Produced conditions	166
Table 5.13 : 3D parameters conditions	166
Table 5.14 : Thermal temperature of PLA:CA blends	167
Table 5.15 : Comparative analysis of the tested properties of CA-40 and LDPE as reported in the literature	172
Table 6.1 : PLA biocomposites and bionanocomposites conditions	183
Table 6.2 : Parameters used for the 3D printing process.....	184
Table 6.3 : Zero-shear viscosity η_0 of PLA, biocomposites and bionanocomposites determined by the Cross equation	189
Table 6.4 : DSC results for biocomposites and bionanocomposites	191
Table 6.5 : Thermal stability of biocomposites and bionanocomposites	192
Table 6.6 : Porosity of the 3D-printed samples measured by permittivity-derived method	195
Table 6.7 : Produced composites by extrusion	205
Table 6.8 : 3D printing parameters	206
Table 6.9 : Configuration of the used factorial design	206
Table 6.10 : Configuration of the PLA specimens	207
Table 6.11 : ANOVA results with F values for dielectric results. * significant at 0,05; ** significant at 0,01; *** significant at 0,001; n.s. not significant.....	213
Table 6.12 : ANOVA results with F values for mechanical results. * significant at 0,05; ** significant at 0,01; *** significant at 0,001; n.s. not significant.....	215
Table 6.13 : ANOVA results with F values for impact strength. * significant at 0,05; ** significant at 0,01; *** significant at 0,001; n.s. not significant.....	216
Table 6.14 : Comparative study of M7 and N7 composites with 3D-printed neat PLA	217
Table 6.15 : Étude comparative du biocomposite M7 ($W_{MCC} = 15\%$, taux de remplissage = 50 % and $T_{impression} = 200\text{ °C}$) et bionanocomposite N7 ($W_{MCC} = 5\%$, taux de remplissage = 50 % and $T_{impression} = 200\text{ °C}$) comparé au valeurs de la littérature du PP	220

Table des Annexes

Annexe 1 : Chapitre 3 - Analyses FTIR et ATG de la MCC et la NCC greffée	229
Annexe 2 : Chapitre 3 - Granulométrie de la MCC greffée	232
Annexe 3 : Chapitre 3 - Balayage en amplitude des tests rhéologiques.....	233
Annexe 4 : Chapitre 4 - Compléments des analyses diélectriques.....	234
Annexe 5 : Chapitre 4 - Analyses thermiques.....	239
Annexe 6 : Chapitre 4 - Analyses DMA	243
Annexe 7 : Chapitre 5 - Compléments des analyses diélectriques.....	245
Annexe 8 : Chapitre 5 - Compléments des analyses statistiques du plan Taguchi	247
Annexe 9 : Chapitre 5 - Analyses thermiques.....	251

Glossaire des sigles et des unités

Sigles

ABS :	Poly(acrylonitrile butadiène styrène)
AC :	Courant électrique alternatif
AgCB :	Noir de carbone enrobé d'argent
Al ₂ O ₃ :	Alumine
APTES :	(3-aminopropyl)triéthoxysilane
ASTM :	American Society for Testing Materials
ATG, TGA :	Analyse thermogravimétrique
BA :	Butadiène adipate
BaTiO ₃ :	Titanate de baryum
BDS :	Spectromètre diélectrique fréquentiel à large bande
BST :	Titanate de baryum strontium
CA :	Acétate de cellulose
CAD :	Conception assistée par ordinateur
CB :	Noir de carbone
CFO :	Ferrite de cobalt
CNT :	Nanotubes de carbone
CS :	Chitosane
DC :	Courant électrique continu
DS :	Degré de substitution
DSC :	Analyse calorimétrique différentielle à balayage
EMI :	Interférence électromagnétiques
FET :	Transistor à effet de champs
FFF, FDM :	Fabrication additive par dépôt de fil
FTIR :	Analyse infrarouge à transformée de Fourier
GNP :	Nanofeuillets de graphène
HV :	Hydroxyvalérate
H ₂ O ₂ :	Peroxyde d'hydrogène
H ₂ SO ₄ :	Acide sulfurique
ISO :	Organisation internationale de normalisation
ITO :	Oxyde d'indium-étain
KCl :	Chlorure de potassium
K ₄ Fe(CN) ₆ :	Ferrocyanure de potassium
LAGP :	Phosphate de lithium aluminium germanium
Li :	Lithium
LiTFSI :	Bis(trifluorométhanesulfonyl)imidure de lithium

LVE :	Limite viscoélastique
MAR, RAM :	Matériau absorbeur d'ondes électromagnétiques
MCC :	Microcristaux de cellulose
MEB, SEM :	Microscopie électronique à balayage
MET :	Microscopie électronique à transmission
MFC :	Microfibrilles de cellulose
MFI :	Indice de fluidité
mNR :	Caoutchouc naturel
MW :	Masse moléculaire
MWCNT :	Nanotubes de carbone multiparois
MWS :	Relaxation Maxwell-Wagner-Sillars
NADH :	Nicotinamide adénine dinucléotide sous forme réduite
NCC :	Nanocristaux de cellulose
NFC :	Nanofibrilles de cellulose
NH ₄ I :	Iodure d'ammonium
OECT :	Transistor électrochimique organique
OFET:	Transistor à effet de champs organique
OVS :	Capteur de tension optique
P3HT :	Poly(3-hexylthiophène)
PAni :	Polyaniline
PBS :	Poly(succinate de butyle)
PBAT :	Poly(téréphtalate-co-adipate de butyle)
PBSA :	Poly(succinate-co-adipate de butyle)
PBST :	Poly(succinate-co-téréphtalate de butyle)
PCB :	Circuit électronique
PCL :	Polycaprolactone
PE:	Polyéthylène
PEBD, LDPE :	Polyéthylène haute densité
PEHD, HDPE :	Polyéthylène haute densité
PEDOT :	Poly(3,4-éthylènedioxythiophène)
PEG, PEO :	Polyéthylène glycol, poly(oxyde d'éthylène)
PET :	Poly(téréphtalate d'éthylène)
PHA :	Polyhydroxyalcanoate
PHB :	Polyhydroxybutyrate
PHBV :	Poly(hydroxybutyrate-co-valérate)
PIL :	Poly(méthoxy poly(éthylène glycol)monométhacrylate-co-1-vinyl-3 éthylimidazolium bromide)
PLA :	Acide polylactique
PMMA :	Poly(méthacrylate de méthyle)
POM :	Polyoxyméthylène
PP :	Polypropylène

PPy :	Polypyrrole
PS :	Polystyrène
PTFE :	Polytétrafluoroéthylène
PVA :	Alcool polyvinylique
PVC :	Poly(chlorure de vinyle)
PVDF :	Poly(fluorure de vinylidène)
PVP :	Polyvidone
RH :	Humidité relative
RFID :	Radio-identification
RPM :	Tour par minutes
SLA :	Stéréolithographie
SLS :	Frittage sélectif par laser
T_g :	Température de transition vitreuse
T_c :	Température de cristallisation
T_{cc} :	Température de cristallisation froide
TiO_2 :	Dioxyde de titane
T_m, T_f :	Température de fusion
TPS :	Amidon thermoplastique
UV :	Ultraviolet
W_x :	Proportion en masse d'un composant x
XLPE :	Polyéthylène réticulé
XRD :	Diffraction à rayons X
ZnO :	Oxyde de zinc
ZnPP :	Protoporphyrine zinc

Unités

kt :	Milliers de tonnes
Mt :	Millions de tonnes
S :	Section (en m ² ou mm ²)
ep :	Épaisseur (en m ² ou mm ²)
f :	Fréquence (en Hz)
ω :	Fréquence angulaire (en °·s ⁻¹ ou rad·s ⁻¹)
δ :	Déphasage (en ° ou rad)
tan δ :	Tangente de perte (sans unité)
X _{cr} :	Taux de cristallinité (en %)
dH :	Enthalpie de fusion mesurée (en J·g ⁻¹)
dH ₀ :	Enthalpie de fusion théorique (en J·g ⁻¹)
T ₉₀ :	Température lorsque 10 % de matière a été perdue durant un test ATG (en °C)
T ₉₅ :	Température lorsque 5 % de matière a été perdue durant un test ATG (en °C)
eV :	Electronvolt (1 eV = 1,602176*10 ⁻¹⁹ J)
χ :	Electronégativité (sans unité)
C _p :	Capacité électrique (en F)
ϵ^* :	Permittivité complexe
ϵ' , k :	Constante diélectrique (sans unité)
ϵ'' :	Perte diélectrique (sans unité)
ϵ_0 :	Permittivité du vide (8,854187*10 ⁻¹² F·m ⁻¹)
R :	Résistance électrique (en Ω)
σ :	Conductivité électrique (en S·m ⁻¹ , S·cm ⁻¹)
ρ_v :	Résistivité volumique (en $\Omega\cdot m$)
σ_{AC} :	Conductivité électrique en courant alternatif (en S·m ⁻¹ , S·cm ⁻¹)
σ_{DC} :	Conductivité électrique en courant continu (en S·m ⁻¹ , S·cm ⁻¹)
E _{BR} , χ_S :	Rigidité diélectrique (en kV·mm ⁻¹)
V _{BR} :	Tension de claquage (en kV)
α_{BR} :	Tension électrique théorique où une rupture a 63,2 % de chances de se produire (en kV)
β_{BR} :	Facteur de forme de la dispersion des données de la loi de Weibull (sans unité)
γ_0 :	Déformation maximale du système (sans unité)
σ_0 :	Contrainte maximale du système (en Pa ou GPa)
E* :	Module mécanique complexe mesuré par DMA (en GPa)
E' :	Module de stockage (en GPa)
E'' :	Module de perte (en GPa)
G* :	Module mécanique complexe mesuré par rhéologie (en Pa)
G' :	Module de stockage (en Pa)
G'' :	Module de perte (en Pa)

η^* :	Viscosité complexe (en Pa·s)
η_0 :	Viscosité théorique sans cisaillement (en Pa·s)
L_{t0} :	Longueur utile de l'échantillon (en mm)
ΔL_t :	Allongement subie par l'éprouvette durant le test (en mm)
L_f :	Distance entre les supports en test de flexion (en mm)
δ_C :	Déflexion de l'éprouvette (en mm)
F :	Force mécanique appliquée sur l'échantillon (en N)
F_{\max} :	Force mécanique maximale que l'échantillon peut supporter (en N)
E :	Module d'élasticité, ou de Young (en GPa)
E_t :	Module d'élasticité en traction (en GPa)
E_f :	Module d'élasticité en flexion (en GPa)
σ_t :	Contrainte maximale en traction (en MPa)
σ_f :	Contrainte maximale en flexion (en MPa)
ε_t :	Allongement en contrainte maximale traction (en %)
ε_f :	Allongement en contrainte maximale flexion (en %)
K :	Résistance au choc de l'échantillon (en $\text{kJ}\cdot\text{mm}^{-2}$)
E_j :	Énergie nécessaire pour rompre l'éprouvette (en kJ)

Chapitre 1) Introduction générale

1.1. Mise en contexte

Les matériaux diélectriques sont devenus des matériaux incontournables de notre société de consommation. Le marché diélectrique représentait entre 61 et 66 milliards de dollars en 2022, avec une croissance de 30 % d'ici 2030 (TechSci Research, 2023; Zion Market Research, 2023). Ce domaine connaît de nombreuses applications diverses et variées, telles que l'isolation et la conduction électriques (Barbosa et al., 2018; Nakatsuka, 2011), les matériaux absorbeurs d'ondes radar (MAR) (Boss et al., 2020; Thomassin et al., 2008) et les panneaux de circuits électroniques (PCB) (Kosbar et al., 2000; Yuen et al., 2020). Les matériaux les plus représentatifs de ce domaine sont le verre, les céramiques techniques et les polymères. Ces derniers sont apparus dans nos sociétés au début du XX^{ème} siècle et se sont fortement démocratisés depuis. Même s'ils présentent des propriétés intéressantes, de bonnes capacités de production et une facilité de mise en œuvre, leur dépendance au pétrole et leurs impacts environnementaux déplorables les rendent incompatibles avec un développement économique durable (Butturi et al., 2020; CNRS, 2021). Par exemple, les plastiques conventionnels représentent un risque majeur sur les écosystèmes marins à cause de leur haute toxicité et de leur persistance dans le temps (CNRS, 2021). Comme environ 54 millions de tonnes de E-déchets ont été produits en 2019 (Forti et al., 2020), avec uniquement 17 % de cette masse triée et recyclée, cela amène à des problématiques de pollution environnementale de plus en plus préoccupantes.

Dans ce contexte de développement durable et de sensibilisation du public envers les problématiques environnementales, les polymères biosourcés représentent une niche d'avenir dans le secteur diélectrique, avec une forte dynamique de croissance. En effet, les polymères biosourcés et/ou biodégradables sont plus adaptés que les polymères conventionnels en raison de leurs nombreux avantages écologiques, tels que des capacités de biodégradation accélérées pour certaines applications, des propriétés de biocompatibilité, avec une capacité de production quasi illimitée (Deshmukh et al., 2017; Filimon et al., 2019; Hegde, 2017; Hirai et al., 2007; Mano and Niarova, 2003; Platnieks et al., 2020). En 2023, l'association *European Bioplastics* prévoyait une production de 7,43 millions de tonnes (Mt) pour 2028, avec une proportion de polymères à la fois biosourcés et biodégradables de 62 % (European Bioplastics, 2023a). Ces nouveaux matériaux prennent une place privilégiée dans les secteurs utilisant des polymères

conventionnels, tels que l'emballage alimentaire, les biens de consommation, l'agriculture et la construction. Le domaine diélectrique représentait en 2023 environ 87,2 milliers de tonnes (kt) de polymères biosourcés et/ou biodégradables, soit 4 % de la production totale, et connaît aussi une croissance exponentielle (European Bioplastics, 2023b), démontrant un intérêt des industriels pour de tels matériaux.

1.2. Problématique générale

Bien que des travaux aient déjà été réalisés, de nombreuses limitations existent encore pour bénéficier pleinement des performances diélectriques de ces nouveaux matériaux biosourcés. Par exemple, la faible stabilité thermomécanique de l'acide polylactique (PLA) à l'état caoutchouteux pourrait limiter son applicabilité. De plus, la grande majorité des travaux de recherche actuels menés se concentre sur l'augmentation de la conductivité électrique des polymères biosourcés. Très peu de travaux existent concernant le potentiel des polymères biosourcés pour le domaine de l'isolation électrique, ou pour fabriquer des matériaux à faible permittivité (matériaux « *low-k* »). Or ces deux domaines regroupent de nombreux produits finis, comme les isolateurs électriques, les PCB et isolants de câbles électriques. De plus, les condensateurs électriques et les transistors ont besoin de tels matériaux pour assurer leur bon fonctionnement.

1.3. Originalité du projet

L'originalité du projet sera triple. Premièrement, nous proposons une étude rationnelle de mélanges binaires de polymères biosourcés. Cette étude portera sur la comparaison des propriétés diélectriques et mécaniques de 3 types de mélanges polymériques en parallèle. En plus d'aider à déterminer le meilleur mélange pour une application future en impression 3D, nous avons appliqué un plan expérimental de mélange. Le plan de mélange est un plan répandu en pharmacutique et pour la création de béton, mais à notre connaissance, ce type de plan n'est que très peu appliqué pour concevoir des mélanges de polymères. Deuxièmement, nous proposons d'imprimer en 3D des mélanges de PLA et d'acétate de cellulose (CA). Ce sont des mélanges qui ne sont que très peu étudiés. De plus et à notre connaissance, de tels mélanges n'ont jamais été mis en œuvre par impression 3D, et jamais pour une application en isolation électrique. Pouvoir combiner

ces deux derniers points permettra d'apporter une profondeur supplémentaire à l'innovation apportée par le projet. Troisièmement, nous proposons d'imprimer en 3D des biocomposites et des bionanocomposites. Même si l'utilisation de biocomposites dans l'impression 3D est de plus en plus courante, combiner à la fois impression 3D et une application en isolation électrique est innovant.

1.4. Objectifs du projet

1.4.1. Objectif général

L'objectif général de la thèse vise à explorer les performances diélectriques des polymères biodégradables et/ou biosourcés.

1.4.2. Objectifs spécifiques et hypothèses de recherche associées

Pour atteindre l'objectif principal, les trois objectifs spécifiques du projet sont les suivants :

- Recenser les applications potentielles des matériaux biosourcés dans le domaine diélectrique
 - Hypothèse : les polymères issus de la transformation de bioressources (biosourcés) seraient de potentiels candidats pour remplacer les matériaux diélectriques polymériques
- Concevoir et caractériser les propriétés diélectriques de matériaux biosourcés
 - Hypothèse : les propriétés diélectriques des polymères biosourcés seront plus élevées que leurs contreparties synthétiques
- Optimiser les matériaux biosourcés pour les rendre compétitifs face aux matériaux conventionnels du domaine diélectrique
 - Hypothèse : en combinant l'impression 3D et des plans d'expérience, il serait possible de rendre les polymères biosourcés compétitifs face à leurs contreparties synthétiques pour l'isolation électrique

1.5. Contenu de la thèse

Cette présente thèse est constituée de six grands chapitres, dont trois regroupent les résultats expérimentaux. Le présent chapitre traite du contexte général des matériaux diélectriques, mais aussi du besoin de trouver des alternatives durables et biosourcées à ces matériaux. Une brève discussion concernant le potentiel des polymères biosourcés pour remplacer les matériaux diélectriques conventionnels a été présentée. Cette première partie a aussi présenté la problématique générale, les objectifs, ainsi que les hypothèses de recherche associées. Pour finir, ce chapitre présente l'organisation générale du document.

Le deuxième chapitre propose un état de l'art détaillé axé sur les propriétés diélectriques des polymères biosourcés. Ce chapitre est divisé en deux parties. La première partie vise à présenter la théorie sur les matériaux diélectriques, ainsi que les différents polymères biosourcés rencontrés dans la littérature. Une analyse comparée des propriétés diélectriques des polymères biosourcés, ainsi que différents polymères synthétiques couramment utilisés dans le domaine diélectrique, est ensuite proposée et discutée. La seconde partie, présentée sous la forme d'une revue de la littérature [R1], présente différentes stratégies permettant de favoriser l'application des matériaux biosourcés dans des applications d'isolation électrique et les récentes applications proposées par différentes équipes de recherche. Ce chapitre permet d'identifier les polymères biosourcés avec les potentiels d'application les plus intéressants pour une application en isolation électrique, ainsi que les différentes stratégies applicables pour favoriser l'utilisation des polymères biosourcés.

Le troisième chapitre présente les différentes démarches expérimentales menées durant le projet. Les matières, méthodologies statistiques, ainsi que les méthodes de fabrication et caractérisations sont systématiquement présentées pour chacune des phases expérimentales.

Le quatrième chapitre présente la conception et caractérisation de mélanges polymériques à base de PLA, de polyhydroxybutyrate-co-valérate (PHBV) et de CA. Les résultats sont présentés sous la forme d'un article [A1] réalisant un focus majoritairement sur les

propriétés diélectriques et rhéologiques. Cet article est ensuite discuté et mis en perspective avec des analyses mécaniques dynamiques et thermiques afin d'identifier le mélange polymérique avec le plus fort potentiel pour son utilisation en impression 3D programmée dans la suite du projet.

Le cinquième chapitre présente la conception et caractérisation du mélange précédemment sélectionné pour l'impression 3D de biocomposites, ainsi que leurs performances diélectriques, rhéologiques et mécaniques. Les résultats sont présentés sous la forme de deux articles. L'article [A2] présente une analyse des propriétés diélectriques et mécaniques de mélanges PLA:CA afin d'étudier l'influence de la teneur en CA et du procédé d'impression 3D sur les propriétés diélectriques, mécaniques dynamiques et rhéologiques des mélanges PLA:CA. L'article [A3] traite de l'utilisation d'un plan de Taguchi pour comprendre comment les paramètres d'impression et le taux de CA dans le mélange influencent les propriétés mécaniques et diélectriques des mélanges PLA:CA, tout en proposant des optimisations diélectriques et mécaniques. Pour finir, l'article [A4] propose une étude synthétique des matériaux développés durant ce chapitre. Les résultats de ces travaux combinés ont permis d'étudier le potentiel des mélanges PLA:CA imprimé en 3D pour promouvoir l'intégration de matériaux biosourcés pour des applications d'isolation électrique.

Le sixième chapitre présente la conception et caractérisation de composites à base cellulosique, ainsi que leurs performances diélectriques, rhéologiques et mécaniques. Les résultats sont présentés sous la forme de deux articles. L'article [A5] est une analyse des propriétés diélectriques et mécaniques de biocomposites PLA:microcristaux de cellulose (MCC) et de bionanocomposites PLA:nanocristaux de cellulose (NCC) afin d'étudier l'influence des charges cellulosiques et du procédé d'impression 3D sur les propriétés diélectriques, mécaniques dynamiques et rhéologiques des biocomposites et bionanocomposites. L'article [A6] proposé se concentre sur l'utilisation d'un plan d'expérience factoriel pour comprendre comment les paramètres d'impression et le taux de charge cellulosiques du mélange influencent les propriétés mécaniques et diélectriques, tout en proposant des matériaux optimisés. Les résultats de ces articles combinés permettent d'étudier le potentiel des biocomposites et bionanocomposites à base de cellulose, imprimés en 3D, pour promouvoir l'intégration de matériaux biosourcés pour des applications d'isolation électrique.

La fin du manuscrit présentera une conclusion globale du projet et les potentielles perspectives ouvertes.

1.6. Organisation de la thèse

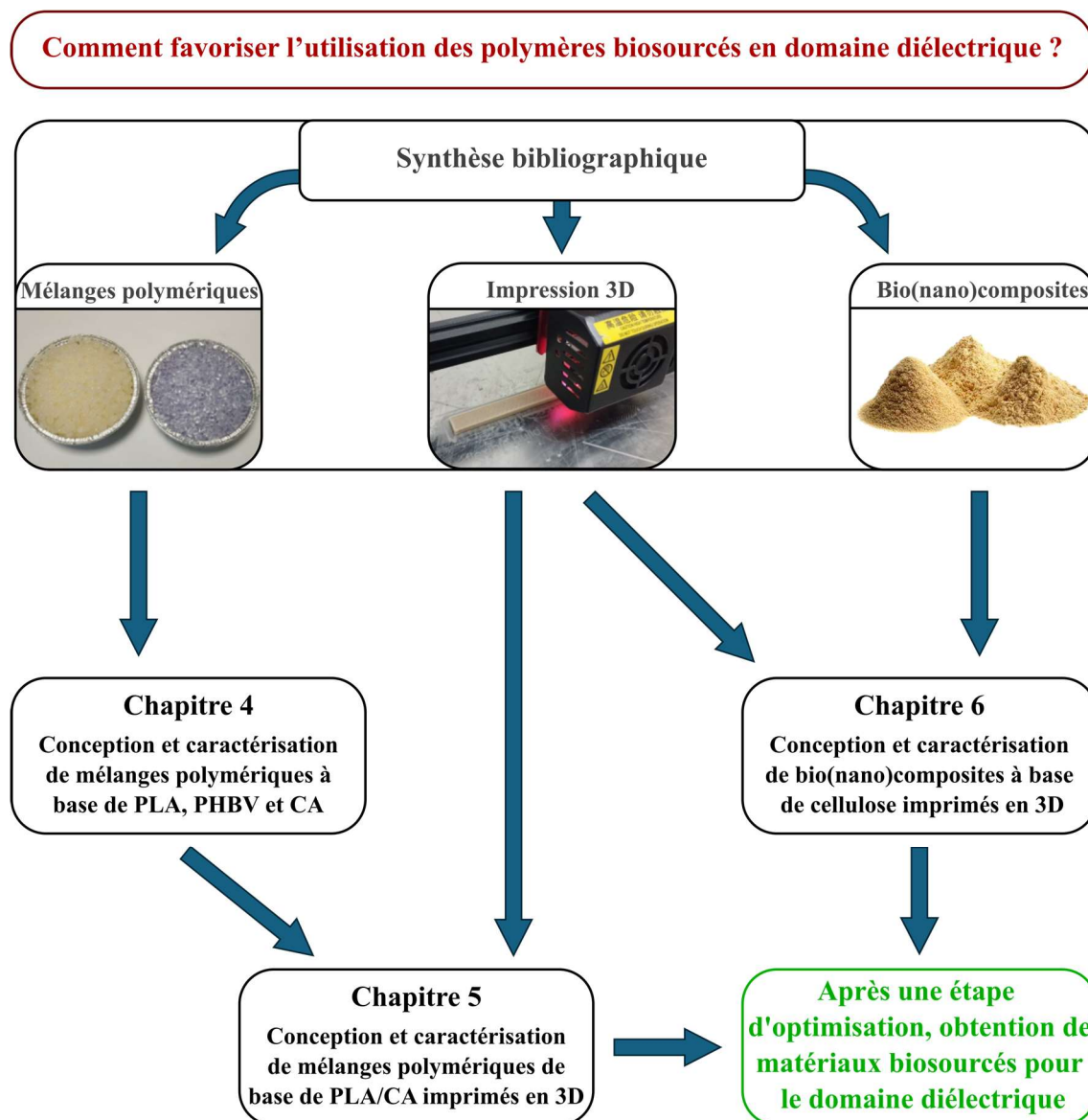


Figure 1.1 : Organisation de la thèse

Chapitre 2) Synthèse bibliographique

2.1. Notions diélectriques

2.1.1. Partie théorique

Les matériaux diélectriques sont des matériaux généralement considérés comme des matériaux isolants, dont la bande interdite (à savoir la plage d'énergie entre la bande de valence et la bande de conduction électronique) est supérieure à 3 eV (Psarras, 2018). Les matériaux diélectriques les plus courants et utilisés sont le bois, les polymères et les céramiques. Ces matériaux sont néanmoins capables d'interagir sous l'effet d'un courant électrique alternatif (AC), en acquérant un moment dipolaire, formant ainsi une polarisation à l'échelle microscopique et/ou nanoscopique. À l'échelle macroscopique, cette polarisation conduit à la notion de permittivité (Psarras, 2018). La **Figure 2.1** illustre la variation de la permittivité d'un matériau diélectrique théorique en fonction de la fréquence du champ électrique (Psarras, 2018) :

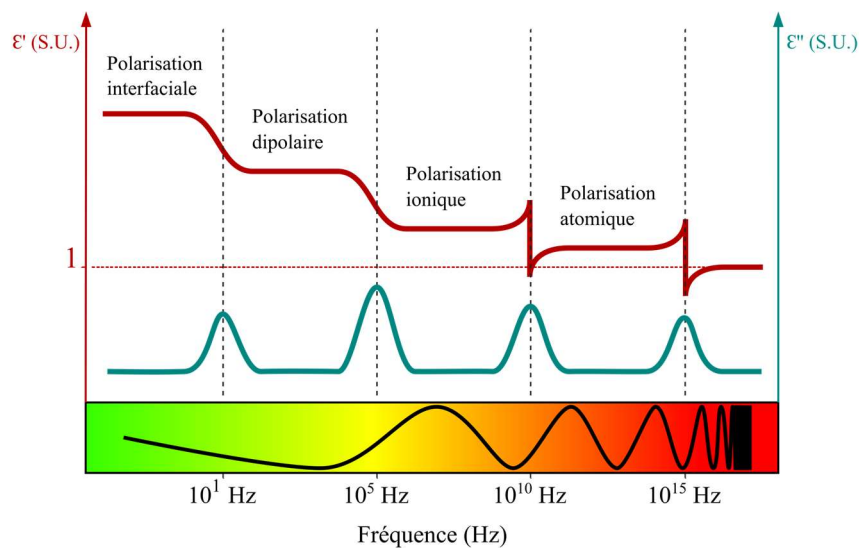


Figure 2.1 : Variation théorique de la constante diélectrique (ϵ') et perte diélectrique (ϵ'') d'un matériau polaire, en fonction de la fréquence électrique appliquée (Psarras, 2018)

Plusieurs types de polarisations différentes induisent la permittivité finale d'un matériau, chacune dépendante d'une gamme de fréquences électriques et associée à une échelle de matériau propre :

- La polarisation interfaciale (aussi appelée Maxwell-Wagner-Sillars (MWS) ou polarisation de charge d'espace) est une polarisation caractéristique que l'on retrouve dans les matériaux hétérogènes (Gallot-Lavallee and Heux, 2013; Jeszka et al., 2010; Psarras, 2018). Lorsqu'un champ électrique est appliqué, des charges électriques s'accumulent entre deux phases d'un matériau dont la conductivité et la permittivité sont suffisamment différentes (Psarras, 2018). Cette polarisation peut être observée dans les composites, où la polarisation se produit à l'interface matrice-charge (Jeszka et al., 2010; Larguech et al., 2021). Dans les systèmes polymériques, cette polarisation peut également se manifester entre les phases amorphes et cristallines (Gallot-Lavallee and Heux, 2013; Hegde et al., 2016). La polarisation MWS est particulièrement visible à basse fréquence et à haute température, où elle joue un rôle majeur dans la permittivité (Gallot-Lavallee and Heux, 2013; Hegde et al., 2016; Jeszka et al., 2010; Larguech et al., 2021).
- La polarisation dipolaire (également appelée polarisation rotationnelle ou moléculaire) est provoquée par la présence de molécules asymétriques dans le matériau (Psarras, 2018). La teneur en humidité du matériau peut également être responsable d'une forte polarisation dipolaire (Koubaa et al., 2008). La **Figure 2.2** présente une classification de quelques groupes fonctionnels typiques rencontrés dans la composition des polymères.

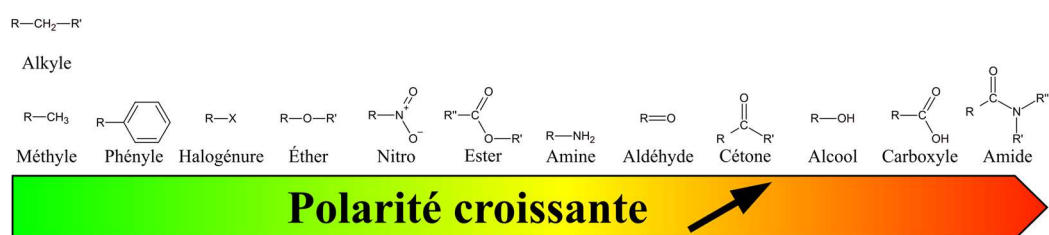


Figure 2.2 : Classification des groupes chimiques par leur polarité
(Adapté de Ophardt, 2003; Young and Weigland, 2002)

À titre d'exemple, le polypropylène (PP) a une polarité très faible, car il ne possède que des groupes alkyles et méthyles. En revanche, le poly(chlorure de vinyle) (PVC) possède des groupes halogénures lui donnant une morphologie chimique comparable à ceux du PP, mais avec une asymétrie moléculaire le rendant plus polaire que ce dernier. Pour rappel, l'électronégativité (χ) de

l'hydrogène, du carbone et du chlore est respectivement de 2,1, 2,5 et 3 (unité sans dimension) (Ouellette and Rawn, 2015). La fréquence électrique appliquée au système a un impact négatif sur la polarisation dipolaire du système. À mesure que la fréquence augmente, le dipôle a moins de temps pour s'adapter à la variation de fréquence du champ électrique. Cette relation fréquence/polarisation dipolaire est largement observée dans la littérature (Billah, 2016; Elloumi et al., 2021; Fredin et al., 2013; Gallot-Lavallee and Heux, 2013; Hegde et al., 2016; Khouaja et al., 2021; Maeno et al., 2005).

- La polarisation ionique (également appelée polarisation vibratoire ou atomique) est une polarisation favorisée dans les structures ioniques telles que les céramiques. Elle se produit lorsque le champ électrique interagit avec un système ionique, attirant ou repoussant les ions positifs (cations) et les ions négatifs (anions), liés par des liaisons ioniques ou non covalentes (Balasubramanyam et al., 2014). Les cristaux ioniques peuvent engendrer des phénomènes physiques tels que la ferroélectricité (Jow and Cygan, 1992), la piézoélectricité (Ando et al., 1986), et la pyroélectricité (Colbrook and Roberts, 1989). Selon le système ionique testé, cette polarisation se produit à des fréquences électriques comprises entre 10^{10} et 10^{13} Hz (Billah, 2016; Fredin et al., 2013).
- La polarisation électronique intervient à l'échelle atomique. Vers les fréquences de l'ordre du pétahertz (10^{15} Hz), l'atome se déforme sous l'effet d'un champ électrique (Fredin et al., 2013). Les charges positives (protons) et négatives (nuage électronique) migrent pour suivre la très haute fréquence du champ électrique, selon Psarras (2018). Cette polarisation est directement liée au nombre d'électrons de l'atome/ion présent, et l'intensité du champ électrique a un impact proportionnel sur la polarisation électronique (Balasubramanyam et al., 2014).

Selon leurs structures chimiques et leurs polarités, les polymères peuvent être séparés en deux catégories (Dubois, 2001) :

- Les polymères polaires présentent une dissymétrie polaire plus ou moins prononcée, en fonction de leurs groupements électro-négatifs présents ($=O$, $-N-$, $-S-$, $C=O$, $C\equiv N$...), et de leurs positions relative par rapport à la chaîne carbonée

principale (Dubois, 2001). Le PVC, le chitosane (CS), le polyméthacrylate de méthyle (PMMA), le polyvidone (PVP), le poly(fluorure de vinylidène) (PVDF) et l'alcool polyvinylique (PVA) sont des polymères polaires typiques (Aziz et al., 2020a). Ces polarités élevées sont particulièrement intéressantes pour la fabrication d'électrolytes solides, où ces matériaux offrent la faible conductivité électrique et la haute conductivité ionique requises pour un séparateur anode-cathode efficace (Li and Li, 2022).

- Les polymères apolaires sont principalement utilisés comme isolants électriques et sont généralement composés de carbone et d'hydrogène. Le polyéthylène (PE) et le PP sont des polymères apolaires courants. S'ils contiennent des atomes fortement électronégatifs tels que le fluor, le chlore ou l'oxygène, ces derniers sont disposés symétriquement autour du squelette carboné, annulant partiellement leur apport de polarité à la molécule (Dubois, 2001). Le polytétrafluoroéthylène (PTFE) est un exemple typique de polymère illustrant ces propriétés.

2.1.2. Grandeurs physiques dans le domaine diélectrique

2.1.2.a. Permittivité complexe : constante diélectrique ϵ' et perte diélectrique ϵ''

Les mesures diélectriques sont généralement effectuées à l'aide d'un spectromètre diélectrique fréquentiel large bande (BDS). L'appareil se présente comme suit : un générateur électrique applique un signal sinusoïdal à deux électrodes. Un voltmètre et un ampèremètre recueillent les signaux électriques résultants. La **Figure 2.3a**) illustre le schéma électrique théorique du système. Le système électrode/échantillon/électrode peut ainsi être considéré comme un condensateur plan, l'échantillon inséré jouant le rôle de l'isolant diélectrique.

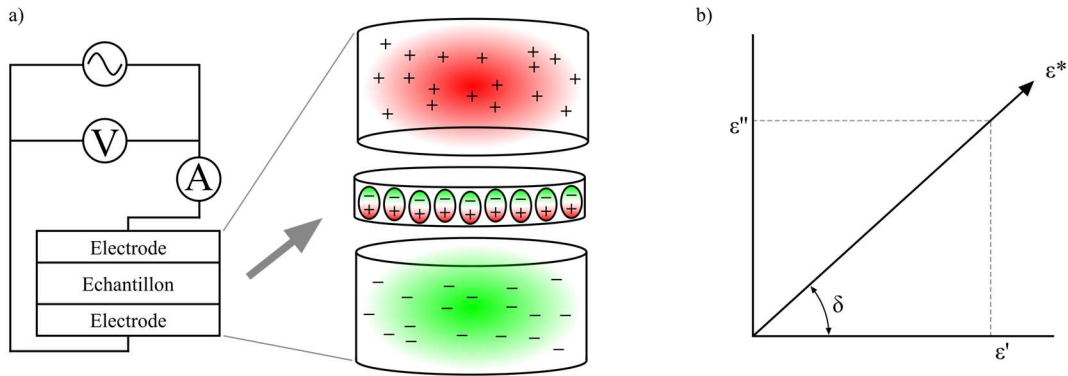


Figure 2.3 : a) Représentation schématique du spectromètre diélectrique et de la polarisation de l'échantillon soumis à un champ électrique, b) projection de la constante diélectrique et du facteur de perte dans le plan complexe (Adapté de (Hegde, 2017; Schönhals, 2010))

L'échantillon est positionné entre ces deux électrodes et sa permittivité peut être exprimée sous forme complexe par les **Équations 1** et **2** (Benabed and Seghier, 2015; Jacob et al., 2006) :

$$\varepsilon' = \frac{C_p * ep}{\varepsilon_0 * S} \quad \text{Équation 1}$$

$$\varepsilon'' = \tan \delta * \varepsilon' \quad \text{Équation 2}$$

Où C_p est la capacité électrique donnée en Farad, S est la section de l'échantillon (en m^2), ep est la distance entre les électrodes (en m), et ε_0 est la permittivité du vide (donnée à $8,541878 * 10^{-12} \text{ F} \cdot \text{m}^{-1}$). La constante diélectrique ε' est la composante réelle de la permittivité complexe et correspond à la réponse du matériau testé au champ électrique appliqué. La perte diélectrique ε'' est la composante imaginaire de la permittivité, et peut être reliée à l'énergie électromagnétique convertie en chaleur par le matériau (Koubaa et al., 2008), pouvant accélérer les phénomènes de dégradation des polymères. La perte diélectrique est calculée en fonction de la composante réelle et la tangente de perte $\tan \delta$ (**Équation 2**). Le déphasage δ , illustré en **Figure 2.3b**), correspond au déphasage induit par le matériau entre l'onde électromagnétique transmise et reçue entre les électrodes.

2.1.2.b. Conductivité électrique σ_{AC} et σ_{DC}

La conductivité électrique d'un matériau désigne sa capacité à laisser passer un flux d'électrons. Ce flux d'électrons crée un courant électrique passant au travers du matériau. Cette conductivité, également nommée conductivité volumique, peut être exprimée par les **Équations 3** et **4** (Jacob et al., 2006) :

$$\sigma = \frac{ep}{R * S} \quad \text{Équation 3}$$

$$\sigma = \frac{1}{\rho_v} \quad \text{Équation 4}$$

Où σ est donné en $S \cdot m^{-1}$, R correspondant à la résistance électrique de l'échantillon (en Ω). S et ep correspondent respectivement à la surface (en m^2) et à l'épaisseur (en m) des échantillons. La conductivité électrique peut également être exprimée comme l'inverse de la résistivité volumique ρ_v (en $\Omega \cdot m$) (**Équation 4**). En fonction de la nature du courant électrique appliqué, deux types de conductivité existent : la conductivité en courant alternatif σ_{AC} et la conductivité en courant continu (DC) σ_{DC} . Sous la présence d'un champ électrique alternatif, la conductivité électrique σ_{AC} peut être déterminée avec l'**Équation 5** (Benabed and Seghier, 2015; Kim et al., 2018) :

$$\sigma_{ac} = \omega * \varepsilon'' * \varepsilon_0 = 2\pi f * \varepsilon'' * \varepsilon_0 \quad \text{Équation 5}$$

Où σ_{AC} est exprimé en $S \cdot m^{-1}$, ω est la fréquence angulaire et f est la fréquence électrique appliquée (en Hz). La conductivité électrique est fortement dépendante de la nature du matériau traversé. Trois catégories de matériaux existent en fonction de leur conductivité : isolant ($\sigma < 10^{-8} S \cdot cm^{-1}$), semiconducteur ($10^{-8} S \cdot cm^{-1} < \sigma < 10^2 S \cdot cm^{-1}$) et conducteur ($\sigma > 10^2 S \cdot cm^{-1}$) comme présenté en **Figure 2.4**.

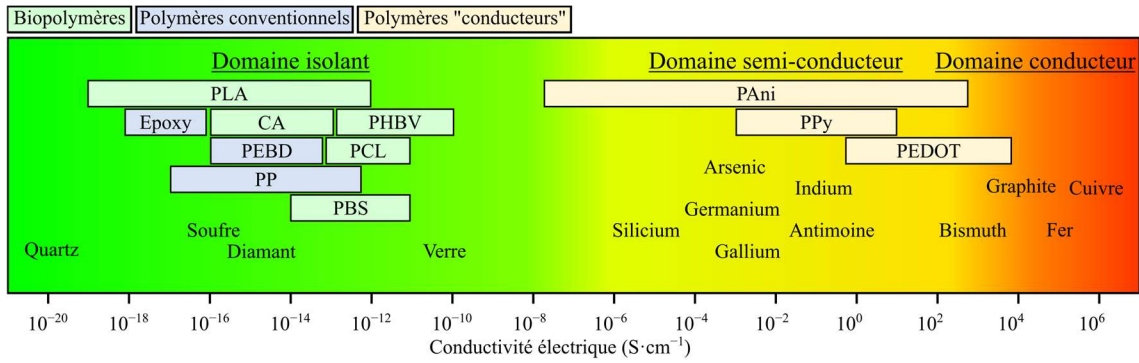


Figure 2.4 : Conductivité électrique de polymères et de divers matériaux (adapté de Solazzo et al. (2019))

Les polymères sont des matériaux généralement classés comme isolants en raison de leur conductivité relativement faible par rapport à d'autres matériaux (Solazzo et al., 2019). Cependant, des polymères tels que le polypyrrole (PPy) (Liu et al., 2018), la polyaniline (PAni) (Fang et al., 2023; Peidavosi et al., 2022), et le poly(3,4-ethylenedioxythiophene) (PEDOT) (Chen et al., 2015) présentent de bonnes propriétés de conductivité électrique en raison de leurs chaînes macromoléculaires conjuguées (alternance de simples et doubles liaisons covalentes), donnant des polymères conducteurs intrinsèques (Dubois, 2001). Ces liaisons facilitent le mouvement électronique, rendant ainsi le matériau conducteur et les plaçant dans la gamme des semi-conducteurs (Solazzo et al., 2019).

2.1.2.c. Rigidité diélectrique E_{BR}

La rigidité diélectrique correspond à la tension maximale qu'un matériau peut subir avant de rompre. Cette rupture se manifeste par la création d'un court-circuit via un arc électrique. Cette tension de rupture est aussi nommée tension de claquage. La relation entre la rigidité diélectrique et la tension de claquage est présentée par l'Équation 6 (Ahmed Dabbak et al., 2018) :

$$E_{BR} = \frac{V_{BR}}{ep} \quad \text{Équation 6}$$

Où V_{BR} est la tension de claquage exprimée en kV, ep est l'épaisseur de l'échantillon (en mm) et E_{BR} est la rigidité diélectrique de l'échantillon (en kV·mm⁻¹). Comme les

mesures d'E_{BR} sont très sensibles à l'homogénéité du matériau, les essais utilisent les méthodes statistiques de distribution de Weibull. La probabilité qu'un matériau subisse un claquage est donnée par l'Équation 7 (Ahmed Dabbak et al., 2018) :

$$F(x) = 1 - e^{\left(\frac{-E_{BR}}{\alpha_{BR}}\right)^{\beta_{BR}}} \quad \text{Équation 7}$$

Où α_{BR} correspond à la tension théorique où un claquage à 63,2 % de chances d'apparaître (en kV) et β_{BR} est le facteur de forme associé à la dispersion des données (sans unité).

2.2. Généralités sur les polymères biosourcés et/ou biodégradables

2.2.1. Les polymères biosourcés et/ou biodégradables

2.2.1.a. *Acide polylactique (PLA)*

L'acide polylactique (PLA) est un polyester biosourcé, dérivé de l'amidon de maïs. Selon le choix de la stéréoisométrie du précurseur, il est possible de former trois PLA différents : le poly(acide L-lactique) (PLLA), le poly(acide D-lactique) (PDLA) et le poly(acide D,L-lactique) (PDLLA) (Newman et al., 2009). Afin d'obtenir des chaînes macromoléculaires à haute masse moléculaire (MW) (> 100 000 Daltons), Auras et al. (2004) ont mentionné trois voies principales de polymérisation, toutes utilisant des énantiomères de l'acide lactique comme monomères. Ces synthèses sont présentées dans la **Table 2.1**. Pour des raisons d'industrialisation et de simplicité, la production industrielle actuelle de PLA est principalement basée sur la synthèse par ouverture de cycle (Yu et al., 2023). La **Figure 2.5** illustre les différents isomères, ainsi que la structure chimique du PLA obtenu par ouverture du cycle du lactide. L'isométrie du précurseur utilisé pour le PLA est un concept important, car elle a un impact direct sur sa cristallisation. Les PLLA et PDLA sont des polymères semi-cristallins, tandis que le PDLLA est un polymère amorphe (Newman et al., 2009).

Table 2.1 : Principales voies de synthèse du PLA (*)

Procédés de synthèse	Avantages	Inconvénients
Polycondensation directe	Économique et simple (Auras et al., 2004; Yu et al., 2023; Zhao et al., 2004)	Relative faible masse molaire comparée aux autres procédés et nécessite une purge de l'eau produite lors de la réaction (Auras et al., 2004; Yu et al., 2023)
Polymérisation par condensation azéotropique	Haute masse molaire atteignable (Auras et al., 2004; Yu et al., 2023)	Des étapes supplémentaires sont nécessaires pour purger la solution azéotropique à la fin du procédé (Yu et al., 2023; Zhao et al., 2004)
Polymérisation par ouverture de cycles	Haute masse molaire atteignable et réaction facilement contrôlable (Auras et al., 2004; Yu et al., 2023)	Une étape de réaction supplémentaire et une grande pureté des monomères sont nécessaires (Yu et al., 2023)

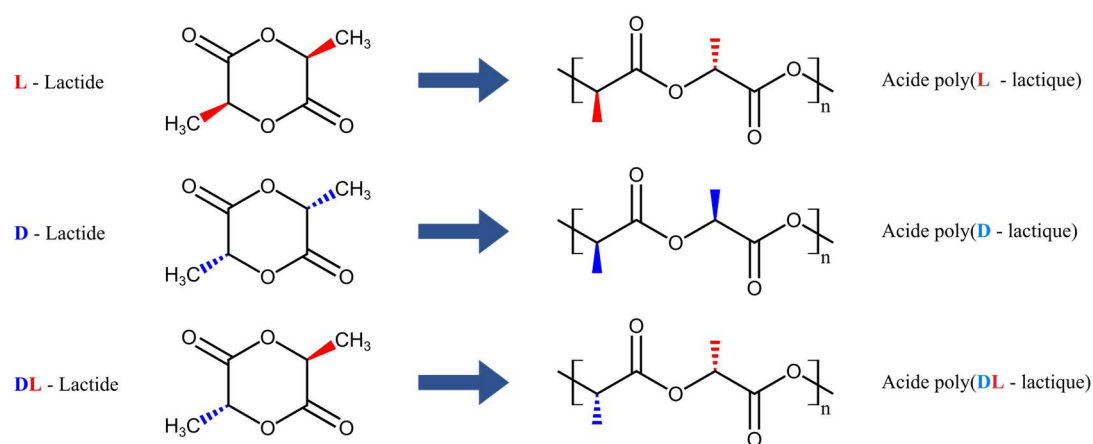


Figure 2.5 : Synthèse par ouverture de cycles du PLA par différents isomères de lactides

La cristallinité du PLA a une influence directe sur les propriétés mécaniques (Guinault et al., 2010; Tsuji, 2016), thermiques (Tsuji, 2016), physiques (Guinault et al., 2010), diélectriques (Dichtl et al., 2017) et de biodégradation (Pantani and Sorrentino, 2013). La phase cristalline du PLA peut se trouver sous trois formes différentes : α , β , et γ , avec leurs propriétés mécaniques spécifiques selon Müller et al. (2014). Les auteurs ont constaté que la phase cristalline la plus fréquemment observée était la phase α . Sa bonne compatibilité biologique (compostabilité, biocompatibilité et faible toxicité) rend le PLA intéressant dans les domaines biomédicaux, de l'emballage et de chimie verte (Scaffaro et al., 2020). Ses propriétés et sa processabilité en font une alternative pertinente au polystyrène (PS), au poly(téréphtalate d'éthylène) (PET) et au PP (Hamad et al., 2016). L'impression 3D est un autre domaine d'application majeur du PLA. Cette technologie

(*) Pour des raisons de logique et de concordance tout le long du manuscrit, le terme de table a été choisi en place du terme tableau.

de transformation prometteuse présente de nombreux avantages, tels que son faible coût, sa rapidité et sa polyvalence (Chen et al., 2023; Kuzmanic et al., 2023; Spinelli et al., 2020; Tabriz et al., 2023). Cette technologie ferait du PLA un choix aussi pertinent pour les applications diélectriques avancées.

2.2.1.b. Polyhydroxyalcanoates (PHAs)

Les polyhydroxyalcanoates (PHAs) sont une classe de biopolyesters biodégradables linéaires, pouvant être classifiées en trois classes en fonction de la longueur de leurs chaînes R : les PHAs à chaîne courte ($R < 6$ atomes de carbone), les PHAs à chaîne moyenne ($6 < R < 13$ atomes de carbone) et les PHAs à chaîne longue ($R > 14$ atomes de carbone) (**Figure 2.6**).

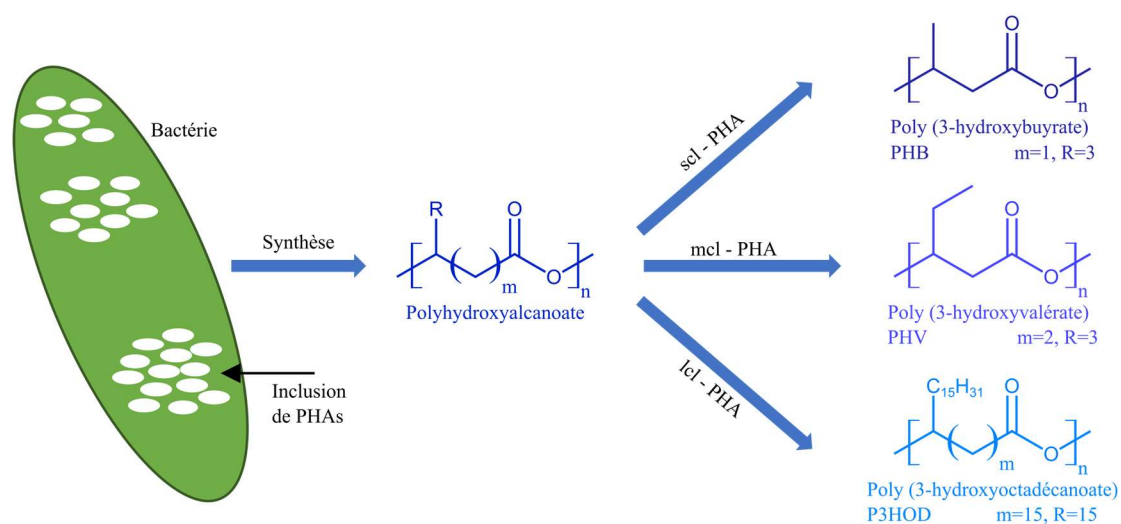


Figure 2.6 : Synthèse de polyhydroxyalcanoate (PHA) et formulations chimiques de différents PHAs

Les PHAs peuvent être synthétisés par des cellules végétales naturelles ou transgéniques (Bohmert-Tatarev et al., 2011, 2000; Snell et al., 2015) et des bactéries (Blandón et al., 2020; Koller et al., 2005; Taga et al., 1997). Snell et al. (2015) ont rapporté un rendement en polyhydroxybutyrate (PHB) à partir de cellules végétales d'environ 10 % entre 1992 et 2012. Un rendement de 18,8 % en masse sèche totale a été obtenu dans des plastides de plantes de tabac par Bohmert-Tatarev et al. (2011). Des rendements de 40 % en masse sèche totale ont même été obtenus dans de l'arabette de *Thalium* transgénique (*Arabidopsis thaliana*) par le même auteur (Bohmert-Tatarev et al., 2000), mais avec un

effet cytotoxique observé en raison d'une teneur excessive en PHAs. En comparaison, les bactéries peuvent atteindre des rendements plus élevés (Castilho et al., 2009). Les rendements en polyhydroxybutyrates et polyhydroxybutyrate-co-valérates ont été rapportés à 81,4 et 76 % respectivement (Koller et al., 2005; Taga et al., 1997). Les propriétés mécaniques du PHB sont proches de celles du PLA, mais sa phase cristalline plus élevée le rend très cassant, et sa processabilité très limitée rend son exploitation industrielle difficile (Gasmi et al., 2019; Shang et al., 2012). L'incorporation d'hydroxyvalérate (HV) dans la structure pour former le copolymère polyhydroxybutyrate-co-valérate (**Figure 2.7**) peut partiellement atténuer ce problème en diminuant sa cristallinité. (Shang et al., 2012). Les applications de ces deux polymères restent néanmoins vastes et comprennent l'emballage alimentaire, l'agriculture et certains domaines biomédicaux (Ibrahim et al., 2021; Rhim et al., 2013).

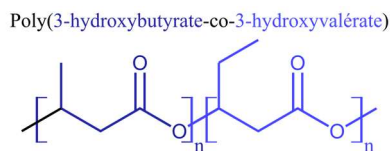


Figure 2.7 : Structure chimique du PHBV

2.2.1.c. *Poly(succinate de butyle) (PBS)*

Le poly(succinate de butyle) (PBS) est un polyester aliphatique biodégradable. Il peut être polymérisé de nombreuses façons, comme par exemple par polycondensation directe de l'acide butane-1,4-dioïque (acide succinique) avec du 1,4-butanediol (Rafiqah et al., 2021) (**Figure 2.8**).

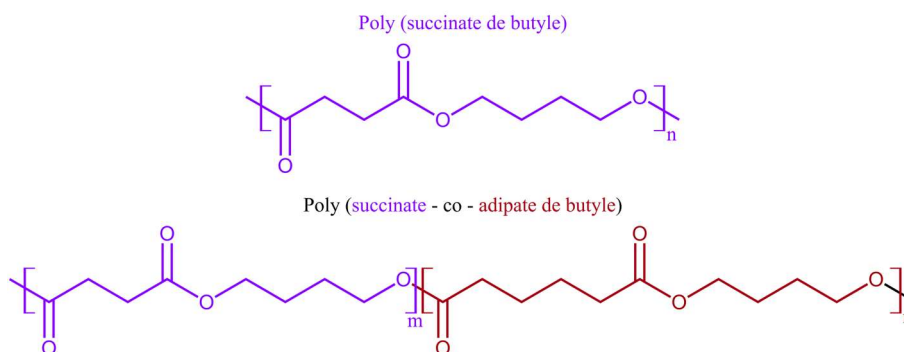


Figure 2.8 : Structures chimique du PBS et du PBSA

Les monomères peuvent être synthétisés par des voies à la fois fossiles et renouvelables (Meynial-Salles et al., 2008). Ce double procédé de synthèse fait du PBS un polymère de transition synthétique-biologique intéressant. En raison de sa faible température de transition vitreuse (T_g) et de fusion (T_f), il possède une excellente processabilité, équivalente au PE et au PP, le rendant adapté pour des applications d'emballage, de films pour agriculture, fibres textiles et nécessitant des besoins de biodégradation (Cristofaro et al., 2018; Platnieks et al., 2020; Sahoo et al., 2011). Sa biocompatibilité le rend également intéressant pour le domaine biomédical, comme les applications d'encapsulation pour les médicaments biodégradables, les prothèses de cartilage et prothèses osseuses (Brunner et al., 2011; Cristofaro et al., 2018; Wang et al., 2009). Les copolymères à base de PBS peuvent également être synthétisés pour améliorer certaines propriétés spécifiques. Le poly(succinate-co-adipate de butyle) (PBSA) est un copolymère de PBS obtenu en copolymérisant de l'acide succinique et de l'acide adipique avec du butane-1,4-diol (Brunner et al., 2011) (**Figure 2.8**). Selon Xu and Guo (2010), l'ajout du motif adipate de butylène (BA) diminue la cristallinité du PBS, impactant positivement sur son élongation à la rupture et sa résistance au choc IZOD. Ils ont également montré que les copolymères de PBSA ont un taux de biodégradation amélioré dans les boues activées. Le poly(succinate-co-téréphtalate de butyle) (PBST) est obtenu par copolymérisation de l'acide succinique, du butane 1,4 diol et de l'acide téréphtalique (Li et al., 2013). Selon Luo et al. (2012), ce copolymère a une application potentielle dans les fibres élastiques, avec une bonne capacité de restructuration après le stress.

2.2.1.d. Polycaprolactone (PCL)

Le polycaprolactone (PCL) est un polyester aliphatique synthétique et biodégradable. Selon Labet and Thielemans (2009), le PCL peut être obtenu par deux synthèses principales : par polycondensation de l'acide 6-hydroxyhexanoïque et par polymérisation via ouverture de cycle d' ϵ -caprolactone. La **Figure 2.9** montre la synthèse du PCL par ouverture de cycles d' ϵ -caprolactone. Le PCL est un polymère semi-cristallin et hydrophobe. Sa cristallinité atteint 69 %, mesurée par analyse calorimétrique différentielle à balayage (DSC) (Ong and Price, 2007) et 57 %, mesuré par diffraction à rayons X (XRD) (Salehi et al., 2014). Il présente une bonne stabilité chimique à de nombreux solvants, comme l'eau, l'huile et le chlore (Mohamed and Yusoh, 2015).

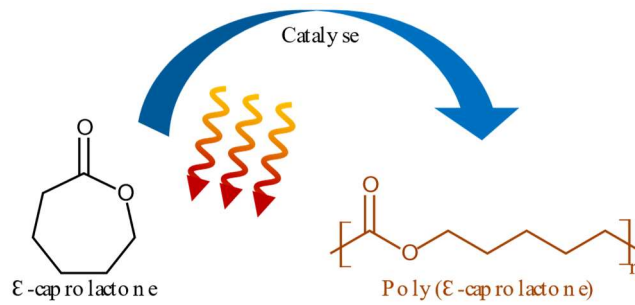


Figure 2.9 : Synthèse du PCL par ouverture de cycle du ϵ -caprolactone

Sa bonne compatibilité avec d'autres polymères tels que le PVC, le PVA et le poly(acrylonitrile butadiène styrène) (ABS) en fait un candidat idéal pour les mélanges de polymères avancés (Labet and Thielemans, 2009). Ses propriétés thermiques ($T_g \sim -60$ °C et $T_f \sim 60$ °C) (Bartnikowski et al., 2019; Hegde et al., 2016; Hirai et al., 2007; Hrichi et al., 2019; Ishak et al., 2021) restreignent son application, mais confèrent au PCL un comportement caoutchoutique à température ambiante (Dhakal et al., 2018). Il présente une cinétique de biodégradation relativement lente, allant de plusieurs mois à plusieurs années, directement reliée à son taux de cristallisation (Bartnikowski et al., 2019).

2.2.1.e. Acétate de cellulose (CA)

L'acétate de cellulose (CA) est un ester organique de cellulose (Fischer et al., 2008), directement dérivé de la cellulose, le principal biopolymère disponible sur Terre (Liu and Sun, 2010). Il est synthétisé par une réaction d'acétylation de la cellulose dans un environnement acide (Fischer et al., 2008). L'acétate de cellulose est une famille définie par son degré de substitution (DS). Le degré de substitution correspond au taux de conversion des groupes hydroxyles de la cellulose en groupes acétyles. Il est compris entre 0 (cellulose) et 3 (triacétate de cellulose). Les degrés intermédiaires correspondent au diacétate de cellulose. Un DS de 2,5 est le plus fréquemment rencontré, car il optimise les propriétés de fusion, de structure moléculaire et de solubilité (Puls et al., 2011). La **Figure 2.10** montre la synthèse du triacétate de cellulose et du diacétate de cellulose.

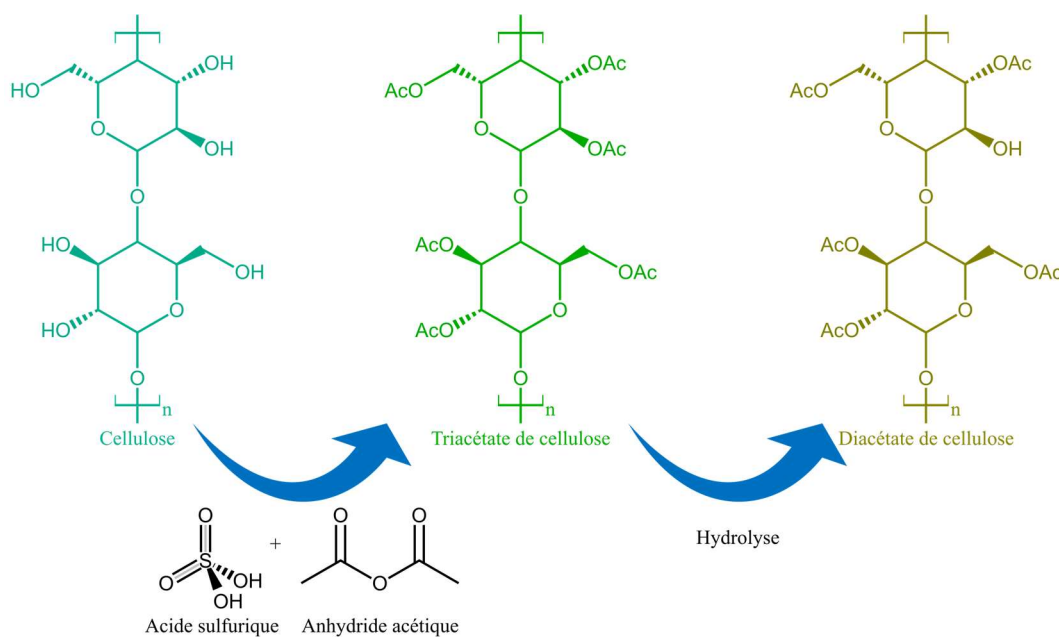


Figure 2.10 : Synthèse de différents acétates de cellulose

Étant une famille de polymères faiblement cristallins, leurs propriétés multiphysiques sont majoritairement déterminées par leurs DS. De Freitas et al. (2017) ont trouvé une influence négative du DS sur la température de transition vitreuse de l'acétate de cellulose. L'augmentation de la proportion de groupes acétyles diminue le nombre de groupes hydroxyles et donc l'énergie d'activation de la transition vitreuse. De plus, ils ont également déterminé que l'augmentation du degré de substitution diminuait le taux de cristallinité des polymères, et donc augmentait sa transparence et par corollaire sa rigidité mécanique. Concernant son utilisation pratique, il a été l'un des premiers polymères utilisés industriellement au XX^{ème} siècle pour des applications photographiques (Sata et al., 2004). Une fois plastifié, il est également utilisable dans des objets de la vie quotidienne tels que les dés, les crayons et les filtres à cigarettes. Ils possèdent des propriétés chimiques et thermiques avancées (Wsoo et al., 2020). L'acétate de cellulose peut être électrofilé, lui offrant des possibilités d'application en ingénierie tissulaire, en pansements biodégradable et en voie d'administration de médicaments (Khan et al., 2019; Khoshnevisan et al., 2018; Ravikumar et al., 2017; Wsoo et al., 2020).

2.2.1.f. *Autres polymères biosourcés*

Comme la cellulose ou le PHA, de nombreux polymères biosourcés sont produits par voie biologique, tels que la kératine, le collagène, la pectine et la gélatine. Certains polymères

biosourcés, comme l'amidon et le chitosane, ont récemment suscité l'intérêt de l'industrie, notamment en raison de leur abondance sur Terre et de leur facilité de traitement par rapport aux polymères conventionnels (**Figure 2.11**).

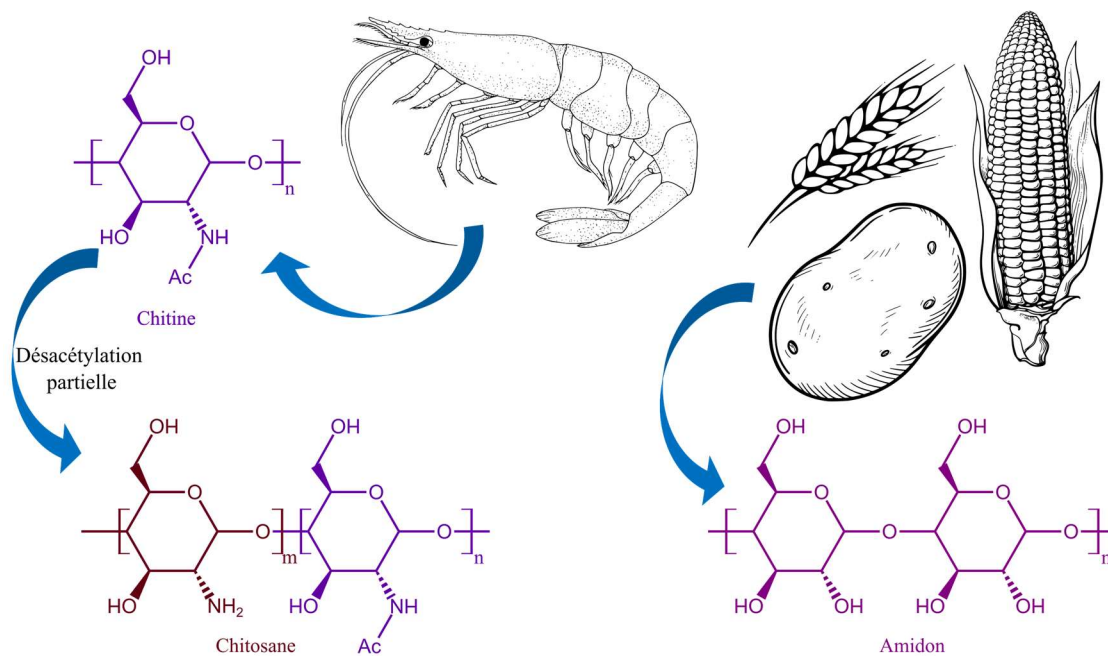


Figure 2.11 : Chitine, chitosane et amidon

L'amidon est un polysaccharide ramifié composé de deux substances distinctes : d'amylose linéaire (composée de D-glucose) et d'amylopectine ramifiée (Drakopoulos et al., 2017). Ce biopolymère est présent dans de nombreuses plantes, notamment le blé, les pommes de terre et le maïs. La différence entre l'amidon et la cellulose réside dans la nature des liaisons du glucose : la cellulose possède des liaisons β -1,4, tandis que l'amidon possède des liaisons α -1,4. L'amidon brut ne convient pas aux applications polymères en raison de sa rigidité excessive. Une étape de plastification est nécessaire pour former de l'amidon thermoplastique (TPS). Avec un plastifiant adapté, le TPS peut être utilisé pour des applications respectueuses de l'homme telles que les emballages alimentaires (Drakopoulos et al., 2020, 2017). Mano and Niarova (2003) ont également proposé une utilisation de TPS pour les tissus osseux et les applications biomédicales dans les mélanges de polymères. Dans le domaine diélectrique, Shukur et al. (2014) ont déjà étudié son utilisation comme électrolyte en condensateurs électrochimiques à double couche. Le chitosane (CS) est un copolymère saccharidique cationique et est obtenu par

désacétylation partielle de chitine et se compose de D-glucosamine acétylés et désacétylés (Monika et al., 2018; Petrov et al., 2016). La chitine est présente dans la biomasse faunistique, et est le deuxième polymère le plus abondant sur Terre après la cellulose, selon Monika et al. (2018). Ce polymère est principalement transformé par voie solvant (Misenan et al., 2018; Nainggolan et al., 2018; Petrov et al., 2016). Ses propriétés antifongiques, antioxydantes et antimicrobiennes le rendent attractif pour les emballages alimentaires (Monika et al., 2018). Le CS a également vu des applications dans le domaine biomédical, comme tous les polymères biosourcés mentionnés ci-dessus. Comme pour les TPS, le CS a un potentiel adapté dans le domaine électrique, que ce soit pour la création d'électrolytes (Misenan et al., 2018), de matériau diélectrique pour condensateurs électrostatiques (Nainggolan et al., 2018) et de membranes pour la régénération osseuse (Petrov et al., 2016).

2.2.2. Performances diélectriques des polymères biosourcés et/ou biodégradables

2.2.2.a. Constante diélectrique

La constante diélectrique ϵ' des polymères biosourcés et/ou biodégradables, et des polymères conventionnels rapportées dans la littérature (Abou-Aiad et al., 2002, 2007; Ahmed Dabbak et al., 2018; Ando et al., 1986; Anh et al., 2016; Badia et al., 2014; Benabed and Seghier, 2015; Cao et al., 2014; Dawy and Nada, 2003; Dhal and Mishra, 2013; Erdönmez and Güven Özdemir, 2020; Ezzeddine et al., 2021; Fahmy et al., 2016; Fal et al., 2021; Fryń et al., 2021; Gallot-Lavallee and Heux, 2013; Gojayevev et al., 2019; Han et al., 2020; He et al., 2020; Hegde, 2017; Hegde et al., 2016; Heid et al., 2016; Hikosaka et al., 2008; Hirai et al., 2007, 2004; Hrichi et al., 2019; Huang et al., 2013; Ishikawa et al., 2007; Ishikawa and Ohki, 2008; Izci and Bowler, 2019; Kemari et al., 2020; Kotp, 2010; Kumar and Kumar, 2012; Madbouly et al., 2007; Maeno et al., 2005; Mike Chung, 2012; Mohiuddin et al., 2015; Musto et al., 2015; Nemoto et al., 2008; Ohki et al., 2009; Ohki and Hirai, 2006; Platnieks et al., 2020; Pratt and Smith, 1997, 1999; Ren et al., 2003; Seghier and Benabed, 2015; Shafee, 2001; Shinyama and Fujita, 2005; Sics et al., 1998; Spinelli et al., 2020; Tagami et al., 2008; Ten et al., 2012; Uyor et al., 2022; Wan et al., 2015; Q. Wang et al., 2017; Xu et al., 2021; L. Yu et al., 2011; H. Zhang et al., 2021) est résumée dans la **Figure 2.12**. Cette étude montre que :

- Les valeurs médianes d' ϵ' observées pour les polymères biosourcés et/ou biodégradables étudiés sont comprises entre 2,8 et 4,8. Selon Dubois (2001), ces valeurs de constante diélectriques sont typiques de polymères faiblement polaires.
- Le PLA est le polymère biosourcé le plus étudié en termes de constante diélectrique, comme l'avait noté Hegde (2017).
- Le PLA et le PHBV présentent les constantes diélectriques médianes et moyennes les plus faibles, aux alentours de 3. En revanche, le PBS et l'acétate de cellulose ont les constantes diélectriques les plus élevées, jusqu'à 4,8 pour le PBS.

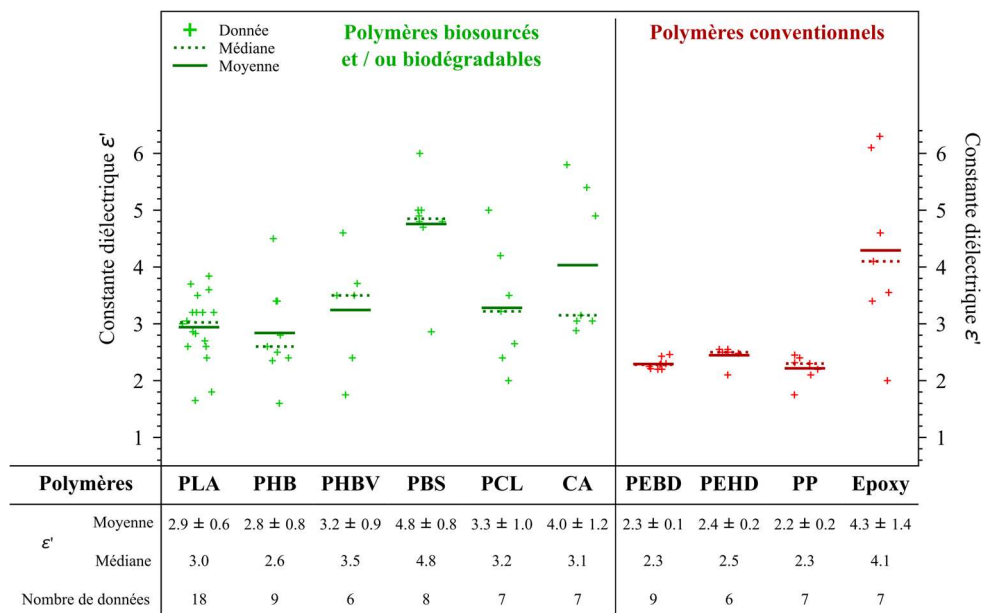


Figure 2.12 : Synthèse bibliographique de la constante diélectrique ϵ' de polymères biosourcés et/ou biodégradables, et de polymères conventionnels, mesurées à 100 Hz

- Le polyéthylène basse densité (LDPE), le polyéthylène haute densité (HDPE) et le PP affichent des valeurs médianes de constantes diélectriques autour de 2,4 en raison de leur composition atomique ne contenant que des atomes apolaires (carbone et hydrogène). Il convient de noter que ces trois polymères conventionnels présentent des écarts types très faibles et sont considérés comme polymères apolaires par Dubois (2001).

- L'époxy a une constante diélectrique plus élevée que les autres polymères synthétiques, et avec un écart type important, pouvant être attribué à sa constitution chimique plus polaire, ainsi qu'à son degré de réticulation (J. Li et al., 2022; Ogura, 1999).
- À l'exception du PBS, les polymères biosourcés et/ou biodégradables présentent des écarts types relativement importants, imputables à plusieurs facteurs (précision de la mesure, grade du polymère/lot, cristallinité du polymère, par exemple).
- Les propriétés diélectriques du CA dépendent principalement de leur degré de substitution.
- Plus le DS est élevé, plus la constante diélectrique du CA est faible, car le groupe acétyle a un pouvoir polaire inférieur au groupe hydroxyle. Cela pourrait expliquer la large distribution des ϵ' du CA présente dans la littérature (Dawy and Nada, 2003).

2.2.2.b. *Perte diélectrique*

La **Figure 2.13** synthétise les valeurs de facteur de perte diélectrique ϵ'' des polymères biosourcés et/ou biodégradables, et des polymères conventionnels mesurées par différentes études (Abdel Moteleb et al., 1992; Abou-Aiad et al., 2002, 2007; Ahmed Dabbak et al., 2018; Ando et al., 1986; Anh et al., 2016; Bello et al., 2007; Benabed and Seghier, 2015; Bergmann and Owen, 2004; Bian et al., 2019; Brás et al., 2008; Cao et al., 2014; Chambers et al., 2001; Crétois et al., 2013; Dawy and Nada, 2003; Erdönmez and Güven Özdemir, 2020; Ezzeddine et al., 2021; Fahmy et al., 2016; Fal et al., 2021; Fryń et al., 2021; Fu et al., 2007; Gallot-Lavallee and Heux, 2013; Gasmi et al., 2019; Gojayev et al., 2019; Hamciuc et al., 2013; He et al., 2020; Hegde, 2017; Heid et al., 2016; Hirai et al., 2007; Hrichi et al., 2019; Ishikawa and Ohki, 2008; Izci and Bowler, 2019; Katayama et al., 2013; Kemari et al., 2020; Kortaberria et al., 2006; Kotp, 2010; Larguech et al., 2021; Mierzwa et al., 2002; Mohiuddin et al., 2015; Nabiyeve et al., 2014; Nemoto et al., 2008; Norshamira and Mariatti, 2014; Ohki et al., 2009; Pachekoski et al., 2012;

Platnieks et al., 2020; Pratt and Smith, 1999; Reddy et al., 1993; Ren et al., 2015, 2003; Saad et al., 1992; Saravanamoorthy et al., 2015; Seghier and Benabed, 2015; Shinyama and Fujita, 2005; Sics et al., 1998; Takala et al., 2010; Uyor et al., 2022; Wan et al., 2015; Q. Wang et al., 2017; Wang et al., 2019; Wu et al., 2013; Xu et al., 2021; L. Yu et al., 2011; H. Zhang et al., 2021). Comme le montre le graphique :

- Les valeurs ϵ'' les plus faibles sont observées pour le PBS et le PLA, tandis que les valeurs les plus élevées sont observées pour le PHB et le PHBV.
- Les polymères thermoplastiques conventionnels sélectionnés ont des ϵ'' plus faibles que leurs homologues biosourcés et/ou biodégradables, avec un écart plus important entre leurs valeurs moyennes et médianes. L'époxy a des ϵ'' similaires à ceux des polymères biosourcés et/ou biodégradables.

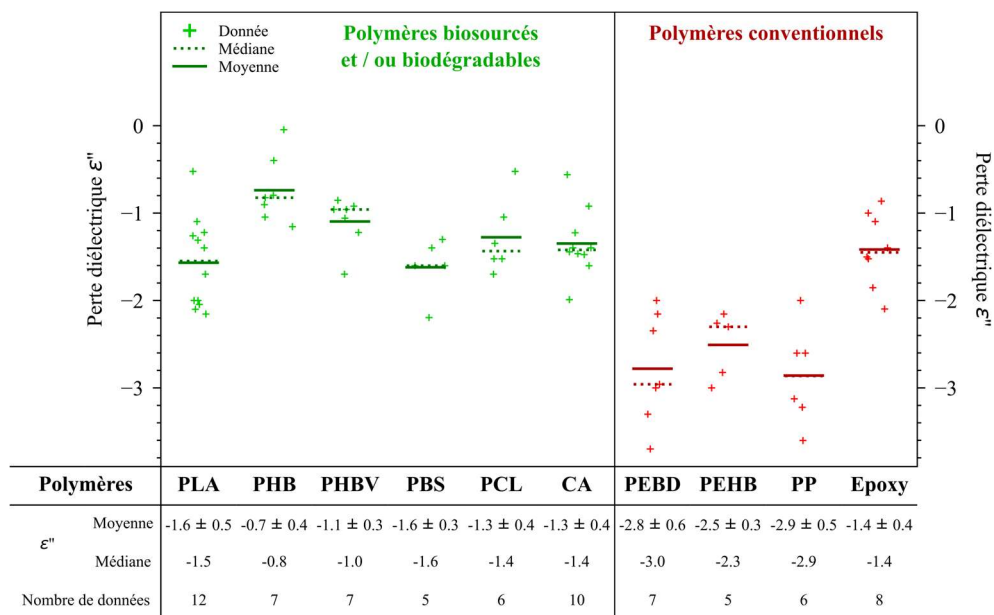


Figure 2.13 : Synthèse bibliographique de la log (perte diélectrique ϵ'') de polymères biosourcés et/ou biodégradables, et de polymères conventionnels, mesurées à 100 Hz

- Les ϵ'' les plus élevés du PHB et du PHBV peuvent être dus à la fois à la relaxation α se produisant dans cette gamme de température et à la forte polarisation interfaciale induite par leur cristallinité élevée.

2.2.2.c. Conductivité électrique

Les **Figure 2.14a)** et b) présentent une vue d'ensemble des conductivités en courant continu et en courant alternatif des polymères d'origine biologique et des polymères conventionnels observées dans différentes études (Chen et al., 2017, 2019; Chiteme et al., 2007; Ciuprina and Plesa, 2011; Dalai and Parida, 2022; Dawy and Nada, 2003; Ebrahim et al., 2007; Erdönmez and Güven Özdemir, 2020; Fahmy et al., 2016; Fal et al., 2021; Filimon et al., 2019; Hamciuc et al., 2013; Hegde, 2017; Hegde et al., 2016, 2015; Hrichi et al., 2019; Huang et al., 2013; Ishak et al., 2021; Ishikawa et al., 2007; Islam et al., 2021; Jeon et al., 2012; Khare et al., 2008; Lamberti et al., 2018; Lee and Kim, 2021; Li et al., 2010; Liang and Tjong, 2006; Matsushita et al., 2005; Montanheiro et al., 2015; Nuriev et al., 2018; Oi et al., 2012; Perumal Ramasamy et al., 2014; Platnieks et al., 2020; Reddy et al., 1993; Russo et al., 2018; Rytöluoto et al., 2022; Saravanamoorthy et al., 2015; Stancu et al., 2013; Su et al., 2013; Sui et al., 2008; Vieira et al., 2021; Virtanen et al., 2017, 2016; Wan et al., 2015; C.-R. Yu et al., 2011; L. Yu et al., 2011). Comme le montre les graphiques :

- En mode DC, la conductivité moyenne des polymères biosourcés et/ou biodégradables varie de $1,6 \cdot 10^{-16}$ à $1,2 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$, les plaçant dans la catégorie des isolants électriques. Le PLA et le CA présentent les valeurs médianes de conductivité électrique les plus faibles, proches des polymères synthétiques. En revanche, le PHBV et le PCL possèdent les conductivités les plus élevées, avec des valeurs autour de $1 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$.
- En mode AC, la conductivité électrique médiane des polymères biosourcés et/ou biodégradables se situe entre $1,6 \cdot 10^{-12}$ et $1,2 \cdot 10^{-10} \text{ S} \cdot \text{cm}^{-1}$, les plaçant également dans la catégorie des matériaux isolants électriques. Dans ce mode, le PBS et le PLA présentent les plus faibles conductivités, avec des valeurs moyennes et médianes comprises entre $6 \cdot 10^{-13}$ et $4 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$. Dans ce mode, tous les polymères biosourcés et/ou biodégradables examinés présentent une conductivité électrique similaire à celle des polymères conventionnels.

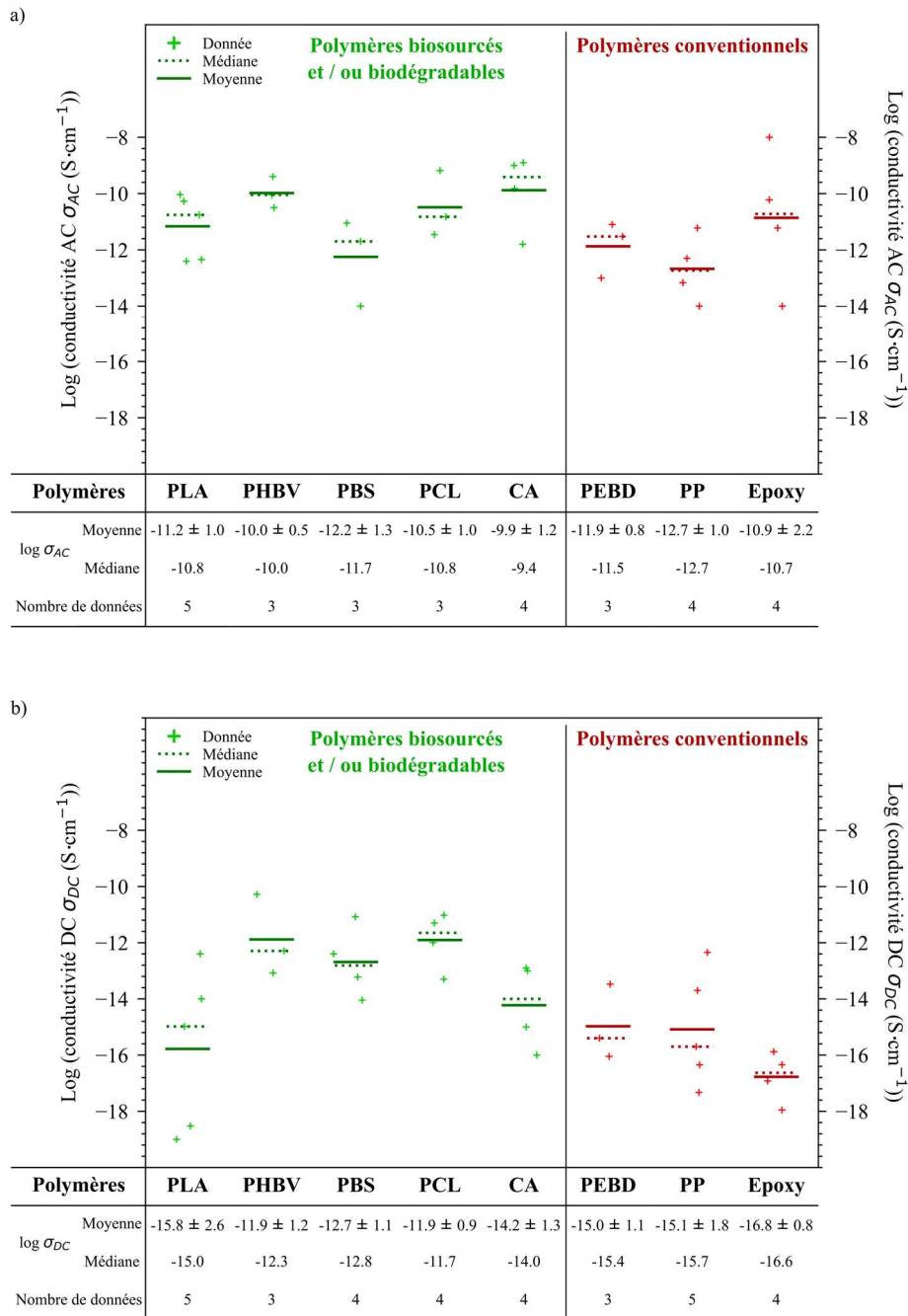


Figure 2.14 : Synthèse bibliographique de la log (conductivité électrique) de polymères biosourcés et/ou biodégradables, et de polymères conventionnels, a) en mode AC σ_{AC} , b) en mode DC σ_{DC} . Les valeurs en mode AC sont mesurées à 100 Hz

- Comparé au mode DC, le mode AC présente les valeurs de conductivité les plus élevées en raison du « *hopping carrier phenomenon* » favorisé à plus haute fréquence électrique (Ciuprina and Plesa, 2011).

2.2.2.d. Rigidité diélectrique

La **Figure 2.15** présente la rigidité diélectrique en mode continu et alternatif des polymères biosourcés et/ou biodégradables, et des polymères conventionnels observées dans différentes études (Andritsch et al., 2010; Anh et al., 2016; Azmi et al., 2018; Chen et al., 2017; Desmars et al., 2018; Eesaee et al., 2018; Fang et al., 2014; Feng et al., 2018; Hegde, 2017; Kato et al., 2006; Lau et al., 2017; Li et al., 2016; Nemoto et al., 2008; Ohki and Hirai, 2007; Oi et al., 2012; Takala et al., 2010; Warnakulasooriya, 2022; Wu et al., 2013; Yeung and Vaughan, 2016; Yu et al., 2012) Comme le montre le graphique :

- En mode DC, les valeurs médianes et moyennes de l' E_{BR} pour les polymères biosourcés et/ou biodégradables sont comprises entre 250 et 600 $\text{kV}\cdot\text{mm}^{-1}$, la valeur maximale étant obtenue pour le PLA. Les valeurs E_{BR} les plus faibles sont obtenues pour le PCL.

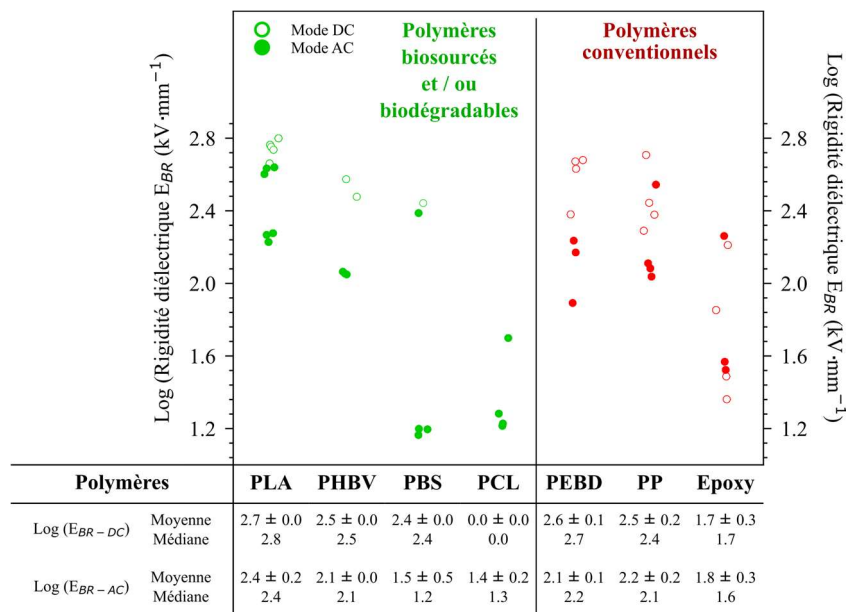


Figure 2.15 : Synthèse bibliographique de la rigidité diélectrique E_{BR} de polymères biosourcés et/ou biodégradables, et de polymères conventionnels. Les valeurs en mode AC sont mesurées à 100 Hz

- En mode AC, les valeurs E_{BR} médianes et moyennes des polymères biosourcés et/ou biodégradables sont comprises entre 16 et 250 $\text{kV}\cdot\text{mm}^{-1}$, les valeurs maximales sont obtenues pour le PLA et les valeurs minimales pour le PBS et le PCL.

- La rigidité diélectrique dépend du courant électrique appliqué, le mode AC étant plus sévère que le mode DC pour le matériau. Le PLA et le PHBV, par exemple, ont montré des valeurs moyennes et médianes environ deux fois plus faibles pour le mode AC que pour le mode DC.
- Le PLA et le PHBV ont donné des résultats similaires à ceux de leurs équivalents synthétiques, le LDPE et le PP, les rendant aptes à être utilisés dans des champs électriques intenses.

2.3. Dielectric properties of biobased polymers – A review

Morgan Lecoublet^{1,2}, Raphaël Lack², Mohamed Ragoubi¹, Nathalie Leblanc¹ and Ahmed Koubaa²

¹ UniLaSalle, Unité de Recherche Transformations et Agro-Ressources (ULR 7519 UniLaSalle-Université d'Artois), Mont-Saint-Aignan, France

² UQAT, Campus de Rouyn-Noranda, 445, boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

*Correspondence to: morgan.lecoublet@unilasalle.fr; mohamed.ragoubi@unilasalle.fr,

2.3.1. Abstract

In a world increasingly demanding materials for electrical and electronic applications, biobased materials are a welcome opportunity to achieve a sustainable economy and limit our dependence on petrobased materials. This review proposes an analysis of biobased polymers and their dielectric performance for suitable applications. Three different strategies are proposed to promote the application of such materials. Polymer blending combines the properties of different polymer matrices in a single material. Composites based on cellulosic fillers can improve the mechanical properties of biobased polymers, which are generally mediocre while retaining low dielectric properties. The third strategy concerns using 3D printing to rethink the design of biobased materials and adjust their dielectric properties. The last part of the review presents the various applications proposed in the literature. This review highlights that achieving 100 % biobased materials that retain biodegradation potential without cytotoxic particles, biobased polymers would be well suited to electrical insulation and low-dielectric-constant (low-k) applications.

2.3.2. Résumé en français

Dans un monde de plus en plus demandeur de matériaux applicables en électricité ou en électronique, les matériaux biosourcés sont une opportunité bienvenue pour atteindre une économie durable et de limiter notre dépendance aux matériaux pétrosourcés. Afin d'y voir plus clair, cette revue propose une analyse des polymères biosourcés ainsi que leurs performances diélectriques pour une application adaptée. Trois stratégies différentes sont proposées pour promouvoir l'application de ces matériaux. Les mélanges polymériques permettent de cumuler les propriétés de différentes matrices polymériques en un seul matériau. La réalisation de composites à base de charge cellulosiques permet d'améliorer

les propriétés mécaniques des polymères biosourcés, notoirement faibles, tout en gardant des propriétés diélectriques basses. La troisième stratégie concerne l'utilisation de l'impression 3D comme outil afin de repenser la conception des pièces et ajuster leurs propriétés diélectriques. La dernière partie de la revue présente les différentes applications proposées dans la littérature. Cette revue a permis de mettre en lumière que pour atteindre une philosophie de matériaux 100 % biosourcés gardant un potentiel de biodégradation sans particules cytotoxiques, les polymères biosourcés seraient parfaitement adaptés dans des applications d'isolation électrique et à faible constante diélectrique (low-k).

2.3.3. Introduction

In an emerging bioeconomy and public awareness context, biobased polymers represent a future niche in the industrial sector with strong dynamic growth. Conventional polymers appeared in our societies at the beginning of the XXth century and have been strongly democratized. Even if they have interesting properties, good production capacities, and processing easiness, their petroleum dependency and deplorable environmental impacts make them incompatible with sustainable economic development. In this context, biobased and/or biodegradable polymers are more adapted than conventional polymers due to their numerous ecological benefits, such as accelerated biodegradation capacities and biocompatibility properties, with a virtually unlimited production capacity (Deshmukh et al., 2017; Filimon et al., 2019; Hegde, 2017; Hirai et al., 2007; Mano and Niarova, 2003; Platnieks et al., 2020). In 2023, the "European Bioplastics" association forecasted a bioplastics production of 7,43 Mt for 2028. 62 % of this production is biobased and biodegradable, as shown in **Figure 2.16a**) (European Bioplastics, 2023a). An increase of 340 % over 2023 production is planned. These new materials have a strong position in sectors using conventional polymers, such as food packaging, consumer goods, agriculture, and construction (**Figure 2.16b**). The dielectric field represented in 2023 about 87,2 kt of bioplastic and is growing exponentially (European Bioplastics, 2023b).

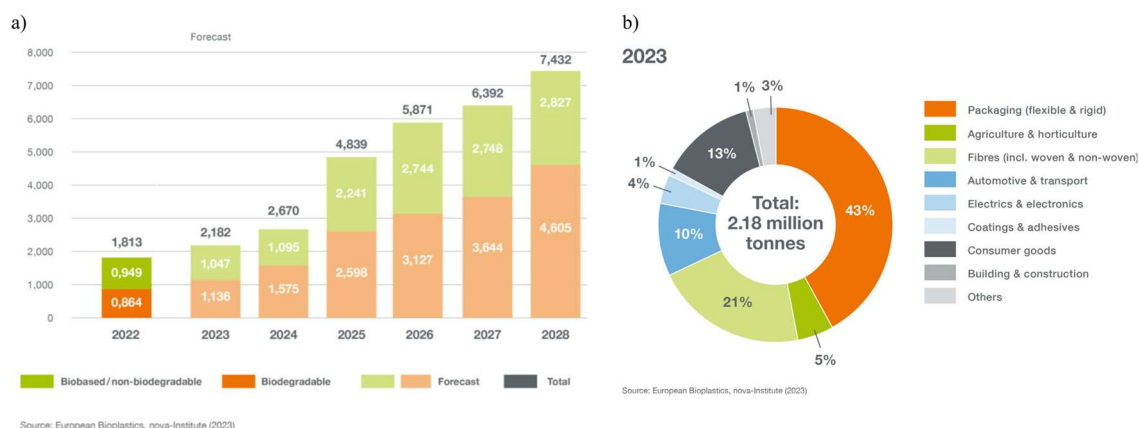


Figure 2.16 : a) Global production capacity of bioplastics and forecast for 2028, b) Distribution of bioplastics production in 2022 by applications fields (European Bioplastics, 2023a, 2023b)

In the dielectric field, many applications exist, such as electrical insulation and conduction (Barbosa et al., 2018; Nakatsuka, 2011), radio wave-absorbing materials (RAM) (Boss et al., 2020; Thomassin et al., 2008), and printed circuit boards (PCB) (Kosbar et al., 2000; Yuen et al., 2020). Polymers with a low dielectric constant can be used to manufacture thin films with high breakdown strength and high-temperature stability. The growth of biobased composites and the limitation of fossil resources create a favorable context for developing new biobased and/or biodegradable structures suitable for many dielectric applications (Kosbar et al., 2000). Although work has already been done in this area of materials science, numerous limitations of biopolymeric matrices still exist to benefit entirely from the dielectric performances of these new materials. Several research teams have focused on their development and optimization to investigate the dielectric performance of biocomposite materials further.

The present review will focus on integrating these new materials into dielectric applications. The following section analyzes different parameters that can influence the dielectric properties of biobased materials, using polymer blending, the creation of biocomposite via the addition of cellulosic micro- or nanofillers, or innovative processing techniques such as 3D printing. Finally, different applications of such biobased materials will be presented.

2.3.4. Biobased polymer improvements for dielectric applications

Biobased polymers have great potential for dielectric applications, but they are subject to several limitations compared with synthetic polymers, such as low thermal stability and relatively high polarity. Some improvement tactics already used in polymers can be considered to facilitate their integration into the dielectric field. In this section, we will focus on three strategy paths from both a material and a process point of view.

2.3.4.a. *Influence of polymer blending strategy*

A polymer blend combines two or more polymers in a single material, providing specific and tuned properties to the final material. Different morphologies can be obtained depending on polymer compatibility. Two polymers are compatible if they have similar surface tensions. A too-great surface tension difference makes them immiscible (Ajitha A.R. and Thomas, 2020). Blends of immiscible polymers form differentiated morphologies with visible phases, depending on their component proportions, as shown in **Figure 2.17**. When one component forms the main constituent, the blend exhibits a "sea-island" morphology, forming inclusions of the minority polymer ("island") into the main polymer ("sea") (Gasmi et al., 2019). This morphology can be applied to reduce polylactic acid's (PLA) brittleness (Larguech et al. 2021).

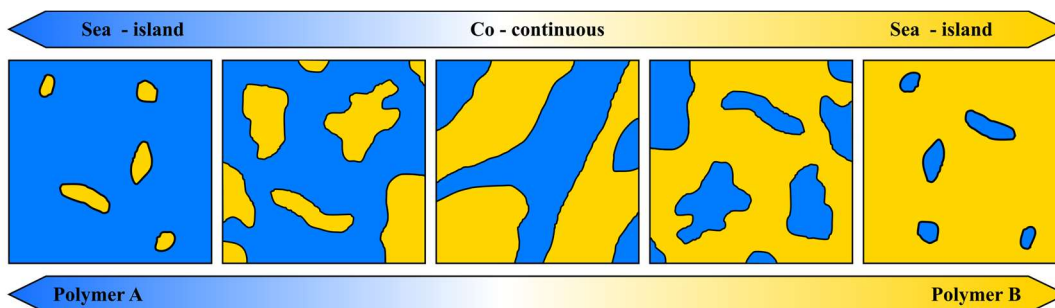


Figure 2.17 : Morphologies of immiscible binary blends in function of their ratio

A co-continuous morphology is present when the two polymers are at comparable levels, forming two interconnected and interpenetrated continuous structures. This morphology is highly desired in the electric field since creating a composite with good mechanical and conductive properties with the appropriate matrixes is possible. Nowadays, several blends have been studied and produced, presenting a range of properties capable of covering a

wide spectrum of specific needs. Two types of biobased polymer blends could be considered: to improve the material conductivity or to provide new functionality.

- *Case of insulating:insulating blends*

In the dielectric field, the case of insulating:insulating blends mainly involve the addition of complementary properties. Concerning lowly-polar polymeric blends, Torğut and Gürler (2021) observed blends of PLA and an unknown polyhydroxyalkanoate (PHA) with different proportions. They noted that at room temperature and 10 kHz, PLA-rich PLA:PHA blends possessed a higher dielectric constant and electrical conductivity. Measured at 10 kHz, a blend with a weight content of PLA (W_{PLA}) = 30 % had an electrical conductivity in the alternative current mode (σ_{AC}) of $1,1 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$ and the blend with a $W_{PLA} = 70 \%$ had a σ_{AC} of $3,9 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$. These values were within the range of electrical insulators, despite the co-continuous morphology that could promote electrical conduction phenomenon. The proposed blends were cost-effective and can be easily produced, validating their applications in electronics, packaging materials, and biomedical applications requiring low dielectric properties. To minimize the processing difficulties of polyhydroxybutyrate-co-valerate (PHBV) and the low heat deflection temperature of PLA, Gasmi et al. (2019) focused on the production of PLA:PHBV blends. They noted that the dielectric constant (ϵ') of the PLA:PHBV blend varied proportionally with the proportion of PLA and PHBV, a behavior analogous to a rule of mixtures. However, the α -relaxation of PLA and PHBV measured by BDS seemed not affected by the blend constitution, indicating that PLA and PHBV were immiscible. This statement was confirmed by scanning electron microscopy (SEM) analysis. Finally, mechanical properties did not follow a rule of mixture, probably due to the specific sea-island morphology observed.

Adding a low amount of polybutylene succinate (PBS) to PLA can improve the PLA toughness. By BDS analysis, Larguech et al. (2021) conceived such blends and observed partial miscibility between PLA and PBS. Adding PBS into a PLA matrix (blend ratio PLA:PBS of 98,76:1,24) decreased the ϵ' at low frequencies and temperatures. It was associated with the partial miscibility of PLA:PBS blends. In addition, the dielectric loss ϵ'' analyses showed a new relaxation, non-existent in neat PLA. This β -relaxation came

from a twisting motion of the PLA main chains linked to the observed partial miscibility. Blending PBS and PLA increased their electrical insulating properties slightly, according to Sivanjineyulu et al. (2018). Adding 10 % of PLA into PBS not only increased the Young's modulus of PBS, but also brought a slight surface resistivity increasing. PLA, PBS and PLA:PBS blend showed a surface resistivities of $1,1 \cdot 10^{13}$, $4,5 \cdot 10^{13}$, and $4,1 \cdot 10^{14} \text{ sq}^{-1}$, respectively.

Concerning apolar/polar blends, Mishra et al. (2021) designed PLA:polyvinylidene fluoride (PVDF) blends for broadening the application of piezoelectric PVDF. At 1 kHz and room temperature, PLA presented a ϵ' of 4,5 and PVDF a ϵ' of 9. Adding PVDF into PLA increased the dielectric constant of the latter. However, the blend containing 70 % PVDF showed a dielectric constant of 10,5, higher than its constituents. The authors suggested that a particular ionic interaction between PLA and PVDF could facilitate the apparition of interfacial polarization and, as a corollary, increased the polarization potential an offering a potential application for polymer film capacitors. Elsayy et al. (2016) studied a PLA:chitosan (CS) blend to widen the PLA application field by apporring antibacterial and barrier functionalities. At 10 kHz and 40 °C, neat PLA showed a ϵ' of 2,7 and the PLA:CS containing 5 % of CS a ϵ' of 4. Moreover, the dielectric loss showed a broadening of the α -relaxation of PLA with the addition of CS. This enhancement of dielectric properties was associated with the chemical structure of CS, which is more polar than PLA. A deeper dielectric analysis of the imaginary part has proven that CS gave to PLA a more “fragile” behavior than PLA, due to a decrease in chain mobility of PLA, and was associated with a hydrogen bonding occurring between hydroxyl/amino groups of CS and carbonyl groups of PLA.

- *Case of insulating:conductive blends*

Blending a conductive polymer with a biobased polymer can functionalize the latter by enhancing the material's electrical conductivity. In recent literature, polyaniline (PAni) has been mainly used to improve biobased polymer electrical conductivity (Ashraf et al., 2020; Shahdan et al., 2020; Wibowo et al., 2020; Wong et al., 2020). To find alternatives to the current costly and toxic antistatic agents like carbon black (CB) and titanium dioxide (TiO₂), Wong et al. (2020) proposed adding PAni to improve the PLA electrical conductivity. The surface resistivity of PLA can be decreased from $1,2 \cdot 10^{12}$ to

$4,3 \cdot 10^8 \Omega \cdot \text{sq}^{-1}$ with a W_{PAni} up to 20 %. However, the authors recommend not exceeding a W_{PAni} of 15 % to meet the suggested standard antistatic range. Moreover, a too high PANi content created aggregates that hindered the full potential of such polymers. Shahdan et al. (2020) studied a PLA blend toughened by natural rubber (mNR) and blended with low levels of PANi (up to $W_{\text{PAni}} = 0,11$ %). Alongside an improvement in mechanical properties, an improvement of the PLA:mNR system's conductivity was observed. The system without PANi showed a conductivity of $3,8 \cdot 10^{-11} \text{ S} \cdot \text{cm}^{-1}$ and the system containing $W_{\text{PAni}} = 0,11$ % a conductivity of $1,2 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$, approaching the values observed for semiconducting materials. Even at $W_{\text{PAni}} = 0,03$ %, a 77 % conductivity improvement was observed compared to the neat system. This significant improvement in conductivity despite a very low loading rate was associated with a preliminary sonication step, which efficiently dispersed the PANi into the PLA:mNR blend.

Although not biobased, PANi is a biocompatible polymer and a potential candidate for polymer blends with a biobased polymer for biomedical applications (Ashraf et al., 2020; Wibowo et al., 2020). Electrospinning is a suitable processing technology for medical applications, providing a lightweight and porous material with good specific surface area. Ashraf et al. (2020) proposed an electrospun PLA: PANi with good electrical performance and capable to undergo a gamma irradiation sterilization process. The authors noted an improvement in electrical conductivity with the addition of PANi. A $W_{\text{PAni}} = 5,55$ % multiplied the electrical conductivity of PLA by 30000, up to $5,4 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$. The obtained conductivities would be sufficiently high to target the conduction of electrical signal for tissue engineering applications. Recently, Wibowo et al. (2020) 3D-printed a polycaprolactone (PCL) blend with low levels of PANi for bone tissue engineering. This polymer blend can create electroactive scaffolds to optimize cell viability. **Figure 2.18** shows the multiphysical properties of the PCL: PANi blend. In addition to improving mechanical properties compared with neat PLA, adding PANi significantly increased electrical conductivity, from $1,1 \cdot 10^{-11}$ to $2,8 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for a $W_{\text{PAni}} = 2$ %. The observed conductivity was close to cortical and cancellous bone electrical conductivities, which could facilitate bone healing. Compressive Young's modulus and compressive strength have also presented an enhancement due to the PANi addition. However, exceeding a $W_{\text{PAni}} = 0,1$ % resulted in a cytotoxic effect of PANi and thus inhibited its

benefits. This study indicated that by using 0,1 % PANi in a PCL matrix, scaffolds with optimal properties for application in bone tissue can be achieved.

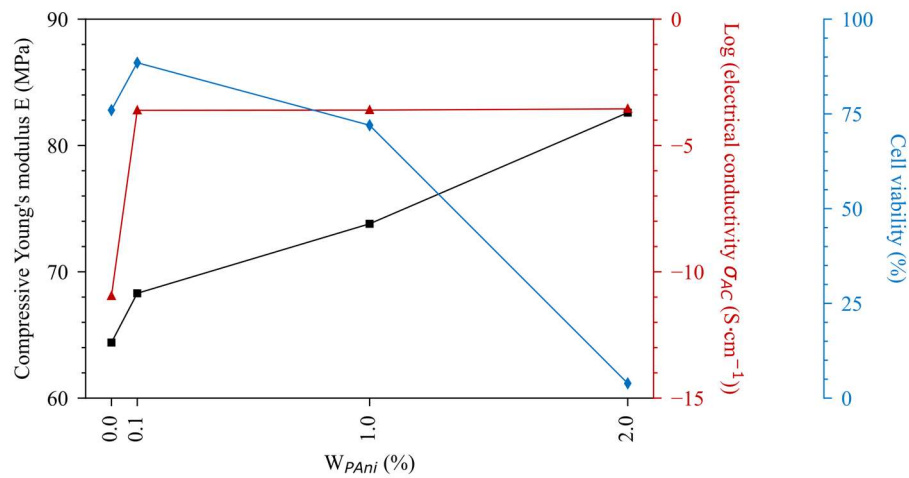


Figure 2.18 : Mechanical, biological and electrical conductivity properties of PCL: PANi blends (Wibowo et al., 2020)

2.3.4.b. Influence of biobased composite strategy

Another way of altering the biobased polymers' properties is by adding fillers to produce composites. In the field of biobased polymers, this mainly involves the use of microfillers or nanofillers. It mainly affects mechanical properties, depending on the form factor of the added filler. In the case of biobased polymers, adding biobased fillers is more appropriate than other fillers for maintaining the philosophy of a 100 % biobased material while keeping the matrix's potential biodegradability. This section presents cellulose fillers at the micro and nanoscale, used for dielectric applications.

- Case of micro-sized cellulose fillers

Microfillers possess a size within the micrometer range. In the field of biobased fillers, the main used shapes are short-fiber fillers, i.e., fillers with a needle-like shape. In their paper, Larguech et al. (2021) went further in their research on PLA:PBS blends by adding jute microfibers. They noted an increase in both the dielectric constant and the dielectric loss, which would be due to the addition of polar groups according to Fourier-transform infrared spectroscopy (FTIR) analysis. In addition, the strength of the Maxwell-Wagner-

Sillars (MWS) polarization increased with the addition of jute microfillers. The authors associated this increase with a decrease in matrix crystallinity due to the addition of charge hindering chain mobility. By comparing PLA:sisal biobased composites with neat PLA, Badia et al. (2017) noted that adding sisal increased the dielectric constant by adding hydrogen bonds (**Figure 2.19**).

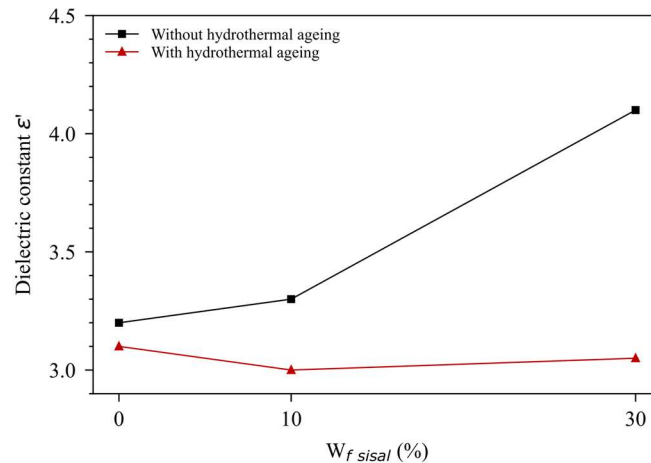


Figure 2.19 : Dielectric constant ϵ' of neat PLA and PLA:sisal biobased composite measured @ 20 °C and 100 Hz (Badia et al., 2017)

Measured at 20 °C and 100 Hz, ϵ'_{PLA} increased by 30 % with the addition of $W_{sisal} = 30$ %. Furthermore, an interaction between sisal's hydrogen bonds and PLA increased the “fragile” behavior of the latter due to a hindering of the chains' mobility. A hydrothermal aging test revealed increased PLA crystallinity due to decreased PLA chain length. This crystallinity variation decreased both the dielectric constant and cold crystallization intensity. The crystallinity enhancement also led to an increase in PLA's “fragile” behavior. Dalai and Parida (2022) irradiated Luffa fibers for application in a PLA matrix. Since the fibers are more polar than the PLA matrix, they increased the dielectric constant of the material, as well as the dielectric loss at low frequencies. These observations were consistent with the rest of the literature (Badia et al., 2014; Khouaja et al., 2021; Larguech et al., 2021). The influence of the gamma irradiation dose absorbed by the microfibers positively influenced the dielectric constant. According to the authors, gamma-irradiation broken down the cellulose polymer chains, allowing more polar functions at the surface. Adding Luffa fibers also increased the σ_{AC} conductivity and the severity of irradiation absorbed by the fibers. In either case, this was explained by the increased polar functions available. The authors noted that such biobased materials could replace barium strontium

titanate (BST) for several applications, such as capacitors, phase shifters, dielectric resonator oscillators, and biomedical electronic devices. Yakubu et al. (2020) filled polycaprolactone with rice husk and studied the size of the charges on the dielectric properties. As well as showing better tensile and impact strength, biobased composites favoring smaller fillers promoted the dielectric constant and dielectric loss at gigahertz frequency. Measured at 10 GHz, 200 μm - and 1000 μm -sized rice husks biobased composites had a dielectric constant of 3,4 and 2,2, respectively (**Table 2.2**). This result may be due to the greater specific surface area of small charges, favoring MWS polarizations. As Dalai and Parida (2022) pointed out, a larger specific surface area gave more polar groups available at the surface of the charges. The authors also suggest this may be due to better dispersion and reduced internal porosity.

Table 2.2 : Dielectric properties of Neat PCL and PCL:rice husks measured at 10 GHz (Yakubu et al., 2020)

Samples	Dielectric constant ϵ'	Loss factor ϵ''
Neat PCL	1,91	0,31
200 μm	3,40	0,59
400 μm	2,81	0,50
800 μm	2,51	0,44
1000 μm	2,20	0,37

Concerning wood-based microfillers, Drakopoulos et al. (2020) studied thermoplastic starch modified with microfibrillated cellulose (MFC), with $W_{\text{MFC}} = 10$ and 20 %. At 1 kHz and 30 °C, neat thermoplastic starch (TPS) exhibited a ϵ' of 20. Adding MFC fillers increased the dielectric constant, reaching 60 in $W_{\text{MFC}} = 10$ %. However, a $W_{\text{MFC}} = 20$ % gave a ϵ' of 40. The authors explained these results by the architectural difference between the linear form of cellulose and the helical form of starch, leading to more water being attracted by cellulose. A higher water absorption could hinder the orientation of polar groups for the biobased composite containing 20 % MFC and thus reduced the dielectric constant. At 1 MHz, however, TPS presented a higher ϵ' at 30 °C than biobased composites. The authors noted that this might be explained by the greater number of free hydroxyl groups (which do not form hydrogen bonds with water) in the starch, enabling a greater polarization potential than in biobased composites. During his thesis, Hegde (2017) also proposed to use MFC, in a PLA matrix. Compared to neat PLA, MFC strongly impacted the dielectric constant, dielectric loss and AC conductivity at low temperatures.

For example, at 20 °C and 0,01 Hz, a $W_{MFC} = 18$ % biobased composite showed a dielectric constant of 7,4 compared to the 3,3 of neat PLA. Moreover, at the same conditions, the σ_{AC} increased over 100 times with the incorporation of MFC.

- *Case of nano-sized cellulose fillers*

Nanocellulose corresponds to two fillers obtained from cellulosic biomass nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). This cellulosic biomass can come from various plants (from wood to sugar beet, including cotton, sisal, ramie, palm and hemp), bacteria and marine animals like tunicates (Ten et al., 2012). This biomass must first be bleached to obtain the various cellulosic fillers. Ten et al. (2012) investigated the influence of NCC on the dielectric and mechanical properties of PHBV-based bionanocomposites. Measured at 1 Hz and at room temperature, the ϵ' increased from 2,1 for neat PHBV to 4,2 at a $W_{NCC} = 2,3$ %. Above this filler content, ϵ' decreased to a value of 2,5. However, for the same conditions, electrical conductivity was positively influenced for all filler content tested and raised from $1 \cdot 10^{-14} \text{ S} \cdot \text{cm}^{-1}$ to $9 \cdot 10^{-14} \text{ S} \cdot \text{cm}^{-1}$ with NCC content of up to 4,6 %. This permittivity increasing can be explained by the presence of hydroxyl groups on the nanofiller surface. At $W_{NCC} > 2,3$ %, the authors suspected the presence of nanofiller aggregation, which reduced the specific surface area of NCC and decreased the MWS polarization power. Complementary dielectric and mechanical analyses confirmed the presence of an optimum NCC content of between 2 and 2,3 %. Bonardd et al. (2018) studied the dielectric properties of a CS:NCC biobased composite. At frequencies < 30 Hz, adding 1 % by weight of NCC increased the ϵ' of CS. It can be explained by the MWS polarization phenomena promoted by the integration of NCC, increasing the heterogeneity of the biobased polymer. This phenomenon is consistent with the previous analyses. However, for frequencies > 30 Hz, the ϵ' of the bionanocomposite was lower than that of neat CS due to the more polar character of the CS. The loss factor was also higher for bionanocomposites, due to the increased MWS relaxation phenomenon. The proposed materials would be suitable for potential applications as capacitor devices.

Silva et al. (2021) proposed a coated-NCC strategy to improve the electrical conductivity of natural rubber. The addition of PANi-coated NCCs considerably increased the rubber's

electrical conductivity in the DC mode (σ_{DC}), from $1,3 \cdot 10^{-14} \text{ S} \cdot \text{cm}^{-1}$ for neat rubber to $8,2 \cdot 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ for a rubber filled with 7 % PANi-coated NCC. A percolation threshold appeared for W_{NCC} between 5 and 7 %, caused by the interconnection of the nanofiller network. This percolation was also found in AC mode. These results were consistent with a theoretical model developed by the authors based on a 2D projection of the Drude and Dyre models. These PANi-coated NCC-filled rubbers have attractive potential applications as capacitors for electroactive materials and dielectric gates for field-effect transistors. Ladhar et al. (2017) compared the dielectric properties of natural rubber and NCC or NFC nanocomposites obtained from date palm stalks. The authors noted that NCC-based nanocomposites had a higher dielectric loss than NFC-based nanocomposites, which can be associated with a higher specific surface area of NCCs. The lower interfacial polarizations observed for NFC showed a better compatibility of the latter with the matrix. The presence of residual hemicellulose and lignin on NFCs may act as a compatibilizer with the matrix, which explains these results. Dynamic mechanical analysis also led to this statement, as the storage modulus was higher, and the loss modulus was lower for NFC than NCC. At 25 °C and 1 Hz, neat natural rubber, natural rubber filled with 2,5 % of NCC and natural rubber filled with 2,5 % NFC presented a storage modulus of 0,55, 2,51 and 6,11 MPa respectively.

Jasim and Ali (2019) investigated nanosized biochar, a pyrolyzed-treated biomass filler, into a plasticized PLA. Biochar is an interesting filler as it has a very large specific surface area, making it suitable for storing molecules such as carbon dioxide. The electrical conductivity gradually increased with the weight content of biochar. Plasticized PLA showed an electrical conductivity at room temperature of $1,46 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$ and biobased composite with $W_{\text{biochar}} = 10 \%$ of $6,1 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$ (**Figure 2.20**), which corresponds to suitable values for anti-static film application.

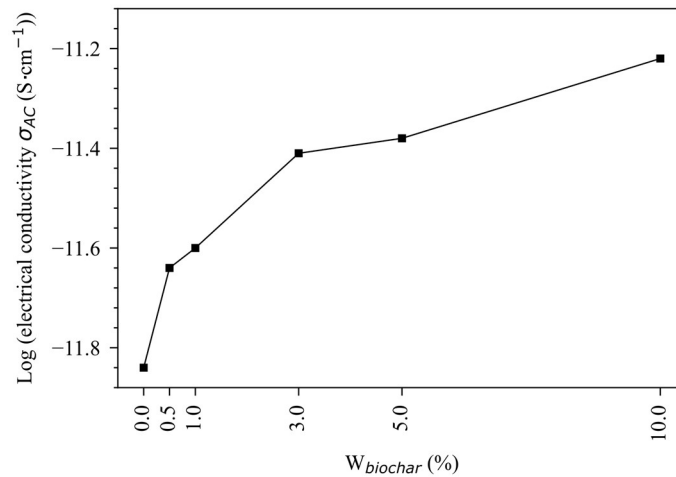


Figure 2.20 : Log (electrical conductivity σ_{AC}) of plasticized PLA filled with nanosized biochar (Jasim and Ali, 2019)

2.3.4.c. *Influence of processing - Case of 3D printing process*

3D printing, or additive manufacturing, revolutionized the creation of physical objects by superimposing layers of material based on 3D digital models. This technology offers immense production, design, and architectural creation possibilities, enabling complex and customized creations. Research into photopolymers usable for 3D printing began in the 1960s at the Battelle Memorial Institute, inaugurating the widely used stereolithography (SLA). The first commercial SLA printed was produced in 1988 by 3D Systems, and the first Selective Laser Melting printer was proposed in the 1990s by Carl Deckard (Su and Al'Aref, 2018). In 1989, S. Scott and Lisa Crump founded Stratasys and patented fused deposition modelling (FDM), a form of rapid prototyping. Around 2005, open source projects such as RepRap and Fab@Home emerged to offer affordable and accessible 3D printers to a wider range of users (Kundu and Mandal, 2022). Thanks to considerable emulation from the research, industry, and the public, various 3D printing technologies are now available and resumed in **Table 2.3**:

- Fused filament fabrication (FFF) is the main used 3D printing technology. The thermoplastic material is melted and then selectively deposited through a nozzle that follows the cross-sectional geometry of the parts to directly produce 3D parts from a computer-assisted design (CAD) model in a layer-by-layer manner (K. Chen et al., 2023; Ngo et al., 2018) (**Figure 2.21a**). These technologies are

very flexible, as many parameters can be tuned for an adapted final material (Figure 2.21b)). However, the numerous tunable parameters make it prone to imperfections and easy printing failures.

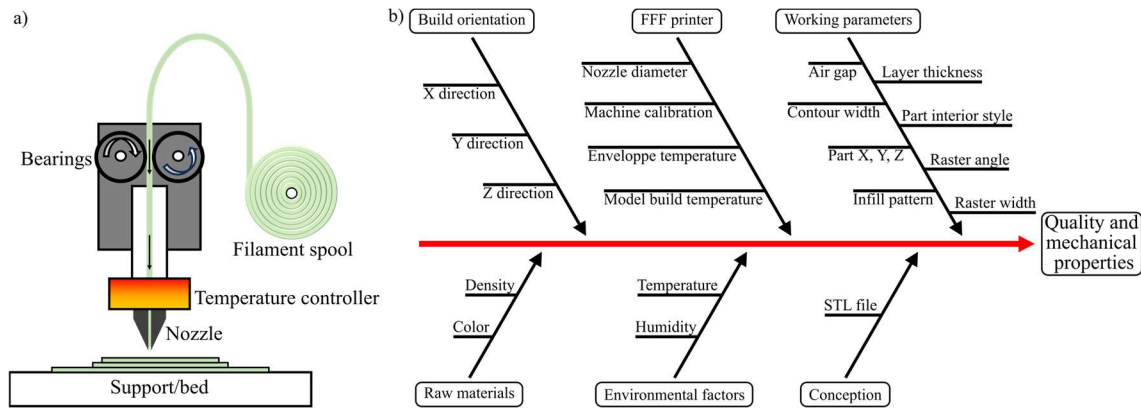


Figure 2.21 : a) Representation of an FFF-type 3D printer, b) Ishikawa diagram of critical process parameter of FFF 3d printing method (Horvath, 2014; Kundu and Mandal, 2022; Su and Al’Aref, 2018; Wohlers and Gornet, 2015)

- Stereolithography (SLA) uses photosensitive resin that solidifies by curing through ultraviolet (UV) laser irradiation to create three-dimensional objects. Like FFF technology, the 3D model is divided into slices and built by successively hardening each resin layer. Although this technology relies mainly on the use of neat resin, some researchers are looking into the possibility of adding additives such as fillers (Jirků et al., 2023; Mhmood and Al-Karkhi, 2023).
- Selective Laser Sintering (SLS) also uses a laser to fuse powdered material to create solid 3D objects. The lack of a preferential printing axis is ideal for complex parts requiring high mechanical strength. The powder used can be polymers, metals, or ceramics. Tabriz et al. (2023) noted that SLS can be an alternative to traditional pharmaceutical oral dosage forms.
- Inkjet 3D printing uses special printers to create objects by depositing droplets of liquid material in successive layers and hardened by UV light. This method offers a variety of materials and accurate color printing, but the surface resolution may be lower and the printing speed slower, sometimes requiring additional post-

processing. This technology can be suitable for the fabrication of microlenses (Magazine et al., 2022).

Table 2.3 : Advantages and drawbacks of the main 3D printing technologies

	Advantages	Drawbacks
FFF	Low production costs, Fast and simple production process, Developed and reliable technology (K. Chen et al., 2023; Chohan et al., 2017; Tabriz et al., 2023)	Poor surface finish (Chohan et al., 2017)
SLA	Developed and reliable technology, complex shape and fine detail, high material variability (Kundu and Mandal, 2022; Mhmood and Al-Karkhi, 2023)	Limited resin shelf life, environment unfriendly, needs a postcuring process, no color printing, (Kundu and Mandal, 2022; Mhmood and Al-Karkhi, 2023)
SLS	No structural support required, porosity control, complex geometry, dimensional control, inexpensive (Kundu and Mandal, 2022; Tabriz et al., 2023)	Long printing time, necessary powder pre-heating, long cooling time, high roughness (Kundu and Mandal, 2022; Tabriz et al., 2023)
InkJet	High precision, precise optical properties adjustment, mass production possible, little material waste (Kundu and Mandal, 2022; Magazine et al., 2022)	Poor mechanical properties, limited knowledge of ink formulation and printing parameters, expensive (Kundu and Mandal, 2022; Magazine et al., 2022)

As presented, the FFF technology is perfect for the rapid industrialization of biobased materials. This technology gives freedom for part design, so dielectric properties can easily be manipulated (Goulas et al., 2019). The following is a selection of some parameters that vary these properties.

- *Case of infill pattern*

The infill pattern is one of the first parameters that can be modified directly in the software. Its effect on electrical conductivity has already been well-measured. Roumy et al. (2023) noted that electrical conductivity varied according to the raster angle in direct current (DC) mode. Their analysis involved 3D-printed PLA samples containing a $W_{CB} = 21,5\%$. A 0° infill pattern (filament in the longitudinal axis) gave a conductivity of $1,2 \cdot 10^{-1} \text{ S} \cdot \text{cm}^{-1}$ and a 90° infill pattern gave a conductivity of $6,6 \cdot 10^{-2} \text{ S} \cdot \text{cm}^{-1}$. The 75% higher conductivity value at 0° was due to easier electrical conduction when the printed conductive filament was directed from one electrode to another than jumping between adjacent ones. The same observation has been made by Pentek et al. (2020) for PLA-based carbon specimens. Truman et al. (2020) also tested a PLA:CB 3D-printed composite with different infill patterns (0° , 45° , 90° , $0^\circ/90^\circ$ and $-45^\circ/45^\circ$). The findings differ from those of the previous article, however, in that although the raster angle of 0°

had a conductivity almost three times greater than that of 90° ($2,18 \cdot 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ vs. $8,03 \cdot 10^{-3} \text{ S} \cdot \text{cm}^{-1}$), it was the $0^\circ/90^\circ$ case that showed the highest conductivity, with a value of $4,37 \cdot 10^{-2} \text{ S} \cdot \text{cm}^{-1}$. To explain these results, the authors performed Monte Carlo simulations. They hypothesized that cross-ply patterns exhibited lower global resistivity because more conductive paths were present for the current to bypass high local resistance zones due to greater local heterogeneity.

Few literatures exist concerning the effect of the infill pattern on the dielectric constant. Kuzmanić et al. (2023) studied 3 different shapes of 3D-printed PLA: the square, triangular, and corrugated shapes, as shown in **Figure 2.22**. The authors noted that at an infill ratio of 33 %, the square, triangular, and corrugated pattern had a dielectric constant of 2,10 2,05 and 1,78 respectively. At an infill ratio of 66 %, the same patterns showed a dielectric constant of 2,45, 2,12 and 2,57 respectively. At low infill ratios, the corrugated pattern had the lowest dielectric constant. However, the triangular pattern had the lowest dielectric constant at high infill ratios. The authors did not give a reason for such a discrepancy. Still, they noted that it was statistically present, and further measurements with more precise equipment were needed to better understand the reason.

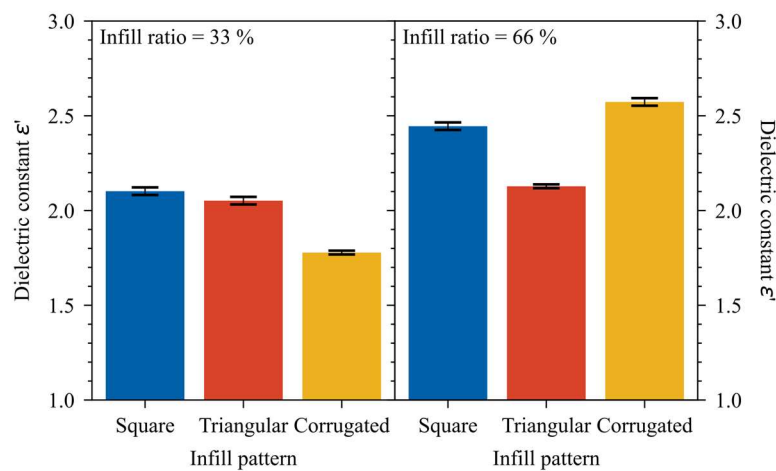


Figure 2.22 : Dielectric constant ϵ' versus the infill pattern of 3D-printed PLA samples (Kuzmanić et al., 2023)

- *Case of infill ratio*

In 3D printing, the infill ratio also plays a crucial role in the properties and performance of the objects produced. The infill ratio refers to the amount of space inside the object filled with material, linked to the total space available. A greater infill ratio increases the mechanical performance but also the total weight of the sample. As dielectric properties are also directly related to material content, it is reasonable to assume that the infill ratio plays a key role in their variation. In addition to investigating the infill pattern, Kuzmanić et al. (2023) also showed that whatever the infill pattern, the infill ratio also played a key role in the dielectric constant, going from 1,78 to 2,81 as example for a corrugated infill pattern, and for an infill ratio from 33 to 100 %, respectively. All the different infill patterns showed increased dielectric constant with increasing material. However, not all internal shapes showed the same behavior. Only the square pattern showed a linear increase with the infill ratio. Colella et al. (2021) showed similar behavior for PLA printed at frequencies close to GHz. A combined increase in dielectric constant and loss factor was noted with an increasing infill ratio. At 20 %, the ϵ' was 1,50 and the ϵ'' was $4,66 \cdot 10^{-3}$. At 100 %, the ϵ' was 2,54 and the ϵ'' was $1,80 \cdot 10^{-2}$. This increase in properties was associated with replacing the air constituting the specimens at low infill ratios with polarizable material. A similar behavior was found with carbon-based PLA, with an increased conductivity as the infill ratio increased (Pentek et al., 2020). By manipulating the infill ratio, Zhang et al. (2016) successfully tuned the dielectric constant of 3D-printed PLA in the GHz frequency range. The authors showed that the ϵ' varied from 1,30 to 2,72 for infill ratios from 10 to 100 % respectively (**Figure 2.23**). A linear regression fitted perfectly with an equation of $0,0159X + 1,1488$ and a correlation factor greater than 0,999. It is worth noting that this equation had 1,15 as a constant term, which is very close to the dielectric constant of air, corresponding to a fully empty material. These observations allowed the authors to produce Fresnel lenses capable of manipulating electromagnetic waves in the GHz range.

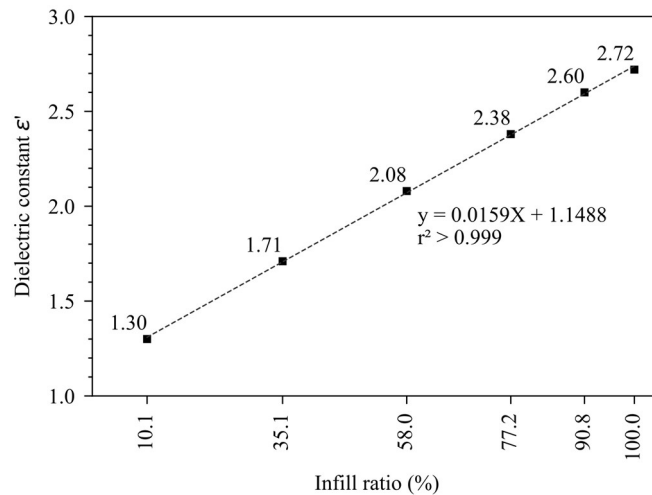


Figure 2.23 : Dielectric constant ϵ' VS infill ratio of 3D-printed PLA (Zhang et al., 2016)

- *Case of layer thickness*

Layer thickness corresponds to the height of a printed layer. Veselý et al. (2018) studied the influence of layer thickness on the dielectric constant and loss factor at 100 Hz of PLA printed materials. The dielectric constant dropped from 2,36 to 1,92 for layer thicknesses of 50 and 200 μm , respectively, with a significant P-Value due to the larger air gap at higher layer thicknesses. On the other hand, the tangent loss ($\tan \delta$) did not vary significantly, as the authors noted that the measurements were difficult to realize and were error-prone. Dielectric strength (E_{BR}) measured at 50 Hz decreased with increasing layer thickness, from 34,1 to 28,7 $\text{kV}\cdot\text{mm}^{-1}$ for layer thicknesses of 50 and 200 μm , respectively. The reason for the decrease in efficiency when using thicker layer thicknesses was associated with a greater proportion of internal air gap. Pentek et al. (2020) also varied the layer thickness between 100 and 400 μm for PLA-based carbon specimens. If the layers are printed in the longitudinal direction, increasing the layer height decreased the conductivity of the composite. In the X orientation and at 27 °C, the electrical resistance value with a layer height of 100 micrometers was $4,63 \cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$, while it was $1,93 \cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 400 micrometers. The decrease of the air gap at smaller layer thicknesses suggested by the previous article could explain the observed phenomenon. However, no significant variation was observed if the layers were printed in the transverse direction. Yang et al. (2019) made the opposite observation. According to them, the electrical conductivity of PLA filled with carbon nanotubes (CNT) increased

with layer thickness. Increasing layer thickness from 100 to 300 μm resulted in a more than 4-times improvement in electrical conductivity. This phenomenon has been associated with a reduction in the number of layer interfaces, which, if they are of poor quality, can generate boundary zones for the electron flow, consequently limiting electrical conductivity.

2.3.4.d. Printing temperature and speed

In addition to investigating the influence of layer thickness, Yang et al. (2019) also noted that extrusion temperature and printing speed play a non-negligible role in electrical conductivity. The printing speed was inversely proportionally linked to a good CNT dispersion, according to complementary SEM analyses. A poor dispersion of the conductive filler inevitably limits the conductivity. Printing temperature was proportionally linked to the electrical conductivity. As mentioned earlier in this section, conductivity depended on the interface quality of the 3D-printed samples. An increase in temperature will promote interfacial adhesion of the layers, reducing the appearance of boundary zones and thus promoting the electron flow.

2.3.5. Biobased materials in the dielectric field application

This part presents a synthetic analysis of recent works studying the possible applications of biobased polymers in electrical insulation/conduction, electronic devices, and electromagnetic shielding.

2.3.5.a. Biobased polymers in electrical insulation and conduction

Electrical insulation encompasses many applications, such as electrical wiring, PCBs, and power system insulators. All three areas require good temperature stability induced by the Joule effect of the current in the vicinity. The IEC 60085:2007 states that at its lowest qualification (Qualification Y), the material should operate under temperatures of 90 °C (International Standard, 2007). These materials must have an increased resistance to thermal combustion and aging. For dielectric properties, insulating materials must have the lowest possible ϵ' and ϵ'' to limit the interaction of the material with the electric field

(Psarras, 2018). If the imaginary permittivity ϵ'' is too high, heating phenomena will occur and could degrade the material. These materials must also have a high resistivity and excellent dielectric strength. For electrical wiring applications, **Table 2.4** presents the dielectric properties of low-density polyethylene (LDPE) and polyvinyl chloride (PVC) polymers, common polymers in these applications.

Table 2.4 : Dielectric properties of LDPE and PVC (Derived from **Figure 2.12**, **Figure 2.13**, **Figure 2.14**, **Figure 2.15** and (Khalaf, 2013; Nakatsuka, 2011; Omnexus, 2022)

Quantities	LDPE	PVC
ϵ' (100 Hz, Room T)	2,3	4,0
ϵ'' (100 Hz, Room T)	$1,6 \cdot 10^{-3}$	$3 \cdot 10^{-2}$
E_{BR} (kV \cdot mm $^{-1}$)	120	10-30
Electrical conductivity (S \cdot cm $^{-1}$)	10^{-16}	10^{-14} - 10^{-11}

Electric cable applications require high flexibility and are currently mainly made of polyethylene (PE), polypropylene (PP), PVC and crosslinked polyethylene (XLPE). PCBs and insulators must be sufficiently rigid to avoid deformation under their own weight at high temperature (Henning et al., 2020). PCBs are mostly made of epoxy: fiberglass and electrical insulators are made of polymers, glass, or ceramic.

- *Case of electrical cable*

Nakatsuka (2011) investigated the interest of PLA-coated electrical cables. He noted that at 60 °C, adding plasticizer into PLA increased the dielectric constant ϵ' from 2,8 to 3,6 and the dielectric loss ϵ'' from $6,4 \cdot 10^{-3}$ to $2,8 \cdot 10^{-2}$. Due to the plasticizer's presence, the electrical conductivity increased from 10^{-15} to 10^{-12} S \cdot cm $^{-1}$. Both cables showed an E_{BR} between 45 and 50 kV for bending stress tests. Unplasticized cables were much more stress-sensitive and suffered electrical failure at 4 times their bending diameter. In contrast, plasticized cables can undergo a self-radiating bending and still achieve a dielectric strength of 25 kV. Plasticized PLA exhibited dielectric properties similar to PVC, confirming the interest in PLA plasticization for applications as an alternative to PVC insulated cable. However, the plasticizer stability over time issues remain to be resolved. To overcome the too-high stiffness of PLA for pertinent use in electrical cables, Shinyama (2018) proposed to blend PLA with polybutylene adipate terephthalate (PBAT), a ductile and biodegradable copolymer. The polymeric blend with a

$W_{\text{PBAT}} = 20\%$ presented a decreased Young modulus and tensile strength. The breaking elongation of PLA was improved by 10 times at room temperature compared to neat PLA. However, the mechanical rigidity of the blend was still greatly higher than LDPE and PVC, two common polymers used in electrical wire (**Table 2.5**). The addition of PBAT respectively decreased and increased the electrical breakdown and dielectric constant of PLA but was still higher better than PVC for electrical insulation application.

Table 2.5 : Mechanical and dielectric properties of PLA, PLA:PBAT 80:20 %, LDPE and PVC (Shinyama, 2018)

Polymer	E (GPa)	Tensile strength (MPa)	Breaking elongation (%)	ϵ' @ 1 kHz	E_{BR} ($\text{kV}\cdot\text{mm}^{-1}$)
PLA	13,2	66,2	7	3,0	416
PLA:PBAT	10,3	40,9	75	3,2	323
LDPE	0,2	13,4	311	2,3	420
PVC	0,04	19,1	756	6,3	165

- *Case of electrical insulator*

Barbosa et al. (2018) developed a 3D-printed PLA electrical insulator combined with an optical voltage sensor (OVS) to develop a new generation of smart grid electrical insulators. 3D printing has successfully produced electrical insulators, validating this technology's interest in rapidly developing smart materials. Finite element simulations carried out on Comsol confirmed that the internal void in the PLA insulator, necessary to insert the crystal measurement system, is the critical area of the system. However, dielectric strength measurement showed that 3D-printed insulators could undergo voltages of 35 kV with no observed degradation. This validates the interest in integrating these new biobased smart isolators for applications targeting a 13,8 kV voltage. Li et al. (2018) also investigated the performances of 3D-printed PLA parts for electrical insulating applications. They compared PLA mechanical and electrical performances with acrylonitrile butadiene styrene (ABS), a common polymer in 3D printing. PLA has better mechanical strength and modulus but has lower impact strength and elongation at break. At 50 Hz and room temperature, they showed comparable dielectric constant ($\epsilon' = 3,25$) and dielectric loss ($\epsilon'' \leq 3 \cdot 10^{-2}$), but the ABS presented better electrical insulation properties ($\sigma_{\text{DC PLA}} = 2 \cdot 10^{-16} \text{ S}\cdot\text{cm}^{-1}$, and $\sigma_{\text{DC ABS}} = 6 \cdot 10^{-17} \text{ S}\cdot\text{cm}^{-1}$), presented in **Figure 2.24**. The dielectric strength of PLA was also slightly lower than ABS, but the

value ($E_{BR} = 30 \text{ kV}\cdot\text{mm}^{-1}$) was still acceptable for low-voltage level system, according to the authors.

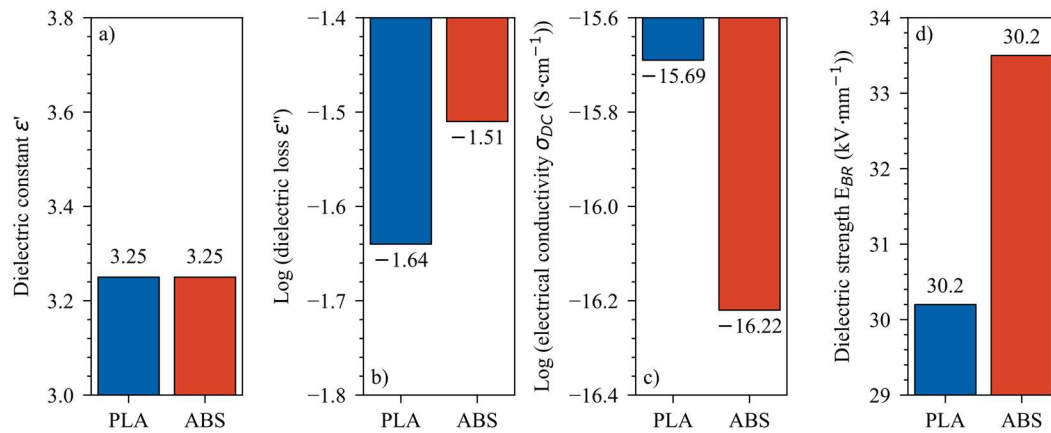


Figure 2.24 : Dielectric properties of 3D-printed PLA and ABS at room temperature.

All tests minus electrical conductivity were performed at 50 Hz (Li et al., 2018)

- Case of PCB

Henning et al. (2019) proposed a PLA:CA ($W_{CA} = 20 \%$) blend filled with zinc pyrophosphate (ZnPP) as a biobased alternative to conventional PCB materials. Dielectric results showed that PLA:CA and PLA:CA blended with $W_{ZnPP} = 5 \%$ had comparable properties to FR4 and FR2 glass:epoxy laminates, except for a significant lower dielectric constant and higher surface resistivity of the binary and ternary blends. They have been successfully used for PCB demonstrators with etching and lamination technologies. However, issues remain to be resolved, such as a warping effect during the component soldering on its surface. In pursuing research for a 100 % biobased PCB, the same team proposed a double-sided PLA biocomposite PCB with a flame-retardant additive (Henning et al., 2020). The galvanization and the engraving of copper circuits on PLA-printed circuit boards have been realized and validated. A copper thickness of $20 \mu\text{m}$ was reached with a galvanization time of 120 minutes. The influence of postcuring was analyzed to improve the mechanical strength of the PCBs at high temperatures. They noted an increase in Young's modulus of 60 %, from 2.1 GPa to 3.6 GPa after a 5-minute postcuring at $100 \text{ }^\circ\text{C}$ due to a more significant crystallization and a lesser mechanical loss above the T_g PLA. By carrying out a controlled postcuring step, they also limit the cold crystallization phenomena that can occur during the use of the final product, facilitating

the use of biobased polymers in PCB at high temperatures. To extend the scope, Nassajfar et al. (2021) investigated the interest of PLA-based PCB from an environmental perspective compared to conventional PCB and other substrates (polyethylene terephthalate (PET) and paper)). They noted that although PLA had to be reinforced with glass fibers ($W_{\text{glass}} = 40\%$) to be sufficiently thermally stable, its environmental impact was similar to PCBs based on PET or paper. Proposed PLA-based PCBs were between 82 % and 97 % less impactful in terms of the different impacts considered than FR4 standard PCB (**Table 2.6**). These results validated the suitability of these materials for electronic applications.

Table 2.6 : Life cycle comparison of FR4-etched copper and PLA biobased composite-silver nanoparticle. The comparison was carried out on 1 m² of four-layer PCB (Nassajfar et al., 2021)

Environmental impact	FR4 – Etched copper	PLA:GF (60:40 %) – silver nanoparticle
Global Warming Potential	34,8 kg CO ₂ eq.	5,2 kg CO ₂ eq.
Abiotic Depletion Potential	525 MJ	84 MJ
Eutrophication Potential	0,29 kg PO ₄ ³⁻ eq.	0,043 kg PO ₄ ³⁻ eq.
Freshwater Aquatic Ecotoxicity Potential	236 kg DCB eq.	42,5 kg DCB eq.
Acidification Potential	0,37 kg SO ₂ eq.	0,041 kg SO ₂ eq.
Ozone Layer Depletion Potential	$5,7 \cdot 10^{-6}$ kg CCl ₃ F eq.	$5,1 \cdot 10^{-7}$ kg CCl ₃ F eq.

- *Case of electrical conduction*

Due to their inherent electrical insulation properties, some strategies must be employed to increase their electrical conductivity. Nanosilver-coated carbon black (AgCB) in PBS can functionalize it by giving attractive electrical conductivity, according to Veranitisagul et al. (2019). Adding 15 % of AgCB into PBS enhanced the electrical conductivity by 20, from $1,7 \cdot 10^{-9}$ to $3,0 \cdot 10^{-8}$ S·cm⁻¹. In addition, microbiological tests showed that such materials inhibited *S. aureus* and *C. albicans* bacteria. The authors proposed numerous applications for these materials, making them suitable for antimicrobial keyboard, antistatic applications, and antifouling paints. Spinelli et al. (2020) added graphene nanoplatelets (GNP) and multiwall carbon nanotubes (MWCNT) into 3D-printed PLA to improve thermal and electrical conductivity, respectively. According to the authors, the shape of the charges played an important role in dielectric and thermal properties. The 1D-shaped MWCNT favored electrical conduction properties. At 100 Hz, the dielectric

constant of PLA with $W_{\text{CNT}} = 12\%$ was multiplied by 1450, and the PLA with $W_{\text{GNP}} = 12\%$ was multiplied by 150 (**Figure 2.25**). In addition, the percolation threshold of σ_{AC} was achieved at lower W_{MWCNT} (between 3 to 6 %) compared to W_{GNP} (between 9 to 12 %). However, the 2D-shaped GNP doubled the thermal conductivity of 3D-printed PLA compared to MWCNT. The authors showed that properties can be tuned according to the filler blend, enabling new multifunctional biobased nanocomposites.

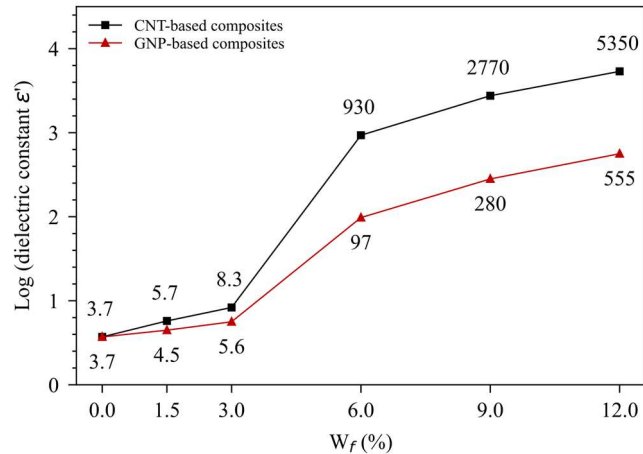


Figure 2.25 : Dielectric constant ϵ' at 100 Hz of neat PLA and PLA-based nanocomposites (Spinelli et al., 2020)

By blending PCL, PANi and barium titanate (BaTiO_3), Peidavosi et al. (2022) produced conductive scaffolds by electrospinning for tissue engineering. BaTiO_3 provided the piezoelectricity properties and PANi provided electrical conductivity properties. Without BaTiO_3 , binary blend with $W_{\text{PANi}} = 5\%$ had a conductivity of $8,1 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$. By subjecting the scaffolds to a cyclic force of 2,66 N and 5 Hz, the addition of $W_{\text{BaTiO}_3} = 40\%$ into the binary blend generated an output voltage of 1,9 V. The mechanical properties of the ternary blends also proved to be superior to neat PCL. In addition, the cell viability of the ternary system was better than the PCL control, due to an improved hydrophilicity of the system and the generation of electrical current. Chen et al. (2019) proposed a foamed PBS:CB composite to produce lightweight composites with high mechanical performance and electrical conductivity for various applications. According to the authors, adding CB nanoparticles reduced the pore size of foamed composites from 24 and 5 μm for neat PBS and PBS biobased composite with $W_{\text{CB}} = 10\%$, respectively. This effect, combined with the reinforcement provided by the CB, explained the improved mechanical strength of foamed composites. The electrical

conductivity of foamed composites increased with CB, and a percolation threshold appeared between $W_{CB} = 3\%$ and 5% . At $W_{CB} = 10\%$, foamed composite gave a density of $0,344 \text{ g}\cdot\text{cm}^{-3}$ for electrical conductivity of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$, validating the interest of such materials for applications requiring both lightweight and conductivity properties.

2.3.5.b. *Electronic device*

- *Case of transistors*

Transistors are electronic devices with 3 inputs/outputs that can control and tune a system's current or voltage. Since the creation of the first bipolar transistor in 1947, new transistors have been developed. Field-effect transistors (FETs) are transistors based on 4 different components: a gate, drain, source, and body (**Figure 2.26**).

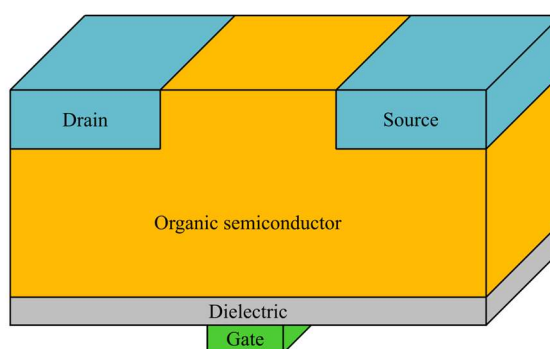


Figure 2.26 : Illustration of a theoretical organic FET (OFET)

The current flow between the source and drain is controlled by adjusting the gate voltage, influencing the body's conductivity (mainly based on a semiconductor). OFETs are organic field transistors, as the semiconductor comprises an organic material. Mattana et al. (2015) have proposed two types of transistors with a PLA part: an organic electrochemical transistor obtained by inkjet printing and an OFET. In the first case, PLA was used as a substrate for the printing step, while in the second, PLA acted both as a substrate and as a bridge between the drain and the source. Electrical and mechanical characterizations validated PLA as a flexible substrate. The recorded transconductance of OECT were promising at $2,75 \text{ mS}$, validating the choice of PLA to replace synthetic substrates. Cho et al. (2018) studied the morphology influence of PLA:poly(3-

hexylthiophene) (P3HT) blends for application in OFET. Blending P3HT into PLA can protect the conjugated polymer from moisture and oxygen. Using a solvent casting process, they noted that the morphology was directly linked to the solvent efficiency for P3HT. A poor solvent for P3HT, like dichloromethane, gave P3HT a nanowire morphology. This morphology provided interesting hole and carrier mobility for OFET applications. Moreover, this morphology offers good mobility even with only 10 % of P3HT through the nanostructured morphology.

Synaptic transistors are transistors based on the OFET structure that can be used to mimic the neurons' synaptic activity. Guo et al. (2018) also proposed using a biobased polymer as an electrolyte for synaptic transistors. A starch electrolyte was prepared, and they observed that an indium tin oxide (ITO):starch electrolyte:ITO sandwich had a capacitance of $0,02 \mu\text{F}\cdot\text{cm}^{-2}$. The proposed system also had a good dissolution capability in deionized water. Lee et al. (2023) investigated using a CS:polyvinyl alcohol (PVA) blend electrolytes for a synaptic transistor. Used in solution, a double layer aluminium:electrolyte:platinum structured capacitor at 100 Hz showed a capacitance of $1,5 \mu\text{F}\cdot\text{cm}^{-2}$. A learning simulation using this kind of synaptic transistor was successfully performed. A neural system was simulated and recognized handwritten digits at a 92 % success rate. These results show that such systems can mimic biological synapse transistors and are expected to provide potential applications for designing new environmental-friendly and biocompatible neuromorphic systems.

- *Case of sensors*

A sensor is an electronic device that converts a physical or chemical quantity into a system's electrical property alteration of the system, such as a variation in its electrical resistance. Accurate measurement of these physical quantities is possible by associating the sensor with an electrical system and a suitable calibration. Sensors can be classified according to the quantity measured. Concerning the humidity sensors, an electrospun cellulose acetate (CA):aluminum bilame sensor was obtained by Meng et al. (2020). The sensor relied on the elongation difference between electrospun CA and aluminum due to the humidity, inducing deformation. By controlling the alignment of the electrospun CA fibers, the authors could control the bilame deformation. The bilame could then be used as an actuator in a circuit for non-contact sensing of the moisture content of a human

hand. In the presence of a nearby finger, the bilame deformed and closed an electric circuit. In addition, the system showed no electrical conductivity degradation of the aluminum part after 5 cycling tests, showing high potential in wearable health monitors and advanced non-contact human-machine interactions. Another humidity sensor was proposed by Parangusan et al. (2021). They used an electrospinning process to produce PLA:PAni-coated ZnO nanocomposites. When this nanocomposite was intercalated between two electrodes, it demonstrated a high capacity to detect water molecules through proton hopping mechanisms. The combined addition of PAni and ZnO into PLA resulted in a relative humidity versus impedance curve with low hysteresis between absorption and desorption curves. Measured at 25 °C, the system featured an impedance variation of 13 M Ω between 20 % and 90 % relative humidity (RH), with response and recovery times of 85 and 120 s, respectively, validating the interest of such systems for humidity sensor applications. Lin et al. (2021) proposed an embedded smart sensor tag encased in PLA to monitor concrete's structural health. The system was based on 3D-printed PLA shells to protect the tags. Sensitivity analyses showed that the PLA shells provided good moisture damage protection for the tags, and the printed shells with a thickness of 3 mm showed the best seeping monitoring capabilities. Once embedded in concrete, the shells protected the tags during compression tests. The authors noted, however, that further research was needed to confirm the results for radio-identification (RFID) applications, but drone applications for unmanned systems monitoring were promising.

Regarding the chemical sensors, Vivaldi et al. (2022) proposed a polymeric sensor for detecting the electrical conductivity of liquids. They conceived a 3D-printed sensor with polystyrene cells and 2*2 cm square PLA:CNT electrodes. The authors found that the system's conductivity varied linearly with the cell length (distance between the two PLA:CNT electrodes) using solutions of 0,05 M potassium chloride (KCl) and a Crison reference solution. The proposed cells determined the conductivity of various bottled water with good accuracy, with similar values to their reported conductivity. The authors pointed out that such sensors can be adapted for ion detection in aqueous and other dielectric media. Junpha et al. (2020) used 3D printing to produce PLA:CNT nanocomposite electrodes filled with copper or zinc oxide (ZnO) for electronic tongue application. 3D printing was used to produce nanocomposites with $W_{\text{CNT}} = 10 \%$ and W_{Cu}

or $W_{\text{ZnO}} = 5 \%$, while maintaining good printability. The 3 different nanocomposites presented different electrical and electrochemical behaviors. The electrical conductivity of PLA:CNT, PLA:CNT:Cu, and PLA:CNT:ZnO nanocomposite presented an electrical conductivity of 1,11, 1,15 and 1,32 $\text{S}\cdot\text{cm}^{-1}$. Used together, they can identify different biochemical such as hydrogen peroxide (H_2O_2), nicotinamide adenine dinucleotide (NADH), potassium hexacyanoferrate ($\text{K}_4\text{Fe}(\text{CN})_6$), while being sufficiently stable over time to create an electronic tongue cost and time-effective for on-site investigation and preliminary observation.

Concerning mechanical sensors, Ma et al. (2022) obtained a foamed polylactide film for disposable sensor applications. Once the film had been subjected to a corona charging method and aluminum-coated, the PLA film showed performances suitable for a pressure or tensile sensor. The systems displayed very good fatigue resistance, with only a slight deterioration after 1 million cycles under a 4.3 kPa pressure, with only a 13 % decrease of the compressive sensitivity compared with the unfatigued value (**Figure 2.27**). The system was applied in-vivo under a shoe and showed a very different load generation depending on the movement applied.

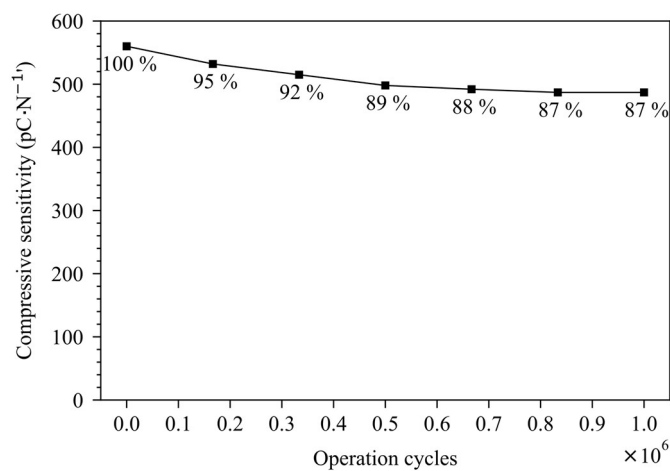


Figure 2.27 : Fatigue test of PLA-based sensor (Ma et al., 2022)

A sensor can also generate its own power. A CS-based self-powered multicomponent triboelectric sensor was made by Ma et al. (2019). A sensor consisting of PET substrate:Kapton:CS film:silver nanowire:PET substrate was used for speed monitoring. The triboelectric sensor can detect a toy car's passage by a voltage variation as a wheel

passes. Using a support vector machine method with a linear kernel model, the team predicted the speed of a toy car with good efficiency, opening their use for speed detection.

- *Case of energy storage*

In electronic applications, energy storage is mainly based on rechargeable batteries. This system relies on reversible electrochemical reactions to store energy. **Figure 2.28a)** shows the schematic diagram of a lithium-ion (Li-ion) battery. In recent years, supercapacitors have been developed to meet the needs of faster energy charge/discharge applications than conventional batteries (schematized in **Figure 2.28b)**).

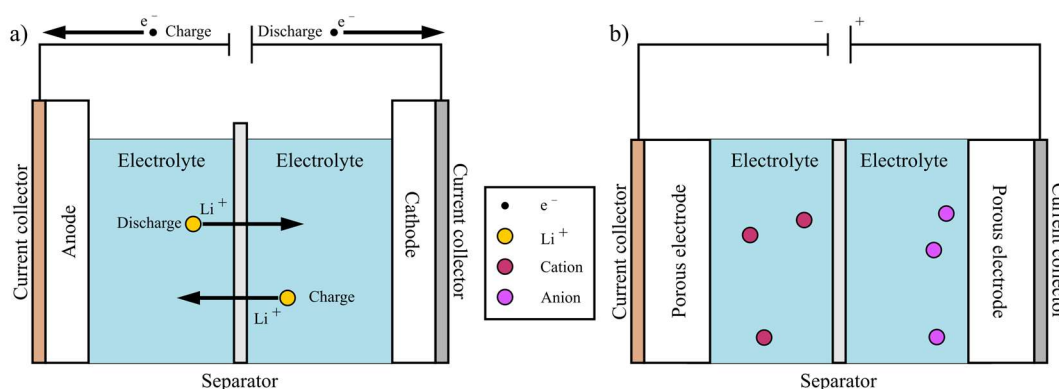


Figure 2.28 : Schematic diagram of a) Lithium-ion battery, b) supercapacitor

Li et al. (2022) coated a foamed PLA with PANi for composite electrodes to produce a symmetric supercapacitor. The foamed PLA presented a porosity of 84 %. By coupling two foamed PLA: PANi electrodes with a PVA: sulfuric acid (H_2SO_4) gel electrolyte, the system delivered a capacitance of around $5,5 \text{ mF} \cdot \text{cm}^{-2}$ when a current density of $0.3 \text{ mA} \cdot \text{cm}^{-1}$ was applied. In addition, the supercapacitor showed good capacitance stability even after 10 000 cycles of charge/discharge. It also demonstrated good performance under bending angles up to 90° , with 66 % of its original capacitance remaining. The authors found that the foamed PLA: PANi supercapacitor had an energy density and power density of $1,89 \text{ } \mu\text{Wh} \cdot \text{cm}^{-2}$ and $35 \text{ } \mu\text{W} \cdot \text{cm}^{-2}$ respectively, values significantly higher than unfoamed PLA: PANi reported in the literature. Fang et al. (2023) also used fabric-based PLA: PANi to produce electrodes. A PVA: H_2SO_4 gel electrolyte was also used to form a symmetrical supercapacitor. Good performance over a wide

temperature range was measured. With a current density of $1 \text{ mA}\cdot\text{cm}^{-2}$, a capacitance of $682,8 \text{ mF}\cdot\text{cm}^{-2}$ and $653,6 \text{ mF}\cdot\text{cm}^{-2}$ was measured at $25 \text{ }^\circ\text{C}$ and $-50 \text{ }^\circ\text{C}$ respectively. Also, good stability after 2000 cycles of charge/discharge was observed for both temperatures. At room temperature, the symmetrical devices showed an energy density of $30,27 \text{ }\mu\text{Wh}\cdot\text{cm}^{-2}$ at a power density of $217 \text{ }\mu\text{W}\cdot\text{cm}^{-2}$, with a capacity to undergo bending up to 180° , which has good application potential in the field of intelligent wearable electronics. Yan et al. (2023) used electrospun CA, on which metal-organic frameworks were anchored to obtain electrodes used in an asymmetric supercapacitor. With a suitable supercapacitor, they achieved a specific capacitance of $175,2 \text{ F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$. In addition, an energy density of $54,8 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ at a power density of $985,5 \text{ W}\cdot\text{kg}^{-1}$ was noted. After 10,000 charge/discharge cycles at a current density of $10 \text{ A}\cdot\text{g}^{-1}$, the supercapacitors retained 91 % of their initial capacity, which, in addition to good flexibility, would enable applications such as artificial skin electronics and flexible portable electronics to be targeted. Mohit and Hashmi (2023) explored using porous PCL for solid-state electrolytes. Once activated by an organic phase, the proposed electrolyte showed a room temperature conductivity of $1,9\cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$. When coupled with an active carbon electrode, derived from sugarcane bagasse to form a symmetrical supercapacitor, a specific capacitance of $170 \text{ F}\cdot\text{g}^{-1}$ at $0,6 \text{ A}\cdot\text{g}^{-1}$ was measured. Moreover, an energy density and a power density of respectively $34 \text{ Wh}\cdot\text{kg}^{-1}$ and $290 \text{ W}\cdot\text{kg}^{-1}$ have been reached. After 10^4 charge/discharge cycles, a loss of 15 % of the initial capacitance was noted while still possessing a coulombic efficiency of 100 %. According to the authors, these measured performances were comparable to PVDF-based electrolytes.

Maurel et al. (2018) used 3D printing to obtain a negative electrode, using PLA, graphite, and a plasticizer for battery application. Adding $W_{\text{plasticizer}} = 40 \text{ \%}$ in PLA provided the best compromise for effective printing with a high W_{graphite} content. The authors successfully produced a negative electrode composite with a weight content of 32,8, 49,8, 13,1 and 4,9 % of PLA, graphite, plasticizer, and carbon nanofibers respectively. This composite achieved an electrical conductivity of $3,8\cdot 10^{-1} \text{ S}\cdot\text{cm}^{-1}$. Furthermore, the 3D-printed disk presented a specific capacity of $200 \text{ mAh}\cdot\text{g}^{-1}$ of active material with a current density of $18,6 \text{ mA}\cdot\text{g}^{-1}$. Optimizations were still required, but according to the authors, this study demonstrated the feasibility of using 3D printing for battery applications. Olmedo-Martínez et al. (2021) realized a PLA:poly(ethylene oxide) (PEO) blend as a solid-state electrolyte for lithium batteries. This blend combined PEO's electrical

conductivity with PLA's mechanical performance. Adding lithium salt to the blend boosted the system's ionic conductivity and counterbalanced the low PLA's electrical conductivity. Such electrolytes exhibited an electrical conductivity of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at $100 \text{ }^\circ\text{C}$. The tests carried out at high temperatures demonstrated that it was possible to make a lithium/metal battery with a solid-state electrolyte based on PEO and PLA capable of exceeding the operating temperature limit of conventional lithium batteries ($\sim 70 \text{ }^\circ\text{C}$). Zhang et al. (2021) also proposed a solid-state electrolyte for a lithium:metal battery. PCL was blended with a lithium salt (LiTFSI) and a lithium aluminium germanium phosphate (LAGP) ceramic. The best conductivity was measured at $W_{\text{LAGP}} = 75 \%$, with a conductivity of $1,7 \cdot 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at $30 \text{ }^\circ\text{C}$. Galvanostatic tests have shown that LAPG also had a positive effect by hindering the growth of lithium dendrites. Electrochemical performances of such system had a specific capacity of $155 \text{ mAh}\cdot\text{g}^{-1}$, with a 96 % retention capacity after 130 cycles. Barbosa et al. (2021) proposed a biobased PHBV:cobalt ferrite (CFO) electrospun membrane separator. The orientation of the fiber obtained influenced the ionic conductivity. With a $W_{\text{CFO}} = 10 \%$, an ionic conductivity of $9,1 \cdot 10^{-3}$ and $5,2 \cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ was reached for random and oriented PHBV:CFO fibers, respectively. However, charge capacity does not appear to be significantly influenced by fiber orientation, around $120 \text{ mAh}\cdot\text{g}^{-1}$ and remaining between $105\text{-}110 \text{ mAh}\cdot\text{g}^{-1}$ after 65 charge/discharge cycles.

2.3.5.c. *Electromagnetic interference shielding materials*

Electromagnetic waves (EM waves) are present in all applications requiring the passage of an electrical current. However, limiting or attenuating these waves for applications such as microwave ovens is sometimes necessary. According to Thomassin et al. (2008) a good electromagnetic interference (EMI) shielding material must have a conductivity higher than $1 \text{ S}\cdot\text{m}^{-1}$ and a dielectric constant as close to air as possible ($\epsilon'_{\text{air}} \simeq 1$) in the desired measurement range. Two strategies can be used to create an effective EMI material based on either conduction or dissipation of the incident wave techniques. The first strategy involves an increase in the conductivity of the composite to improve the material's absorption capacity. The second involves an increase in dielectric loss to convert electromagnetic energy into heat. **Table 2.7** presents a bibliographical summary of some recent articles using biobased polymers for an EMI shielding application.

According to the literature, the technique favoring electrical conductivity was the most favored. In addition, the added fillers were mainly carbon-based nanofillers (CNT or GNP). The best presented results were those obtained by Yang et al. (2021) with a normalized shielding efficiency of $2556 \text{ dB}\cdot\text{mm}^{-1}$, dividing the incident signal by 40000 with only $18 \mu\text{m}$ of thickness, thus meeting the industry-accepted SE requirement of 20 dB. Another point of interest was using a foamed matrix for EMI shielding. This is an attractive strategy, as it reduces the permittivity of the materials by increasing their porosity. Moreover, the formation of porosity in the material favors the percolation threshold of conductive charges at lower weight content levels, which explains the very high nanofiller weight content shown in **Table 2.7** for foamed composite.

Table 2.7 : EMI shielding performances of biobased materials

Matrix	Filler (W_f)	Shielding efficiency SE (dB) @ 10 GHz	Thickness (mm)	Normalized SE ($\text{dB}\cdot\text{mm}^{-1}$)	Ref
PLLA/PDLA/PCL	MWCNT (0.8 %)	17 (SE)	1.5	11,33	Zhang et al., 2017
PHBV	Silver nanowire (5.33 %)	46 (SET)	0,018	2555,56	Yang et al., 2021
PLA/PCL	PIL-modified CNT (8 %)	41 (SET)	1	41	Xu et al., 2022
Foamed PLA	MWCNT (2,5%)	45 (SE)	5	9	Wang et al., 2018
Foamed PHBV	GNP (6 %)	28 (SET)	1	28	Luo et al., 2022
PLLA/POM	MWCNT (10 %)	48.1 (SE)	2	24,05	Li et al., 2020
Foamed PLLA/PDLA	CNT (30 %)	22 (SE)	3,7	5,95	Cui et al., 2017
PLA/PAni textile	-	14 (SET)	-	-	Fang et al., 2023

It should be noted that besides providing good EMI shielding, such biobased materials can offer additional functionality. Adding CNT to foamed PLA also improved its dimensional stability at high temperatures (Cui et al., 2017). At $220 \text{ }^\circ\text{C}$, foamed specimens underwent diameter shrinkage of 15 and 4 % for PLA and PLA:CNT, respectively, as shown by Cui et al.. Fang's team also noted that the PAni coating of PLA fabric can improve their flame retardant properties by enhancing their carbon formation ability (Fang et al., 2023). As the matrix is porous and requires few electrically conductive charges, Wang et al. (2018) noted that their materials could also present good thermal insulation performance, with a thermal conductivity of $27,5 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ with a MWCNT volume fraction of 0,0054 %.

2.3.5.d. *Other applications*

This section will present a few miscellaneous applications that didn't fit into the previous categories but are nevertheless interesting to discuss. A triboelectric nanogenerator was proposed by Zhao et al. (2023). PLA was used in a helicoidal substrate. Pressed by a human hand, the system generated an open-circuit output voltage, short-circuit current, and charge transfer density of 395 V, 28 μA , and 36 $\mu\text{C}\cdot\text{m}^{-2}$, respectively. This power was sufficient to power 300 LEDs connected in series. It could also power small devices such as digital watches when mounted in an electric circuit. Lee et al. (2022) also proposed a PHBV-based triboelectric nanogenerator that can be triggered with an ultrasonic stimulus. By stacking PHBV:PHBV-PEG:magnesium:PHBV sheets, an output voltage of 4,2 V was obtained. The team demonstrated that such a triboelectric nanogenerator can be degraded by ultrasound at an intensity of 3 $\text{W}\cdot\text{cm}^{-2}$, with low cytotoxicity degradation products. These PHBV-based nanogenerators would be ideal for powering in-vivo implantable medical devices while limiting the cumbersome nature of such systems.

3D printing was used to produce PLA:CB composite for Joule heating device by Roumy et al. (2023). They noticed that by adjusting the printing parameters, they could tune the electrical resistance of 70*20*1 mm 3D-printed samples. With a $W_{\text{CB}} = 21,5\%$, they found that specimens printed at an angle of 90° had an electrical resistance 75 % higher than those printed at 0° due to the difficulty of passing electrons between adjacent filaments. On specimens printed at an angle of 0° , when a voltage of 30 V was applied for 200 s, the specimens printed at 0° had a stabilized temperature of 110 $^\circ\text{C}$. In addition, the authors showed that after 10 cycles, the sample temperature reached at a voltage of 30 V was 10 to 15 $^\circ\text{C}$ higher than that of unaged samples. The aging process led to a modification of the internal morphology of the samples, resulting in decreased electrical resistivity.

An electrolyte made of cationic CS and anionic dextran with a mixing ratio of CS:dextran 60:40 and doped with ammonium iodine (NH_4I) was obtained by Aziz et al. (2020). A neat CS:dextran showed a DC conductivity of $5,01\cdot 10^{-10} \text{ S}\cdot\text{cm}^{-1}$, and the CS:dextran with $W_{\text{NH}_4\text{I}} = 40\%$ a DC conductivity of 7 decades higher (**Figure 2.29**). This composite

presented a high ionic mobility, with an ionic transference number of 0,93. Combining this electrolyte with an activated carbon anode and cathode, an energy density and a power density of $3,1 \text{ Wh}\cdot\text{kg}^{-1}$ and $186 \text{ W}\cdot\text{kg}^{-1}$ were respectively reached for a double-layer capacitor application.

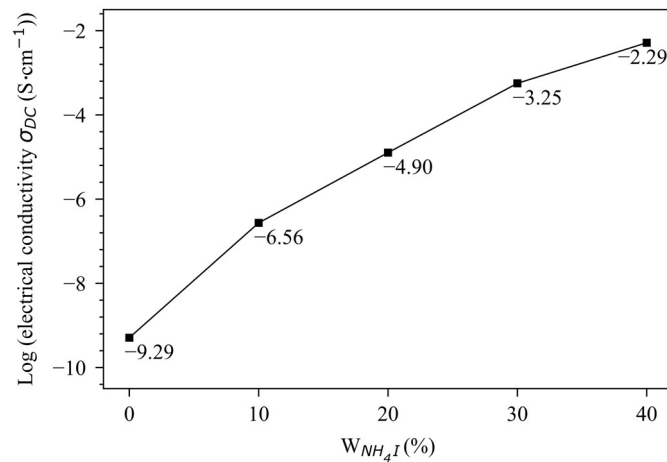


Figure 2.29 : Influence of ammonium iodine on DC conductivity σ_{DC} of CS:Dextran blends (Aziz et al., 2020b)

2.3.6. Conclusion and perspectives

This literature review provided an opportunity to study the dielectric potential of various biobased polymers. Various industrially-applicable strategies are available to modify and facilitate the integration of such dielectric materials. The polymer blend strategy combines the properties of two or more polymers in a final material. Insulator-insulator blends can enhance the multiphysical properties of polymer matrices while retaining high electrical insulating power. Insulator:conductor blends mainly use "conductive" polymers such as polyaniline. One strategy for improving the mechanical properties of the matrix is to create composites by adding fillers. Cellulosic fillers, derived from wood, are very attractive from a sustainable development point of view while only slightly altering the dielectric properties of the materials. Finally, the manufacturing process itself can modify the dielectric properties of materials. Literature results show that varying printing parameters, such as fill ratio and infill pattern, can adjust electrical conductivity and dielectric constant. Furthermore, this process is compatible with the other two improvement strategies.

The last part of the review presents various applications proposed in recent literature. These materials have attractive potential in various applications, from electrical insulation/conduction to electromagnetic shielding, sensors, generators and electrical storage, PCBs, and electrical transistors. However, many applications require the addition of synthetic or non-biobased electrically conductive components to enhance their properties.

2.4. Conclusion de la synthèse bibliographique

Ce chapitre nous a permis de confirmer que l'intégration des polymères biosourcés dans des applications nécessitant une isolation électrique et de faibles valeurs de permittivité est envisageable. Il a été constaté que malgré des valeurs légèrement supérieures aux polymères synthétiques étudiés, les polymères biosourcés ont des performances diélectriques et électriques proches. Le PLA et le PHBV permettraient notamment de concevoir des matériaux ayant les constantes diélectriques et les facteurs de perte les plus faibles possibles, limitant la conversion d'énergie électromagnétique en chaleur. L'acétate de cellulose, bien que possédant des groupes hydroxyles, a une constante diélectrique et un facteur de perte similaire à ceux de l'époxy, composant primordial pour la conception des panneaux de circuits imprimés. De plus, sa conductivité électrique est proche de celle du PLA et du PHBV. En raison de sa capacité de production théorique élevée, l'acétate de cellulose est également prometteur pour une étude approfondie. Le PHB n'a pas été retenu, car il est encore plus complexe à mettre en œuvre par voie fondue que le PHBV, déjà complexe à mettre en œuvre. Le PCL n'est pas retenu non plus, car il n'est pas biosourcé. Pour finir, le PBS possède une trop grande constante diélectrique comparée aux autres polymères, et n'a pas non plus été retenu.

De plus, la revue de la littérature a démontré que les polymères biosourcés avaient une place non négligeable dans le futur des matériaux diélectriques isolants. Afin de pallier les limitations venant des polymères biosourcés, la revue a permis de mettre en évidence différentes stratégies, comme la stratégie de mélange de polymères pour combiner les propriétés des polymères constituants, de création de biocomposites à base de cellulose pour améliorer les propriétés mécaniques, et l'utilisation de nouveaux procédés de mise en œuvre comme l'impression 3D.

Chapitre 3) Approches méthodologique et expérimentale

Ce chapitre présente les différentes méthodologies appliquées durant la recherche expérimentale. La première partie présente les différentes matières premières utilisées, tandis que la deuxième partie met l'accent sur les différents plans expérimentaux utilisés, la mise en œuvre et les techniques de caractérisation appliquées sur la durée du projet.

3.1. Matières premières sélectionnées

Quatre polymères biosourcés différents ont été sélectionnés pour la réalisation du projet de recherche : deux acides polylactiques (Ingeo 2003D et PLI-005), un polyhydroxybutyrate-co-valérate (PHI-002) et un acétate de cellulose (ACI-002). Les polymères sont fournis par Natureworks (Plymouth, MN, USA), BBFil (Heiligenberg, FRA) et Natureplast (Mondeville, FRA). La **Table 3.1** présente les propriétés thermiques et mécaniques des polymères extraites des fiches techniques données par les fournisseurs.

Table 3.1 : Fiches techniques des polymères biosourcés sélectionnés durant le projet de thèse (informations provenant des documents techniques de Natureplast et Natureworks)

	Ingeo 2003D	PLI-005	PHI-002	ACI-002
Polymère	PLA	PLA	PHBV	CA
T _g (°C)	58	-	-	-
T _f (°C)	150-160	170-180	145-155	-
MFI (g·10 min ⁻¹ @ 2,16 kg)	6 (ASTM D1238 @ 210 °C)	25-35 (ISO 1133 @ 190 °C)	15-30 (ISO 1133 @ 190 °C)	15-30 (ISO 1183 @ 190 °C)
Densité (g·cm ⁻³)	1,24 (ASTM D1238)	1,25 (ISO 1183)	1,25 (ISO 1183)	1,27 (ASTM D792)
Module Young (GPa)	3,5 (ASTM D882)	3,5 (ISO 527)	4,2 (ISO 527)	-
Max contrainte (MPa)	60 (ASTM D882)	65 (ISO 527)	-	-
Contrainte rupture (MPa)	53 (ASTM D882)	60 (ISO 527)	35 (ISO 527)	33,1 (ASTM D638)
Elongation rupture (%)	6 (ASTM D882)	4,7 (ISO 527)	4 (ISO 527)	30 (ASTM D 638)
Test impact (kJ·m ⁻²)	-	25 (ISO 527 sans entaille)	5 (ISO 179 sans entaille)	203 (ASTM D 256 entaillé)
Déflexion (°C)	55 (ASTM E2092)	54 (ISO 75-2)	134 (ISO 75-2)	68 (ASTM D 648)
Informations complémentaires	Grade extrusion	Grade injection	Grade injection, dérivé de Enmat Y1000P	Grade injection 29% de plastifiant

Deux grades différents de PLA sont utilisés :

- Le PLA Ingeo 2003D, étant un des grades les plus utilisés et ayant un indice de fluidité adapté pour le procédé d'extrusion, est choisi pour le début du projet. La thermocompression et l'impression 3D ne sont en effet pas des procédés demandant une viscosité particulièrement faible.

- Le PLA PLI-005, grade adapté pour l'injection, est choisi pour la conception des biocomposites à base de cellulose afin d'étudier la faisabilité d'utiliser un grade injection pour l'obtention de biocomposites et bionanocomposites par impression 3D pour le domaine diélectrique. Des recherches menées par Bakrani Balani et al., 2019 ont prouvé la faisabilité d'utiliser ce grade pour impression 3D, tout en notant des problématiques importantes de fluidité à haute température, ce que l'ajout de charges permettrait de limiter.

Deux charges différentes sont utilisées dans le cadre de la partie de conception et caractérisation de biocomposites à base de cellulose. Le principe étant d'étudier l'influence de la taille de la charge, le choix s'est porté sur les microcristaux de cellulose et les nanocristaux de cellulose (respectivement nommées MCC et NCC). Ce duo est pertinent, car ces deux charges sont très proches chimiquement, composées toutes les deux de cellulose pure. La MCC est fournie par J. Rettenmaier (Fosston, MN, USA). Cette MCC est obtenue à partir de pâte kraft blanchie. La densité donnée par le fournisseur est de $0,27-0,33 \text{ g}\cdot\text{cm}^{-3}$. La NCC (DextraCel Nano HP) est fournie par Anomera (Montréal, QC, CAN). La densité apparente donnée par le fournisseur est de $0,3-0,7 \text{ g}\cdot\text{cm}^{-3}$. Une vérification de la densité apparente de la MCC et de la NCC a été réalisée au laboratoire en insérant dans une burette graduée 5 g de matière dans 20 g d'eau distillée. La variation de volume associé à l'apport des charges cellulosique donne par corolaire le volume apparent des charges. Cette densité de vérification est déterminée à $0,35$ et $0,59 \text{ g}\cdot\text{cm}^{-3}$ pour respectivement la MCC et NCC, valeurs correspondantes aux informations données.

Concernant la compatibilisation des charges cellulosiques, du (3-aminopropyl) triéthoxysilane (APTES) est utilisé, fourni par Sigma Aldrich. Ce réactif permet de réaliser une silanisation en suivant le protocole proposé par Dammak (2022) durant son projet de maîtrise au sein de l'UQAT (Rouyn-Noranda, QC, CAN).

3.2. Détermination des plans d'expériences

Pour la partie de la thèse concernant l'utilisation de l'impression 3D, un plan de Taguchi et un plan factoriel sont proposés. En effet, le plan de mélange ne serait pas adapté ici car

aucun des matériaux proposés ne contient trois composants avec des proportions variables. Les plans de Taguchi et factoriel permettent d'optimiser une propriété en faisant varier différents facteurs de manière contrôlée. Chaque facteur se divise en différents niveaux, allant de -1 (la valeur minimale) à $+1$ (la valeur maximale). Pour le projet, le choix s'est porté sur trois facteurs à varier, avec trois niveaux par facteur, soit des plans L27 (3^3). Ces tests nécessitent vingt-sept tests pour un plan complet, soit un temps très important à allouer pour les réaliser. Cependant, l'avantage du plan de Taguchi et du plan factoriel est qu'il est possible de pouvoir raccourcir le volume et le temps de réalisation du plan en ne réalisant qu'une fraction critique des vingt-sept conditions. Donc, pour des raisons de temps de test, les plans L9 (3^3) sont sélectionnés, pour le coût d'une précision légèrement diminuée. La **Figure 3.1** présente visuellement les plans de Taguchi et factoriel incomplet L9 à trois niveaux et trois facteurs (3^3) choisis.

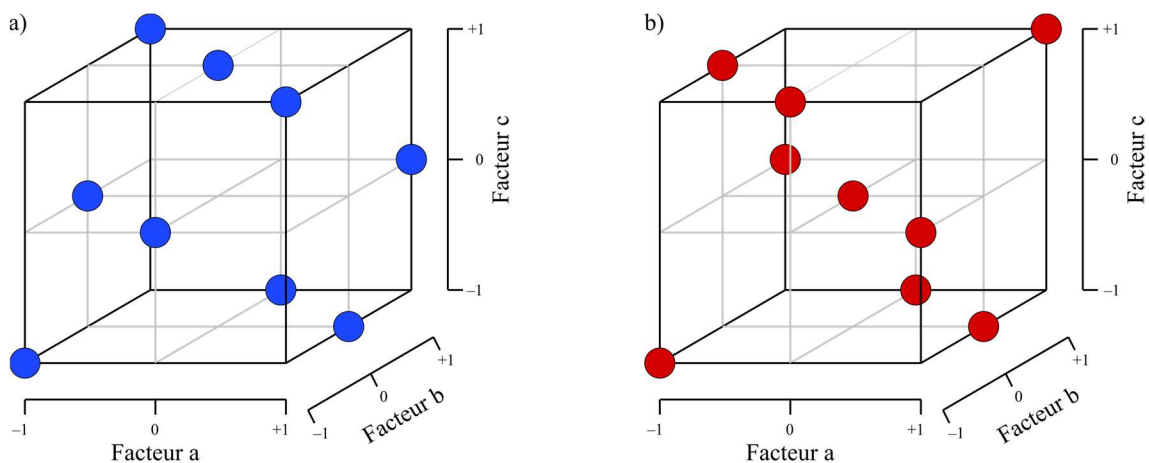


Figure 3.1 : Plan à trois facteurs et trois niveaux (3^3) en plan incomplet L9, a) plan de Taguchi, b) plan factoriel incomplet

3.3. Préparation des fibres cellulosiques et du masterbatch

3.3.1. Préparation des fibres cellulosiques

Cette partie concerne la conception des biocomposites à renforts de cellulose pour impression 3D, car la fabrication de composites n'est pas sans générer des problématiques. Une des plus communes concerne la différence d'énergie de surface entre la matrice et les charges. Les polymères, comme le PLA, sont pour la majorité

relativement hydrophobes, car ils ne possèdent que peu de groupes polaires, comme des groupes hydroxyles.

Les charges cellulosiques, au contraire, possèdent un grand nombre de groupes hydroxyles sur leur surface. Cette différence amène à des défauts structurels comme une mauvaise interface, des phénomènes d'agrégation, et donc à des propriétés physiques moindres que celles attendues. Pour générer une bonne compatibilité entre les constituants, il existe de nombreuses possibilités, comme le greffage de polymères sur les charges, l'hydrophilisation de la matrice ou l'hydrophobisation des charges. Étant donné que le projet vise à produire des matières les moins polaires possibles pour une utilisation adéquate en composant à basse permittivité, la voie de l'hydrophobisation des charges est retenue. Le protocole de silanisation des fibres est dérivé de celui proposé par Dammak (2022) durant son projet de maîtrise au sein du Laboratoire Biomatériaux de l'UQAT. La silanisation est réalisée par agitation magnétique, à température ambiante dans des erlenmeyers d'1 L. La rotation du barreau magnétique est fixée à 500 RPM. Le protocole repose sur une hydrolyse préliminaire de 2 % en masse d'APTES dans une solution de 1:1 d'éthanol (95 % en volume) et d'eau distillée durant 1h à température ambiante. La deuxième étape vise à ajouter de l'acide acétique (99,7 %) pour obtenir un pH compris entre 4 et 5. Pour 1 L de solution, il est trouvé que 20-22 ml d'acide acétique permet d'obtenir un pH de 4,5. Après 15 minutes, les fibres sont ajoutées et laissées en solution durant 3 heures. Une fois la réaction terminée, les fibres sont filtrées et rincées, puis laissées en étuve à 60 °C durant 24h. La **Figure 3.2** résume le processus de silanisation de charges cellulosiques par l'APTES. Afin de vérifier la présence du greffage, des analyses FTIR et analyse thermogravimétrique (ATG) sont réalisées en **Annexe 1**. Les analyses infrarouges confirment la présence de l'APTES sur les MCC et NCC par une diminution du pic associable à l'eau adsorbée, ainsi que la présence d'un nouveau pic associé à la liaison Si-O-C. Des analyses ATG montrent de plus que la NCC-APTES possède une stabilité thermique nettement améliorée par rapport à la NCC non greffée, potentiellement associable à une diminution des groupes hydroxyles et donc atténuant les phénomènes d'oxydation à haute température. Pour finir, une analyse granulométrique est proposée en **Annexe 2**. Les observations microscopiques de 2088 particules donnent une longueur médiane moyenne de respectivement 34,14 et 51,90 μm , ainsi qu'une largeur médiane et moyenne de respectivement 16,60 et 22,86 μm .

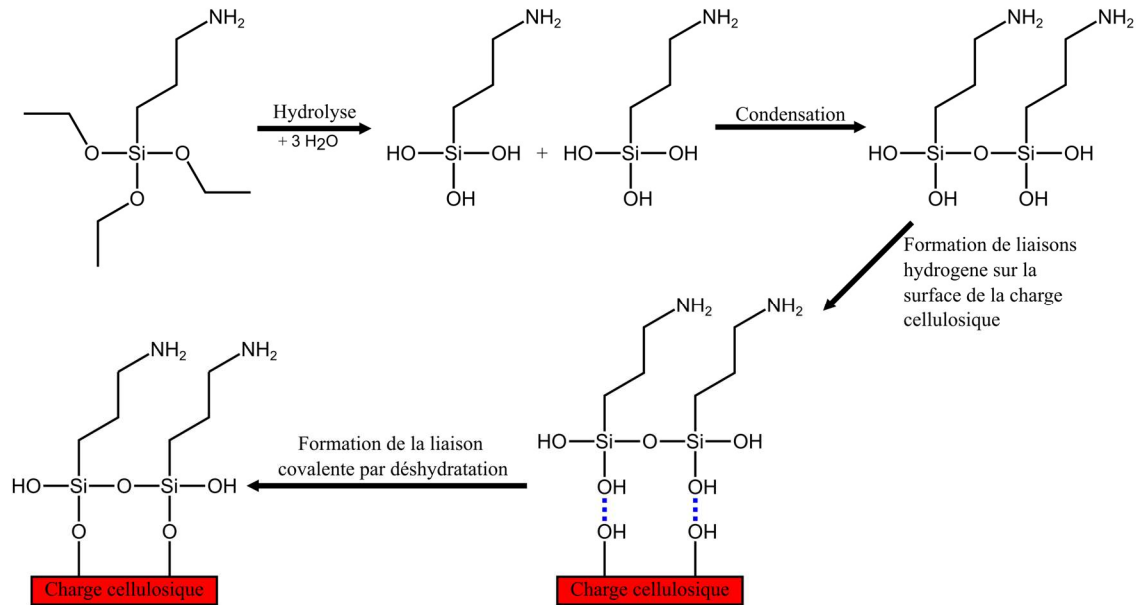


Figure 3.2 : Silanisation des charges cellulosiques (dérivée de Gad et al. (2018))

3.3.2. Préparation du masterbatch de nanocristaux de cellulose (NCC)

Les nanocharges représentent toujours un défi lors de leur mise en œuvre par leurs dimensions. Elles sont plus difficiles à mettre en œuvre que les charges micrométriques, car elles ont tendance à davantage s'agréger à plus faible taux en masse (W_f) que les microcharges. De plus, il est complexe de les homogénéiser avec la matrice durant l'étape d'extrusion. Une solution pour faciliter leur dispersion durant l'extrusion est de réaliser une étape intermédiaire par la création d'un masterbatch. Un masterbatch est généralement une matrice (celle utilisée pour le matériau final) dans laquelle la charge à disperser (pigments, nanocharges ou autres additifs) est mélangée à haut W_f . Ce masterbatch est ensuite dilué dans la matrice pure afin d'obtenir le W_f final souhaité. Si le masterbatch est correctement réalisé, il permet d'améliorer la dispersion des nanocharges. Il existe différentes stratégies pour réaliser un masterbatch, qu'elles soient par voie solvant ou voie fondue. La voie fondue est choisie pour le projet, car plus cohérente avec une application industrielle. Le masterbatch est réalisé avec une mini-extrudeuse Haake Minilab II (Thermo Scientific, Waltham, MA, USA) (**Figure 3.3**). Le microcompounder fonctionne en extrusion discontinue par batchs de 5 g de mélange matrice:NCC. La matière première est conditionnée à 60 °C jusqu'à ce que le taux d'humidité des composants passe en dessous de 1 %. Des tests préliminaires montrent qu'une température de 180 °C est suffisante pour pleinement fusionner le PLA, tout en

limitant le changement de couleur de l'extrudât. De plus, ces tests montrent qu'il est possible de produire un masterbatch avec un $W_{NCC} = 20\%$ tout en gardant une dispersion correcte. Le protocole utilisé consiste en une vitesse de vis de 70 RPM à 180 °C durant 1 minute. Une fois obtenu, l'extrudât est finalement granulé.



Figure 3.3 : Préparation du masterbatch : a) mini-extrudeuse Haake Minilab II, b) système interne de double vis, c) extrusion du masterbatch, d) masterbatch refroidi

3.4. Préparation des mélanges et mises en œuvre des matériaux

3.4.1. Préparation des matériaux

La conception des mélanges polymériques à base de PLA, PHBV et de CA, a été inspirée d'un plan de mélange en « simplex-lattice » {3,3} présenté en **Figure 3.4**. Sur les dix conditions présentées, trois correspondent aux polymères purs et sont présentes aux coins du triangle du plan de mélange. Six conditions correspondent aux mélanges binaires et sont présentes sur les bords du triangle du plan de mélange. Pour la conception des mélanges PLA:CA pour impression 3D, la **Table 3.2** présente les mélanges fabriqués et caractérisés durant cette partie. Il est décidé d'étudier l'influence du CA sur le PLA de 10 à 40 %, car nous manquons de recul concernant l'imprimabilité du CA. La valeur maximale de CA est fixée à 40 %, car les résultats rhéologiques montrent que l'ajout de CA dans le PLA augmente grandement la viscosité des mélanges, risquant de grandement

gêner l'imprimabilité des éprouvettes 3D. A ces mélanges sont ajoutés le PLA et le CA pur pour comparaison.

Table 3.2 : Proportions des différents mélanges de PLA:CA pour impression 3D

Nom	W_{PLA} (%)	W_{CA} (%)
PLA	100	0
CA-10	90	10
CA-20	80	20
CA-30	70	30
CA-40	60	40
CA-100	0	100

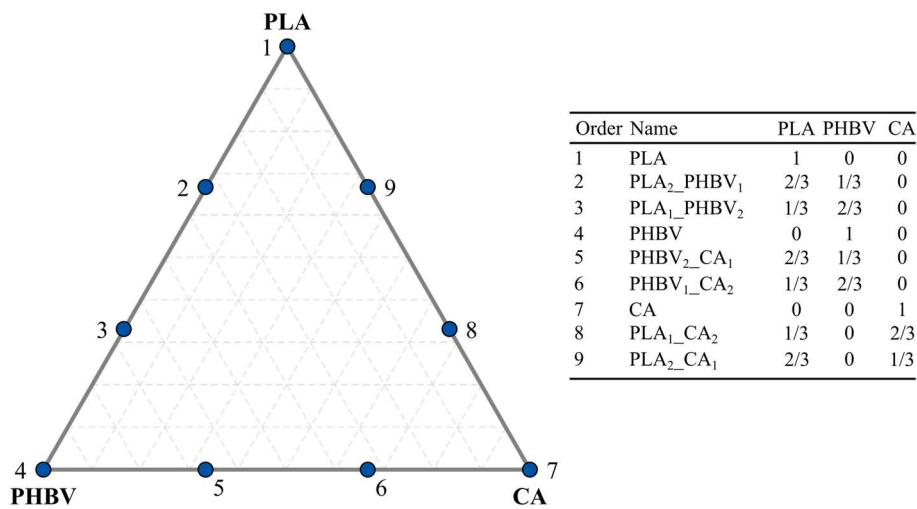


Figure 3.4 : Projection des mélanges de PLA, PHBV et CA confectionnés. La table insérée dans la figure indique les composants en proportion

Pour finir, concernant la conception des biocomposites à renforts de cellulose pour impression 3D, la **Table 3.3** présente les différents biocomposites fabriqués et caractérisés durant cette partie. Il est aussi décidé d'étudier des biocomposites avec un W_{MCC} allant jusqu'à 15 % et des bionanocomposites avec un W_{NCC} allant jusqu'à 5 %. Utiliser un W_{MCC} plus haut risque d'amener à des problèmes d'impression et d'obstruction de la buse. Concernant le W_{NCC} , utiliser des taux supérieurs risque de diminuer la bonne dispersion des fibres par la création d'agrégats, malgré la silanisation. Afin de réaliser le plan factoriel, trois différents taux de charge sont choisis : 5-10-15 % pour la MCC et 1-3-5 % pour la NCC. À ces mélanges sont ajoutés le PLA pur pour comparaison.

Table 3.3 : Proportions des constituants des différents biocomposites à base de cellulose pour impression 3D

	PLA (g)	MCC (g)	Masterbatch (g) (W _{NCC} = 20 %)	NCC final (g)
PLA	1000	0	0	0
MCC-5	950	50	0	0
MCC-10	900	100	0	0
MCC-15	850	150	0	0
NCC-1	950	0	50	10
NCC-3	850	0	150	30
NCC-5	750	0	250	50

3.4.2. Procédé d'extrusion

Pour la conception des mélanges polymériques à base de PLA, PHBV et de CA, ainsi que ceux de mélanges PLA:CA pour impression 3D, l'étape de mise en œuvre est réalisée avec une extrudeuse monovis Scamex 25-20D (Scamex, Isques, FRA). Les matières utilisées ont toutes subi un étuvage durant une nuit à 60 °C pour enlever leur humidité interne. Des tests préliminaires couplés à des analyses DSC sont initialement menés pour déterminer le meilleur compromis de température afin de fondre tous les constituants en dégradant thermiquement le moins possible les polymères. Il est ainsi déterminé que la température de filière de 190 °C est la limite basse pour fusionner totalement le PHBV. Un profil de température de 160-175-190 °C de l'alimentation à la filière et une vitesse de vis de 30 RPM sont donc choisis. Les extrudats produits passent dans un bain de refroidissement rempli d'eau afin de les figer et passent dans un granulateur à couteaux (Scamex, Isques, FRA). Une fois granulée, la matière est restockée en étuve durant une journée pour enlever l'eau ajoutée par la sous-étape de refroidissement. Comme le PHBV n'est pas utilisé durant la phase de fabrication de mélanges PLA:CA pour impression 3D, de nouveaux tests préliminaires sont menés pour déterminer s'il est possible de diminuer la température du procédé. Un profil de 160-170-180 °C est trouvé comme étant un bon compromis pour les polymères purs et leurs mélanges. Les extrudats sont ensuite refroidis, granulés et restockés en étuve durant une journée pour enlever l'eau ajoutée par la sous-étape de refroidissement.

Le partenaire Coalia (Thetford Mines, QC, CAN) s'est chargé d'extruder et de granuler les matériaux pour la conception de biocomposites à renforts de cellulose pour impression

3D. Une extrudeuse baxis a été utilisée pour cette étape. Les différentes zones de l'extrudeuse sont fixées à 190 °C et une vitesse de rotation comprise entre 70 et 100 RPM est utilisée. La pression à la filière est mesurée entre 22 et 24 bars. Une étape d'extrusion complémentaire a dû être réalisée avec la mini-extrudeuse Haake précédemment utilisée pour le masterbatch afin de compléter les pertes durant l'étape de mise en œuvre.

3.4.3. Procédé de thermocompression

Le procédé de thermocompression est choisi dans le projet afin de répondre aux problématiques du matériel possédé par les laboratoires d'accueil. Ce procédé permet d'étudier à la fois les matériaux produits et l'effet de l'impression 3D. La fabrication des échantillons est réalisée sur une thermopresse SCAMEX 20 T 300*300 (Scamex, Isques, FRA), ainsi que sur une LabEcon series (Fontjine Presses, Rotterdam, NLD). Comme pour l'extrusion, toutes les matières sont étuvées à 60 °C afin de retirer le maximum d'humidité. Les protocoles utilisés sont résumés en **Table 3.4**. Des tests préliminaires démontrent qu'un protocole de thermocompression durant 3 minutes suffit pour pleinement fusionner les granulés en une plaque homogène. Les matériaux thermocompressés avec la SCAMEX 20 T sont ensuite directement découpés avec une découpeuse laser ML-W1290 150 W (MLlaser, Pont-à-Mousson, FRA) afin d'obtenir les formes désirées pour les tests. Comme la LabEcon series possède tous les moules nécessaires, aucune étape de découpage laser n'est nécessaire lors de son utilisation.

Table 3.4 : Paramètres utilisés pour la thermocompression des matériaux

	Chapitre 3	Chapitre 4	Chapitre 5
Machine	SCAMEX 20 T	SCAMEX 20 T	LabEcon series
T max (°C)	190	180	180
T (min)	3	3	3
Epaisseur	0,5 mm	2 mm	2 mm
Force/pression max	3 bars	3 bars	100 kN

3.4.4. Procédé d'impression 3D

L'impression 3D est un procédé innovant nécessitant néanmoins une étape intermédiaire pour transformer les granulés en câbles continus (nommés aussi filaments) que l'imprimante 3D convertit en pièces 3D solides.

3.4.4.a. *Obtention des filaments pour impression 3D*

Le procédé de fabrication par filaments fondus (FFF) nécessite un apport de matière première pour l'impression. Cette alimentation se fait grâce à une bobine de polymère sous forme de filaments. Pour convertir les granulés en filaments dans le projet, deux extrudeuses 3DEVO filament maker (3DEVO, Utrecht, NLD) sont utilisées. Ces extrudeuses se situent au sein de L'Institut de Thermique, Mécanique, Matériaux (ITheMM, Charleville-Mézières, FRA), ainsi qu'au sein de l'UQAT. Les profils de température appliqués sont donnés en **Table 3.5**. Concernant les mélanges PLA:CA, des tests préliminaires ont montré qu'il est impossible d'obtenir des diamètres de filaments de 1,75 mm constants. Cette incapacité vient à la fois de l'hétérogénéité du mélange, de la plus grande viscosité du CA, et de la présence du plastifiant. La bien meilleure stabilité des filaments de 2,85 mm viendrait de la meilleure homogénéité globale. Pour la fabrication des biocomposites, aucune présence d'étirement n'est observée, donc des bobines de 1,75 mm ont pu être produites avec succès.

Table 3.5 : Paramètres utilisés pour l'extrusion des filaments

	Chapitre 5	Chapitre 6
Profil de température (T ₁ -T ₂ -T ₃ -T ₄) (°C)	170-180-180-170 °C	170-185-185-180 °C
Masse produite (g)	~ 800	~ 600
Diamètre du filament de bobine (mm)	2,85	1,75
Vitesse vis (RPM)	5	3,5
Vitesse refroidissement (%)	100	40

3.4.4.b. *Impression 3D*

Concernant l'impression 3D en elle-même, toutes les impressions sont réalisées sur une SIGMAX R19 (BCN3D, Gavà, ESP) (**Figure 3.5a**) pour la conception de mélanges PLA:CA. Les biocomposites avec des renforts de cellulose sont quant à eux réalisés avec une CR-10 Max (Creality, Shenzhen, CHN) (**Figure 3.5c**).

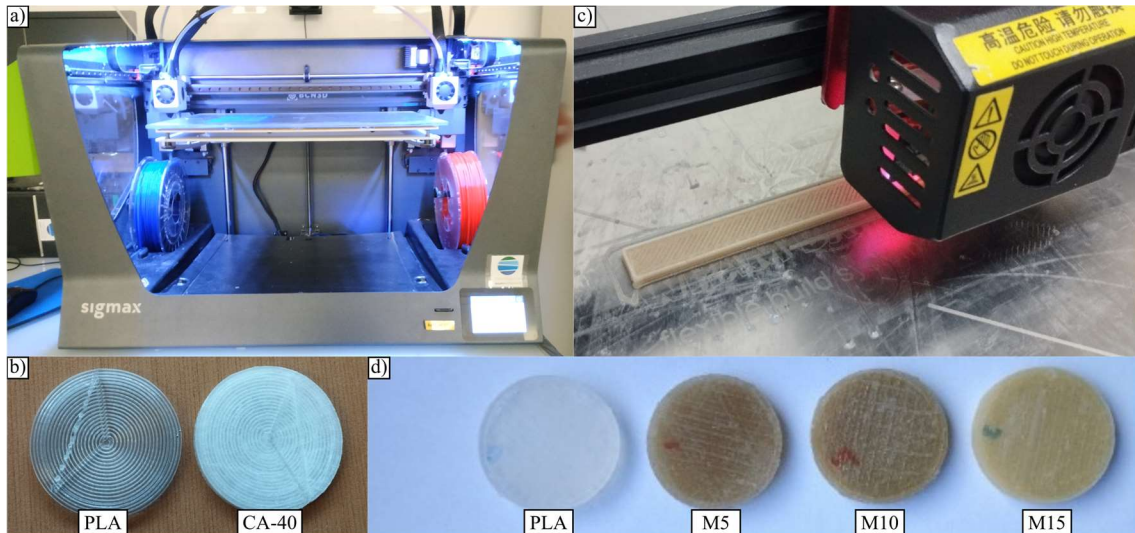


Figure 3.5 : a) Imprimante 3D SIGMAX R19, b) éprouvettes diélectrique de PLA et PLA:CA à 40 % de CA (CA-40), c) Imprimante 3D CR-10 Max, d) éprouvettes diélectriques de PLA et biocomposites PLA:MCC à 5, 10 et 15 % de MCC (M5, M10, M15)

La **Table 3.6** résume les paramètres utilisés durant l'impression. Ces paramètres sont choisis, car ils présentent le meilleur compromis pour toutes les différentes conditions.

Table 3.6 : Paramètres utilisés pour l'étape d'impression 3D

	Chapitre 5	Chapitre 6
Imprimante 3D	SIGMAX R19	CR-10 Max
Température buse (°C)	205-215-225	190-200-210
Diamètre buse (mm)	0,6-0,8	0,8
Vitesse buse (mm·s ⁻¹)	30	40
Température support (°C)	60	60
Épaisseur échantillons (mm)	2-4	3,2-4
Épaisseur couches (mm)	0,1-0,15-0,2-0,3	0,4
Taux remplissage (%)	40-60-80-100	50-75-100
Forme remplissage	Concentrique (BDS) ± 45° (DMA)	± 45°

Le PLA pur n'a posé aucun problème d'impression, mais comme attendu, pour les mélanges et les biocomposites, la pulvérisation de laque sur le support était nécessaire pour améliorer l'adhérence et éviter les phénomènes de décollement durant l'impression. De plus, les bobines sont étuvées juste avant utilisation pour enlever les traces d'humidité pouvant altérer la qualité d'impression.

La **Table 3.7** présente les conditions à créer pour réaliser un plan de Taguchi L9 (3^3) pour le **Chapitre 4**.

Table 3.7 : Configuration du plan Taguchi proposé

Condition	Facteur a W_{CA} (%)	Facteur b Taux remplissage (%)	Facteur c Épaisseur de couche (mm)
1	20	40	0,1
2	20	60	0,2
3	20	80	0,3
4	30	40	0,2
5	30	60	0,3
6	30	80	0,1
7	40	40	0,3
8	40	60	0,1
9	40	80	0,2

Le premier facteur fixé est le taux en CA. Le chapitre précédent a montré que le CA influence négativement les propriétés d'isolation électrique du PLA, mais tout en lui conservant une capacité d'isolation électrique convenable. Intégrer le taux de CA dans le plan de Taguchi permet de comprendre comment cette variation se comporte plus précisément. Les conditions choisies sont CA-20, CA-30 et CA-40, correspondant aux conditions contenant 20, 30 et 40 % en masse de CA. Le deuxième facteur fixé est le taux de remplissage. La littérature montre qu'il est envisageable de modifier les propriétés diélectriques d'éprouvettes imprimées en 3D. Il serait ainsi possible de minimiser la légère dégradation des propriétés diélectriques apportées par le CA grâce à un plus faible taux de remplissage. Mais un tel matériau va aussi présenter des propriétés mécaniques amoindries. Intégrer ce facteur permet de mieux comprendre ces variations. Les valeurs choisies le facteur « taux de remplissage » sont de 40 %, 60 % et 80 %. Le dernier facteur fixé est l'épaisseur de couches. La littérature tend à dire qu'une grande épaisseur de couche augmente la porosité et donc augmente le pouvoir isolant des éprouvettes. Ainsi, les valeurs choisies pour le facteur « épaisseur de couche » fut de 0,1, 0,2 et 0,3 mm.

Avec les connaissances acquises durant la fabrication et la caractérisation des mélanges PLA:CA, le plan factoriel présenté en **Table 3.8** est proposé pour le **Chapitre 5**. Le taux de charge et le taux de remplissage sont choisis en premier et second facteurs. Afin d'éviter des phénomènes d'affaissement dus à une trop grande fluidité du PLA (de grade injection) par manque de matières, le taux de remplissage minimal est fixé à 50 %. Le

troisième facteur choisi est la température d'impression, afin d'étudier comment la température affecte l'imprimabilité des biocomposites. Les extrêmes ont été fixés en fonction de tests préliminaires. Le niveau -1 correspond à la température minimale à laquelle les biocomposites les plus visqueux, à savoir les plus chargés en cellulose (M15 et N5), peuvent être imprimés correctement, tandis que le niveau +1 correspond à la température maximale à laquelle le PLA peut être imprimé correctement. Ces températures sont trouvées à respectivement 190 °C et 210 °C.

Table 3.8 : Configuration du plan factoriel utilisé

Condition	Facteur a	Facteur b	Facteur c
	W_{MCC} (%)	Taux remplissage (%)	$T_{impression}$ (°C)
M1	5	50	190
M2	5	75	210
M3	5	100	200
M4	10	50	210
M5	10	75	200
M6	10	100	190
M7	15	50	200
M8	15	75	190
M9	15	100	210
N1	1	50	190
N2	1	75	210
N3	1	100	200
N4	3	50	210
N5	3	75	200
N6	3	100	190
N7	5	50	200
N8	5	75	190
N9	5	100	210

3.5. Caractérisations des matériaux

Les analyses diélectriques des matériaux préparés durant ce projet ont été les analyses majeures. Cependant, pour parfaitement connaître les matériaux produits, d'autres analyses sont aussi proposées, classées en fonction de leur nature.

Afin d'étudier les propriétés physicochimiques des matériaux, quatre analyses sont menées. Pour connaître les propriétés morphologiques des matériaux, des analyses MEB sont réalisées. Les mesures ATG et DSC permettent par ailleurs de connaître les

propriétés morphologiques et thermiques des échantillons. Enfin, un FTIR est utilisé pour connaître la chimie de surface des matériaux.

Deux autres analyses dynamiques sont aussi réalisées, en parallèle des analyses diélectriques, pour connaître les propriétés viscoélastiques des matériaux préparés. Des analyses mécaniques dynamiques (DMA) permettent de connaître les propriétés viscoélastiques à l'état élastique, tandis que des analyses rhéologiques permettent de connaître les propriétés viscoélastiques à l'état visqueux

Des analyses mécaniques sont aussi réalisées sur les biocomposites pour impression 3D : des tests de mécanique statique en traction (norme ASTM D638 Type 1), en flexion (ASTM D790) et des tests d'impact suivant la norme ASTM D256. La **Table 3.9** résume les caractérisations menées sur les différents matériaux préparés

Table 3.9 : Types de caractérisations réalisées sur les matériaux

		Chapitre 3	Chapitre 4	Chapitre 5
Tests physico chimiques	FTIR	✓	✓	✓
	DSC	✓	✓	✓
	ATG	✓	✓	✓
	MEB	✓	✓	✓
Tests dynamiques	BDS basse fréquence	✓	✓	✓
	BDS haute fréquence	✓	✗	✓
	DMA	✓	✓	✓
	Rhéologie	✓	✓	✓
Tests mécaniques	Traction	✗	✗	✓
	Flexion	✗	✗	✓
	Impact	✗	✗	✓

3.5.1. Caractérisations physicochimiques

3.5.1.a. Analyse infrarouge à transformée de Fourier (FTIR)

L'analyse infrarouge à transformée de Fourier (FTIR) repose sur l'absorption d'ondes électromagnétiques par une molécule dans la gamme des infrarouges. Les liaisons chimiques constituant la matière vont absorber une partie de l'onde infrarouge émise par la machine, cette dernière reçoit le signal altéré par la matière et une courbe d'absorption

peut ainsi être tracée avec ce signal. Comme chaque liaison covalente absorbe à une fréquence précise, il est possible d'associer à chaque pic d'absorption un groupe chimique des molécules constituant la matière. La **Table 3.10** présente quelques groupes chimiques typiques rencontrés dans la chimie des polymères et leur propre fréquence d'absorption.

Table 3.10 : Nombre d'onde d'absorption du spectre électromagnétique de quelques groupes chimiques (dérivé de ("18 Lecture Supplement: Infrared Spectroscopy," Compound Interest, 2015))

Nombres d'onde d'absorption (cm ⁻¹)	Longueurs d'onde (μm)	Groupes	Liaisons	Types de vibrations	Informations supplémentaires
3700-3200	2,70-3,13	Alcool	O–H	Stretching	Intense et large pic
3500-3300	2,86-3,03	Amine/amide	N–H	Stretching	large pic
3100-3000	3,23-3,33	Aryle/vinyle	C–H	Stretching	-
3100-2850	3,23-3,51	Alcane	C–H	Stretching	-
3000-2500	3,33-4,00	Acide carboxylique	O–H	Stretching	Large pic
2900-2700	3,45-3,70	Aldéhyde	C–H	Stretching	2 pics
1750-1735	5,71-5,76	Ester/cétone	C=O	Stretching	Intense pic
1740-1720	5,75-5,81	Aldéhyde	C=O	Stretching	Intense pic
1725-1700	5,80-5,88	Acide carboxylique	C=O	Stretching	Intense pic
1690-1650	5,92-6,06	Amide	C=O	Stretching	Intense pic
1650-1560	6,06-6,41	Alcène	C=C	Stretching	-
1450-1375	6,90-7,27	Méthyle	–CH	Bending	-
1385-1380	7,22-7,25	Alcane	–CH	Bending	-
1300-1000	8,26-6,62	Ester/alcool/acide carboxylique	C–O	Stretching	Intense pic

Il existe trois gammes de fréquence utilisées dans la spectrométrie infrarouge : l'infrarouge proche (longueur d'onde entre 770 nm-2,5 μm), moyen (2,5 μm-20 μm) et lointain (longueur d'onde entre 15 μm-1 mm). Toutes les analyses réalisées durant le projet sont obtenues dans la gamme des infrarouges moyens, avec un spectromètre Nicolet iS10 IR-TF (ThermoFisher Scientific, Waltham, MA, USA), ainsi qu'un IRTracer-100 (Shimadzu, Kyoto, JAP). Tous les échantillons sont analysés grâce à un accessoire de réflectance totale atténuée (ATR), dans la gamme de fréquences allant de 500 cm⁻¹ à 4000 cm⁻¹. Une étape de séchage des échantillons est nécessaire pour ne pas surestimer les observations de la liaison O–H présente à 3400 cm⁻¹ ainsi qu'à 1640 cm⁻¹. Pour cela, les échantillons sont placés en étuve à environ 60 °C.

3.5.1.b. Calorimétrie différentielle à balayage (DSC)

La DSC fait partie des analyses physicochimiques phares dans le domaine des matériaux. Elle permet de mesurer des échanges de chaleur entre l'échantillon à tester et la cellule de mesure. C'est une méthode adaptée pour déterminer les transitions de phase dans un matériau. Les transitions de phase mesurées par DSC sont de deux natures : exothermiques ou endothermiques. Les phénomènes exothermiques émettent de la chaleur (comme la cristallisation), alors que les phénomènes endothermiques (comme la fusion), absorbent de la chaleur dans la cellule de mesure. Le phénomène de transition vitreuse s'observe quant à elle comme un saut dans la courbe flux de chaleur en fonction de la température. Cette méthode de mesure est aussi adaptée pour déterminer le degré de cristallinité d'un polymère semi-cristallin. Dans le cas d'un matériau semi-cristallin pur, la détermination du degré de cristallinité (X_{cr}) peut être calculée avec l'**Équation 8** (Mofokeng and Luyt, 2015a):

$$X_{cr} = \frac{dH}{dH_0} * 100 \quad \text{Équation 8}$$

où dH est la variation d'enthalpie de cristallisation mesurée et dH_0 est la variation d'enthalpie de fusion à 100 % cristallin théorique du polymère, tous deux exprimés en $J \cdot g^{-1}$. Dans le cas d'un matériau multicomposant comme un composite ou un mélange polymérique avec un polymère amorphe, la détermination du degré de cristallinité (X_{cr}) du composant semi-cristallin peut être calculée en ajustant l'**Équation 8** en **Équation 9** (Crétois et al., 2013; El Assimi et al., 2021):

$$X_{cr} = \frac{dH}{dH_0 * (W_{cr})} * 100 \quad \text{Équation 9}$$

où W_{cr} est le pourcentage en masse du polymère cristallisant. Pour réaliser une mesure, la matière est placée dans un creuset en aluminium refermable, puis est chargée dans la cellule de mesure. Un second creuset vide est placé aussi dans l'enceinte pour comparaison. Usuellement un gaz inerte (argon ou azote) est injecté dans la cellule de mesure pour éviter les phénomènes d'oxydation à haute température, ainsi que la formation de glace d'eau dans la cellule à basse température, pouvant altérer la mesure.

Les différences de flux sont habituellement tracées sous la forme de graphiques représentant le flux de chaleur en fonction de la température.

Durant le projet, les mesures DSC sont réalisées sur une DSC Q20 (TA Instruments, New Castle, DE, USA), ainsi que sur une DSC 214 Polyma (Netzsch, Selb, DEU). Les mesures sont effectuées avec 15 mg de matériau, insérés dans des creusets en aluminium, puis refermés. Les vitesses des rampes sont fixées à $10\text{ °C}\cdot\text{min}^{-1}$, choisies comme compromis entre rapidité et précision des résultats. De plus, un flux de gaz inerte de $20\text{ ml}\cdot\text{min}^{-1}$ est utilisé afin d'éviter les phénomènes parasites. Tous les protocoles utilisés sont dérivés du programme proposé durant la caractérisation des mélanges polymériques à base de PLA, PHBV et de CA (**Figure 3.6a**).

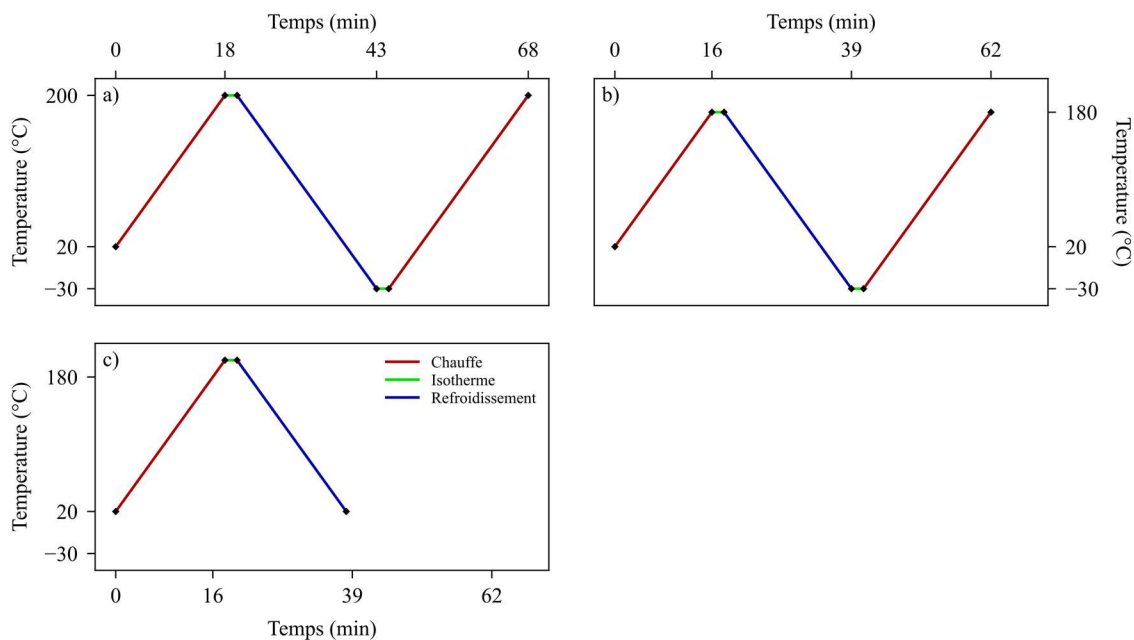


Figure 3.6 : Programmes DSC utilisé pour : a) les mélanges PLA, PHBV et CA, b) les mélanges PLA:CA, c) les biocomposites à base de cellulose

Ce dernier consiste en une première rampe de chauffe entre 20 et 200 °C, afin d'effacer l'histoire thermique de la matière. Cette étape est importante, car elle permet de comparer les échantillons entre eux, car ils auront subi exactement le même traitement thermique. La température de 200 °C est fixée en fonction de la température de fusion du PHBV. Après une isotherme de deux minutes afin de fondre la totalité des cristaux, une rampe de refroidissement de 200 à -30 °C est appliquée. Une dernière rampe de chauffe de -30 à

200 °C est aussi utilisée. La température de -30 °C est utilisée afin d'obtenir la température de transition vitreuse du PHBV.

Pour la conception et caractérisation de mélanges PLA:CA pour impression 3D, un ajustement du protocole précédent est proposé (**Figure 3.6b**). En effet, la température maximale de 200 °C est diminuée à 180 °C pour deux raisons. Le PHBV, polymère à haute température de fusion, est éliminé de cette phase. De plus, les premiers résultats ATG ont démontré que le CA possède une dégradation notable vers les 200 °C. Pour finir, le protocole pour la caractérisation des biocomposites est condensé en une seule chauffe et refroidissement pour des raisons de temps (**Figure 3.6c**). De plus, la température minimale du protocole passe de -30 à 20 °C, car le PLA ne contient pas de plastifiants et ne nécessite donc pas une température aussi basse.

3.5.1.c. *Analyse thermogravimétrique (ATG)*

L'ATG fait partie des analyses physicochimiques phares dans le domaine des matériaux. Elle permet d'observer la stabilité thermique d'un échantillon par une variation de masse en fonction de la température. C'est également une méthode adaptée pour observer certaines transitions ou réactions dans un matériau caractérisé par une variation de masse de l'échantillon. Une variation de masse négative serait associable à une désorption ou une dégradation thermique. Une variation de masse positive serait quant à elle associable à des phénomènes d'adsorption. Pour le domaine des polymères, les analyses sont généralement faites sous gaz inerte pour éviter les phénomènes de combustion. Dans le cas d'échantillons multicomposants, il existera donc plusieurs phénomènes de dégradation, chacun associable à la dégradation d'un composant.

Concernant le projet, les analyses ATG sont menées avec une Tg 209 F1 (Netzsch, Selb, DEU), ainsi qu'une Q50 TGA (TA Instruments, New Castle, DE, USA). Les analyses sont réalisées en mode dynamique, avec une rampe de température de 20 jusqu'à 800 °C et sous gaz inerte (argon ou azote). Une vitesse de balayage de 10 °C·min⁻¹ est utilisée, en accord avec la littérature. Pour chaque échantillon, environ 20 mg de matériaux sont prélevés pour caractérisation.

3.5.1.d. Microscopie électronique à balayage (MEB)

La microscopie électronique à balayage (MEB) est une technique de visualisation d'échantillons à l'échelle micrométrique. Elle est dans le domaine des matériaux composites parfaitement adaptés pour l'observation de la morphologie des polymères, ainsi que la dispersion des renforts dans une matrice polymérique. Contrairement à la microscopie optique, elle repose sur l'utilisation d'électrons à la place de photons pour construire l'image finale. Un faisceau d'électrons envoyé par un canon à électrons est dirigé sur la surface à analyser. Ces électrons vont interagir avec les atomes le constituant, en renvoyant des électrons secondaires. Ces électrons vont ensuite permettre de reconstruire l'image finale. La résolution spatiale des analyses MEB peut aller jusqu'à la centaine de nanomètres. Pour aller plus loin, il existe d'autres techniques de microscopie électronique, comme la microscopie électronique à transmission (MET), plus adaptée pour observer la dispersion des charges nanométriques dans une matrice polymérique. Les analyses MEB nécessitent cependant un vide poussé (environ 40 Pa) pour obtenir une bonne qualité d'image, rendant cette technique inadaptée pour l'observation d'échantillons organiques fragiles. Pour finir, il est possible d'améliorer la qualité des images en réalisant une étape de métallisation des échantillons avec un élément conducteur (or, platine, carbone).

Pour le projet, les analyses sont conduites sur une Jeol JSM IT200 (Jeol, Akishima, JAP). Afin d'assurer une qualité suffisante de la microstructure des matériaux, tous les échantillons subissent une étape de cryofracture avec de l'azote liquide. Cela permet de figer suffisamment les matériaux afin d'éviter des phénomènes d'allongement plastique parasites. Les essais sont réalisés avec une tension d'accélération des électrons entre 5 et 15 kV, ainsi qu'un grossissement allant de x40 à x200.

3.5.2. Caractérisations dynamiques

3.5.2.a. Spectroscopie diélectrique à bande large (BDS)

La spectroscopie diélectrique à bande large (BDS) est utilisée pour connaître les propriétés diélectriques d'un matériau en fonction de la fréquence électrique appliquée. Elle permet de récupérer de nombreuses informations comme la constante diélectrique,

la perte diélectrique et la conductivité électrique. Plus de détails concernant cette analyse, ainsi que sur les équations utilisées, sont donnés dans la synthèse bibliographique (**Chapitre 2**).

Dans ce projet, les analyses sont réalisées sur deux appareils différents : un spectromètre diélectrique à basses fréquences Keysight E4980A Precision LCR Meter (Agilent Technologies, Santa Clara, CA, USA) (**Figure 3.7a**), ainsi qu'un spectromètre diélectrique à haute fréquence Keysight E4991A (Agilent Technologies, Santa Clara, CA, USA) (**Figure 3.7b**).

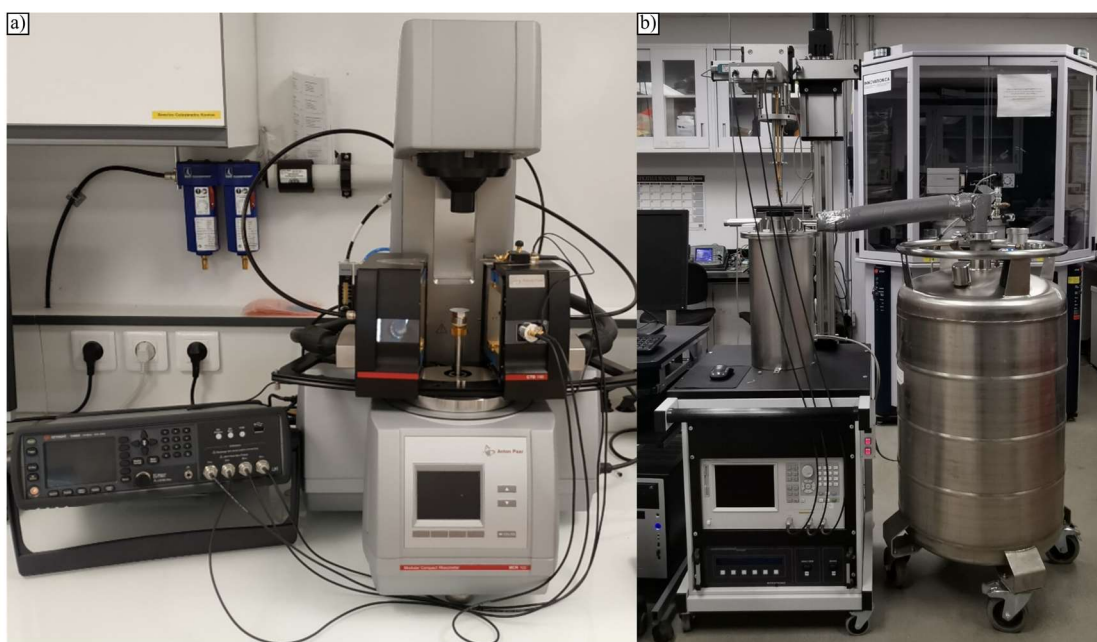


Figure 3.7 : a) Keysight E4980A couplé au rhéomètre MCR 302, b) Keysight E4991A avec le cryostat

La gamme de fréquence atteignable du Keysight E4980A est comprise entre 20 Hz et 2 MHz, et celle du Keysight E4991A est comprise entre 1 MHz et 3 GHz. Comme le Keysight E4980A est couplé avec un rhéomètre plan MCR 302 (Anton Paar, Graz, AUT), il est possible de contrôler la température durant le test dans l'enceinte fermée du rhéomètre. Deux caractérisations différentes sont menées sur les matériaux préparés, à température ambiante et en fonction de la température, détaillées dans les articles du **Chapitre 4.2.** et du **Chapitre 5.2.**

3.5.2.b. Analyse mécanique dynamique (DMA)

Les analyses mécaniques dynamiques sont une gamme de mesures dynamiques comme la BDS. Dans le domaine des polymères, cette méthode est adaptée pour observer le comportement viscoélastique de la matière à des températures en dessous de sa propre température de fusion. Le signal sinusoïdal appliqué est de nature mécanique, contrôlé soit en amplitude, soit en contrainte. L'appareil récupère le signal réémis par l'échantillon et en déduit la contrainte et la déformation du système. Le module complexe E^* se détermine avec les **Équation 10** à **Équation 12** ("2.10: Dynamic Mechanical Analysis," 2016) :

$$E^* = \frac{\sigma_0}{\gamma_0} = E' + iE'' \quad \text{Équation 10}$$

$$E' = E^* \cdot \cos \delta \quad \text{Équation 11}$$

$$E'' = E^* \cdot \sin \delta \quad \text{Équation 12}$$

où E' et E'' sont respectivement le module de stockage et le module de perte, tous deux exprimés en GPa. σ_0 est la contrainte maximale du signal sinusoïdale (en GPa) et γ_0 est la déformation maximale du système sans unités. δ est l'angle de déphasage entre le signal émis et reçu. Comme pour les tests mécaniques statiques, il existe de nombreuses conditions de test possibles, comme des tests en tension, en flexion 3 points, en encastrement simple ou double, voire en cisaillement. Contrairement aux analyses mécaniques statiques, cette technique de mesure peut faire varier la température de l'échantillon et est donc aussi adaptée pour observer des transitions dans les matériaux résultant en une variation des propriétés mécaniques et d'angles de déphasage. Pour le PLA, les transitions mesurables peuvent être la relaxation α , la cristallisation froide et le début de la température de fusion. De plus, si la DMA est couplée avec un système de refroidissement adapté, la relaxation β peut aussi être mesurable.

Durant le projet, les mesures sont réalisées en traction et en double-encastrement sur une DMA 242 E Artemis (Netschz, Selb, DEU). Le choix s'est porté sur l'utilisation du mode double-encastrement pour la caractérisation des matériaux imprimés en 3D, afin d'avoir

une marge d'épaisseur de matériaux suffisamment importante pour tester différents paramètres d'impression (détaillés en **Chapitre 5** et **Chapitre 6**) tout en évitant les phénomènes d'affaissement dus au passage en état caoutchoutique que l'on aurait pu rencontrer en mode flexion 3 points. Les échantillons sont des languettes de 40*10 mm et de 60*10 pour respectivement le mode traction et le mode double-encastrement. Les essais se présentent en une rampe de 0 °C à 140 °C avec une vitesse de chauffage de 5 °C·min⁻¹. Toutes les mesures sont réalisées sous une fréquence de 1 Hz, fréquence majoritairement utilisée pour la mesure du PLA selon la littérature. En mode traction, l'oscillation mécanique est contrôlée par la déformation, avec une amplitude dynamique allant jusqu'à 30 µm et une plage de force entre 4 ± 4 N. En mode double-encastrement, le contrôle se fait via une force contrôlée de 1 N.

3.5.2.c. *Analyses rhéologiques*

Comme la DMA, les tests rhéologiques sont utilisés pour connaître le comportement viscoélastique de la matière, mais cette fois à l'état visqueux. Comme les deux précédentes caractérisations, cette analyse peut aussi être réalisée en mode dynamique. Dans cette configuration, l'oscillation est également d'origine mécanique et se présente sous la forme d'oscillation d'un plan circulaire (appelé géométrie). Le rhéomètre applique une contrainte contrôlée (sous la forme d'un couple) oscillante sur l'échantillon. Cette oscillation va engendrer un cisaillement dans la matière et l'appareil récupère la contrainte de cisaillement ainsi que l'angle de déphasage du système. Grâce à ces informations, il est possible de connaître le module complexe de cisaillement G^* du système selon les **Équation 13** à **Équation 15** ci-contre (Buschow, 2001) :

$$G^* = \frac{\sigma_0}{\gamma_0} = G' + iG'' \quad \text{Équation 13}$$

$$G' = G^* * \cos \delta \quad \text{Équation 14}$$

$$G'' = G^* * \sin \delta \quad \text{Équation 15}$$

où G' et G'' sont respectivement le module de stockage et le module de perte (en Pa), σ_0 est la contrainte maximale du signal sinusoïdal (en Pa) et γ_0 est la déformation maximale

du système (sans unités). δ est l'angle de déphasage entre le signal émis et reçu. Le module de cisaillement calculé permet aussi d'obtenir la viscosité complexe η^* via l'Équation 16 :

$$\eta^* = \frac{G^*}{\omega} = \frac{G^*}{2\pi f} \quad \text{Équation 16}$$

où ω est la fréquence angulaire et f est la fréquence mécanique appliquée (en Hz).

Les essais rhéologiques de ce projet sont réalisés avec un rhéomètre plan MCR 302 (Anton Paar, Graz, AUT). Il est auparavant important de réaliser en amont des tests rhéologiques en fonction de l'amplitude afin de connaître la plage viscoélastique linéaire (LVE) de la matière. Cette plage représente une gamme d'amplitudes où la déformation et la contrainte varient proportionnellement. De plus, l'amplitude de la contrainte n'est pas suffisante pour détruire la microstructure de l'échantillon, souhaitable pour une bonne mesure. Les résultats en amplitude pour tous les tests sont résumés en **Annexe 3**. Une fois cette limite viscoélastique connue, elle est utilisée pour fixer l'amplitude des tests en fréquence. Tous les tests sont réalisés entre 175 et 180 °C avec une épaisseur d'entrefer entre 1 et 1,5 mm sous azote et entre 0,1 et 631 $\text{rads}\cdot\text{s}^{-1}$. Ces paramètres, définis par des analyses préliminaires, semblent être le meilleur compromis pour toutes les matières testées.

3.5.3. Caractérisations de mécanique statique

Pour connaître les propriétés mécaniques statiques des biocomposites, trois tests sont réalisés : des tests de traction, de flexion et d'impact. Les normes utilisées sont respectivement les normes ASTM D638 Type 1, ASTM D790 et ASTM D256 pour les tests de traction, flexion et d'impact. Le design des éprouvettes est donné en **Figure 3.8**. Les tests sont réalisés sur une machine d'essai universelle Zwick Z020 (Zwick Roell Group, Ulm, DEU), ainsi que sur une Zwick IZOD (Zwick Roell Group, Ulm, DEU).

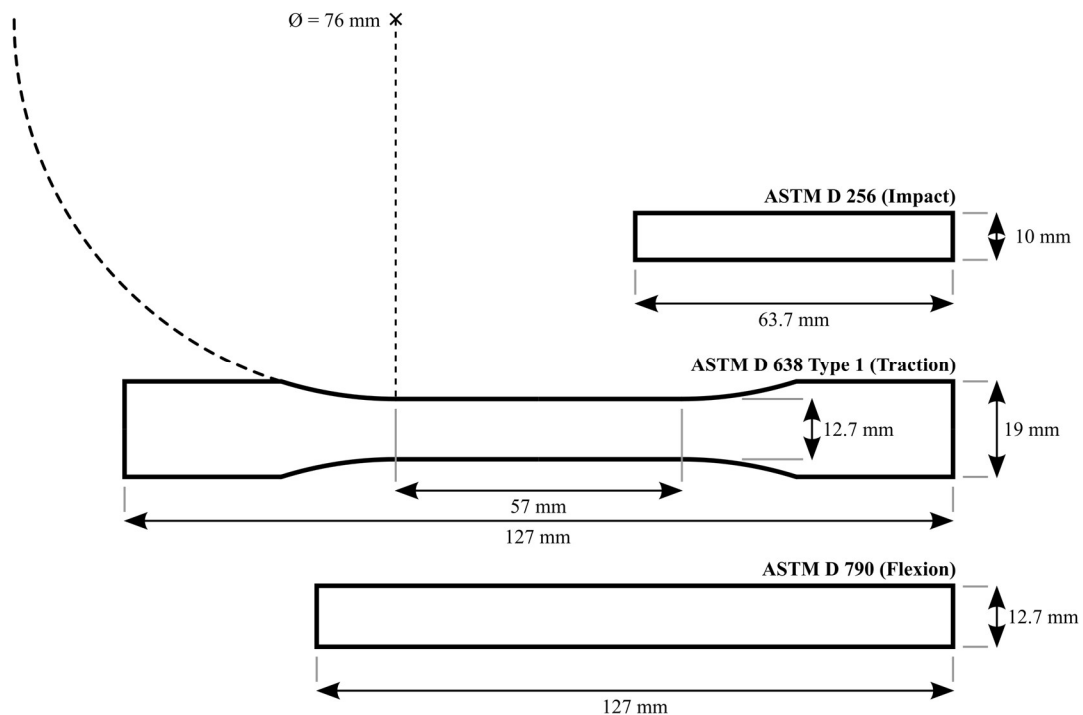


Figure 3.8 : Design des éprouvettes de mécanique statiques

3.5.3.a. Tests de traction

Les tests de traction sont les tests de mécanique statique les plus communs. Ils consistent en la rupture sous contrainte de traction d'éprouvettes pour connaître différentes propriétés physiques comme la rigidité, la ténacité et la fragilité du matériau testé. Les tests de traction sont réalisés usuellement sur des éprouvettes possédant une zone de concentration de contrainte afin de contrôler la rupture, nommées « *dog bones* » en anglais. La rigidité du matériau (E_t), aussi nommé module d'élasticité, correspond au coefficient directeur de la partie linéaire de la courbe, soit la zone d'élasticité du matériau. Cette grandeur est exprimée en $\text{N}\cdot\text{mm}^{-2}$, mais plus régulièrement exprimée en GPa ($1 \text{ GPa} = 1000 \text{ N}\cdot\text{mm}^{-2}$) par simplicité. Concernant la norme ASTM D638 A, cette valeur se calcule usuellement dans la partie de courbe allant jusqu'à 20 N. Une valeur élevée de module reflétera un comportement rigide, là où une faible valeur reflétera un comportement souple. La ténacité du matériau (σ_t), aussi nommée contrainte maximale, correspond à la contrainte maximale que le matériau peut supporter avant soit de se rompre (correspondant à un matériau fragile), soit subir un « *necking effect* ». Une valeur élevée reflétera un comportement homogène résistant, tandis qu'une faible valeur peut refléter un matériau possédant des hétérogénéités (agrégats, porosité), amenant à des

zones de concentration de contraintes et donc de ruptures facilitées. Cette grandeur est exprimée en $\text{N}\cdot\text{mm}^{-2}$, mais plus régulièrement exprimée en MPa ($1 \text{ MPa} = 1 \text{ N}\cdot\text{mm}^{-2}$). Pour finir, l'allongement pour la contrainte maximale (ε_t) est aussi un bon indicateur de la fragilité du matériau. Il correspond à la valeur d'allongement pour laquelle la valeur maximale de contrainte est atteinte, exprimée en pourcentage. Pour déterminer E_t , $\sigma_{t \max}$ et ε_t , les équations sont respectivement **Équation 17**, **Équation 18** et **Équation 19** (Dammak, 2022) :

$$E_t = \frac{\sigma_t}{\varepsilon_t} \quad \text{Équation 17}$$

$$\sigma_{t \max} = F_{\max} * S \quad \text{Équation 18}$$

$$\varepsilon_t = \frac{\Delta L_t}{L_{t0}} \quad \text{Équation 19}$$

où σ_t et ε_t correspondent respectivement à la contrainte et l'allongement pour déterminer le module d'élasticité, respectivement exprimés en $\text{N}\cdot\text{mm}^{-2}$ et en pourcentage. F_{\max} est exprimée en N et correspond à la force maximale supportée par l'échantillon. En divisant cette valeur par la section S de l'échantillon (en mm^2), cela donne la contrainte maximale que peut supporter l'échantillon, exprimée en $\text{N}\cdot\text{mm}^{-2}$. L_{t0} correspond à la longueur utile de l'échantillon et exprimée en mm. Pour finir, ΔL_t correspond à l'allongement subi par l'éprouvette durant le test, aussi exprimé en mm. Un total de 3 éprouvettes par condition ont été testées à température ambiante, avec une vitesse de traverse de $2 \text{ mm}\cdot\text{min}^{-1}$. Pour gagner en précision, l'allongement de l'éprouvette en traction a été monitoré grâce à une jauge placée sur la zone utile des éprouvettes de traction.

3.5.3.b. Tests de flexion

Les tests de flexion sont par nature différents des tests de traction. Plutôt que d'imposer une contrainte de traction dans l'axe de l'éprouvette, la contrainte appliquée est perpendiculaire à la longueur de l'éprouvette. Ce mode de test mécanique induit des phénomènes à la fois de cisaillement, compression et traction dans l'ensemble de l'éprouvette testée. Ces tests sont par exemple très utilisés pour la caractérisation de lames de bois composites, où la sollicitation principale est en flexion. Il est possible d'obtenir

le module d'élasticité en flexion E_f , la contrainte maximale en flexion $\sigma_{f \max}$ et la déformation pour la contrainte maximale ε_f selon les **Équation 20** à **Équation 22** :

$$E_f = \frac{F * L_f^3}{4 * \delta_C * a * ep^3} \quad \text{Équation 20}$$

$$\sigma_{f \max} = \frac{3 * F_{\max} * L_f}{2 * \delta_C * a * ep^2} \quad \text{Équation 21}$$

$$\varepsilon_f = \frac{6 * \sigma_f * ep}{L_f^2} * 100 \quad \text{Équation 22}$$

où L_f correspond à la distance entre les deux supports en mm, δ_C est la déflexion de l'éprouvette (en mm), et $\sigma_{f \max}$ est la contrainte maximale que l'éprouvette peut supporter en flexion (en $N \cdot mm^{-2}$). Afin de respecter la norme ASTM D790, la valeur de L_f est fixée à 64 mm. Un total de 3 éprouvettes par condition ont été testées à température ambiante, avec une vitesse de traverse de $2 \text{ mm} \cdot \text{min}^{-1}$.

3.5.3.c. Tests d'impact

Les tests d'impact, aussi connus sous le nom d'essais au choc, sont également un moyen de connaître la force de cohésion des matériaux. Le test consiste en le lâcher d'un bras lesté sur une éprouvette. Après le choc, l'énergie résiduelle du bras est alors mesurée par le système. L'énergie nécessaire pour rompre la machine correspond donc à l'énergie initiale, moins l'énergie résiduelle du bras. Pour la machine possédée, le bras utilisé a une énergie initiale de 2,75 J. La résistance au choc de l'éprouvette s'exprime alors selon l'**Équation 23** (Dammak, 2022) :

$$K = \frac{E_j}{a * ep} \quad \text{Équation 23}$$

où E_j correspond à l'énergie absorbée nécessaire à la rupture de l'éprouvette et exprimée en kJ. Les grandeurs a et ep correspondent à respectivement la largeur et l'épaisseur de l'échantillon, tous les deux exprimés en mm. Un total de 10 éprouvettes sont testées à température ambiante. Les épaisseurs et largeurs des éprouvettes sont fixées à

respectivement 3,2 mm et 10 mm, en fonction des moules de thermocompression à disposition.

**Chapitre 4) Conception et
caractérisation de mélanges
polymériques à base de PLA, PHBV et
de CA**

4.1. Introduction

La synthèse bibliographique a montré que l'acide polylactique (PLA), le polyhydroxybutyrate-co-valérate (PHBV) et l'acétate de cellulose (CA) ont chacun un bon potentiel dans le domaine diélectrique. De plus, les mélanges polymériques peuvent permettre de produire un matériau final avec les propriétés cumulées de chacun de ses constituants. Les objectifs de ce **Chapitre 4** seront donc de concevoir et de caractériser les propriétés diélectriques de mélanges polymériques de PLA, PHBV et CA. En plus des propriétés diélectriques, il paraît pertinent d'y associer une analyse des propriétés mécaniques pour mieux évaluer leurs potentielles applications. Une analyse rhéologique sera aussi présentée pour connaître davantage le comportement viscoélastique des mélanges à l'état fondu. Les objectifs spécifiques de cette partie seront de :

- Caractériser les propriétés diélectriques, mécaniques et viscoélastiques du PLA, PHBV et CA, ainsi que leurs mélanges binaires obtenus par thermocompression.
- Identifier les mélanges avec un potentiel fort pour une application future en impression 3D.

Au vue des connaissances générales et accumulées durant la synthèse bibliographique, les hypothèses ci-contre sont proposées :

- Le PLA et le PHBV auront des propriétés diélectriques plus faibles que le CA, car ce dernier contient des groupes hydroxyles.
- Le PHBV, par son aspect semi-cristallin prononcé, aura des propriétés diélectriques qui vont beaucoup varier en approchant sa température de fusion ($T \approx 160 \text{ °C}$).
- Le CA, par son caractère amorphe ainsi que sa structure moléculaire, aura des propriétés diélectriques qui vont rester relativement stable jusqu'à des températures de 160 °C .

- Le plastifiant du CA altérera les propriétés mécaniques et les températures de relaxation du PLA et PHBV lorsqu'ils seront mélangés ensemble.

Ce chapitre se présente en deux parties :

- La première partie consiste en un article présentant les résultats MEB et FTIR des mélanges binaires et ternaires, ainsi que les résultats diélectriques et rhéologiques.
- La deuxième partie consiste en une partie discussion, où les résultats de l'article sont mis en perspective avec des résultats mécaniques et thermiques pour sélectionner le candidat avec le plus fort potentiel pour la suite du projet de thèse.

4.2. Dielectric and rheological performances of cellulose acetate, polylactic acid and polyhydroxybutyrate-co-valerate biobased blends *

Morgan Lecoublet^{1,2}, Mohamed Ragoubi¹, Nathalie Leblanc¹ and Ahmed Koubaa²

¹ UniLaSalle, Unité de Recherche Transformations et Agro-Ressources (ULR 7519 UniLaSalle-Université d'Artois), Mont-Saint-Aignan, France

² UQAT, Campus de Rouyn-Noranda, 445, boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

* Article accepté et publié dans *Polymer*, Volume 285, n° 126358, 20 Octobre 2023.

DOI : 10.1016/j.polymer.2023.126358

4.2.1. Abstract

This study presents a new approach to formulating cellulose acetate (CA), polylactic acid (PLA), and polyhydroxybutyrate-co-valerate (PHBV) biobased blends, with a focus on their dielectric and rheological performances for an electrical insulation application. Fourier Transform Infrared (FTIR) and rheological analysis showed a molecular interaction in PHBV:CA and PLA:CA blends between the carbonyl groups of PLA and PHBV, and the hydroxyl groups of CA. Dielectric study showed that temperature, frequency, and polymer nature are key parameters influencing the blends' dielectric constant (ϵ') and dielectric loss (ϵ'') for room and high temperatures. Even though CA-based blends possessed the highest dielectric constants at room temperature, they showed the lowest thermal-sensitive behavior. The measured dielectric properties showed potential applications of PLA-based blends for low-temperature electrical insulation and CA-based blends for high-temperature electrical insulation.

4.2.2. Résumé en français

Cette étude présente notre approche pour la formulation de mélanges biosourcés d'acétate de cellulose (CA), d'acide polylactique (PLA) et de polyhydroxybutyrate-co-valérate (PHBV), en mettant l'accent sur leurs performances diélectriques et rhéologiques pour une application d'isolation électrique. L'analyse FTIR et rhéologique a montré une interaction moléculaire dans les mélanges PHBV:CA et PLA:CA entre les groupes carbonyles du PLA et du PHBV et les groupes hydroxyles du CA. L'étude diélectrique a

montré que la température, la fréquence et la nature du polymère sont des paramètres clés qui influencent la constante diélectrique (ϵ') et le facteur de perte (ϵ'') des mélanges à température ambiante et à haute température. Même si les mélanges à base de CA possèdent les constantes diélectriques les plus élevées à température ambiante, ils présentent le comportement le moins sensible à la chaleur. Les propriétés diélectriques mesurées ont montré les applications potentielles des mélanges à base de PLA pour l'isolation électrique à basse température et des mélanges à base de CA pour l'isolation électrique à haute température.

4.2.3. Introduction

The requirement for materials combining dielectric performances and simplicity of implementation in the microelectronics industry has oriented research towards the elaboration of organic/inorganic composites, combining both the performances of the polymeric matrix with an inorganic filler, such as ferroelectric oxides (Deshmukh et al., 2017; Ioannou et al., 2011; Xia et al., 2020). Moreover, the miniaturization race of electronic components generated by Moore's Law is the reason for the strong attention on this dielectric composite material, which remains a key issue to be resolved. Even if they have attractive properties, good processability, and desirable performances, their oil dependency and deplorable environmental impacts make them incompatible with the development of a sustainable economy. Therefore, biobased and/or biodegradable polymers are better than conventional polymers through their ecological advantages, such as accelerated biodegradation capacities or biocompatibility (Yatigala et al., 2018). The production of bioplastics is expected to reach 7,43 Mt in 2028 according to the association *European Bioplastics* (European Bioplastics, 2023a). Potential applications for these new materials include food packaging, consumer goods, agriculture, and construction. Bioplastics' consumption in the dielectric field reached 87,2 kt in 2023 with exponential growth (European Bioplastics, 2023b). Many biobased and biodegradable polymers are capitalizing on this production frenzy, such as polylactic acid (PLA), polyhydroxybutyrate-co-valerate (PHBV), and cellulose acetate (CA) (Abdul Rahman et al., 2010; Ali, 2020; Avella et al., 2022; Dicker et al., 2014; Gigante et al., 2021; Larguech et al., 2021; Wsoo et al., 2020; P. Zhang et al., 2023).

One industrially viable way to improve the performance of biobased polymers and promote their integration is the polymer blending. A blend is a mixture of two or more polymers that are combined to create a new material with modified physical properties according to the final application. By careful selection, the blend morphology can be tuned, whether it is miscible or not. In the dielectric field, Larguech et al. (2021) observed partial miscibility between PLA and polybutylene succinate (PBS) by broad dielectric spectroscopy (BDS) analysis. The addition of PBS into a PLA matrix decreased the dielectric constant (ϵ') at low frequencies and low temperatures. In addition, the dielectric loss (ϵ'') analyses revealed a new relaxation, not present in neat PLA. This relaxation, named β , is related to the torsional motion of the PLA chain. Melt viscoelastic analysis is a highly relevant tool for studying the behavior of materials in a wide range of sectors (Gonzalez-Garzon et al., 2018; Qi et al., 2022; Xiang et al., 2023; Yang et al., 2023; You et al., 2022). Knowing the melt viscoelastic behavior of biobased polymers is essential to better understand and predict their suitability for processing. For example, You et al. (2022) used viscoelastic analysis to characterize the mechanical behavior of hydrogels based on polysaccharide and poly(tannic acid) nanorods. They found an enhancement in the mechanical properties of the hydrogel with the addition of nanorods, which could suggest hydrogen bond-based crosslinking between polysaccharide and poly(tannic acid). Gonzalez-Garzon et al. (2018) suggested blending PLA with PMMA to extend the life of PLA for engineering applications. They noted that the PLA and PMMA had different melt viscoelastic behavior. The zero shear viscosity of PLA was two orders of magnitude lower than that of PMMA. In addition, the blends followed a logarithmic rule of mixture, indicating good compatibility between PLA and PMMA. The observation of a single relaxation by complex viscosity analysis also supported this observation. Yang et al. (2023) studied blends of PLA and starch at a ratio of 90:10 by weight. These blends showed similar behavior to PLA. However, a compatibilization step by reactive extrusion increased the low-frequency storage modulus by 2 orders of magnitudes and the complex viscosity and low-frequency loss modulus of the PLA:starch blends by 1 order of magnitude due to increased chain entanglement as a result of the occurrence of covalent bonding between PLA and starch by reactive extrusion. Although previous studies have shown the potential of biobased polymers in the dielectric field, very few studies have focused on the analysis of these biobased blends, and even fewer on CA-based blends. To provide answers to these problems, this study presents a novel formulation approach for biobased PLA, PHBV, and CA polymeric blends. While the dielectric performance of

biobased polymers has been widely studied, the originality of the work is based on a simultaneous comparison of the dielectric and rheological properties of PLA, PHBV and CA, as well as 6 associated binary blends, to find the best compromise for electrical insulation applications. Moreover, very few rheological studies have been carried out on CA-based blends. Since hydrophilic polymers can create hydrogen bonds with the other components of the blend, it would therefore be relevant to study its behavior with other biobased polymers.

4.2.4. Materials & Methods

4.2.4.a. *Raw materials and sample preparation*

Three biobased polymers were used. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and cellulose acetate (CA) were purchased from Natureplast (Montdeville, FRA). Polylactic acid (PLA) was supplied by EURL BBFil (Heiligenberg, FRA). All biobased polymers were received as 4 mm diameter pellets in 25 kg bags. The CA had a plasticizer content of $W_{\text{plasticizer}} = 29\%$. The Melt Flow Indexes (MFI at 190 °C with 2,16 kg) of PLA and PHBV provided by suppliers were 7 and 15-30 $\text{g}\cdot 10\text{ min}^{-1}$, respectively. The chemical structure of PLA, PHBV and CA is shown in detail in **Figure 4.1**.

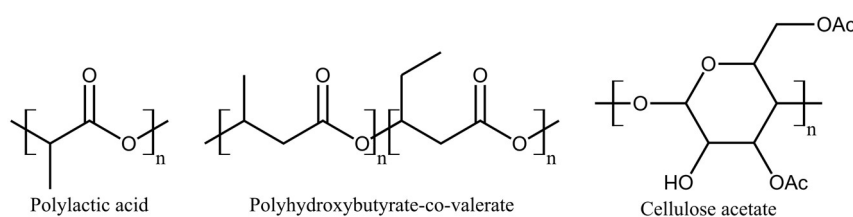


Figure 4.1 : Chemical structure of PLA, PHBV and CA

Different polymeric blends were prepared according to the formulations specified in **Table 4.1**. For this step, all polymer pellets were conditioned in a drying oven at 60 °C at night. The drying phase was repeated at each processing step.

Table 4.1 : Different biobased polymeric blend formulations

Samples	PLA (%)	PHBV (%)	CA (%)
PLA	100	0	0
PLA ₂ _PHBV ₁	200/3	100/3	0
PLA ₁ _PHBV ₂	100/3	200/3	0
PHBV	0	100	0
PHBV ₂ _CA ₁	0	200/3	100/3
PHBV ₁ _CA ₂	0	100/3	200/3
CA	0	0	100
PLA ₁ _CA ₂	100/3	0	200/3
PLA ₂ _CA ₁	200/3	0	100/3

An adaptation of the mixture design was used for a better compromise between several tests and the accuracy of the result (**Figure 4.2**).

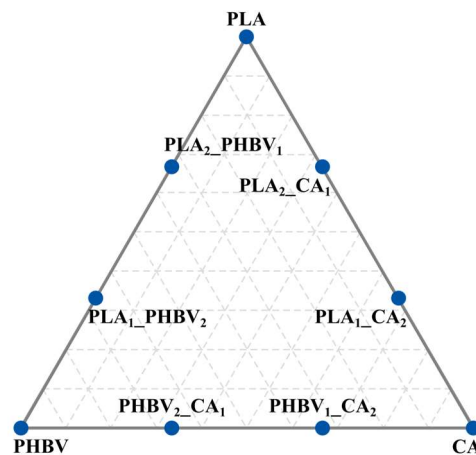


Figure 4.2 : Adapted mixture design used

An extrusion-thermocompression pair was used to process polymeric blends. A single screw extruder Scamex 25-20D (SCAMEX, Isques, FRA) was used, with a temperature profile of 160-175-190 °C from the feeder to the die, with a screw speed of 30 RPM. The parameters were set according to a preliminary processability test. The obtained extrudates were pelletized and hot-pressed with a Scamex 20 T 300*300 press (SCAMEX, Isques, FRA) for 3 minutes at 190 °C. Two plate thicknesses of 0,5 mm and 2 mm were obtained for each neat or blended polymer. All samples were stored in a desiccator before being characterised.

4.2.4.b. *Methods used*

- *Broad Dielectric Spectroscopy (BDS) analysis*

Measurements were made with an Keysight E4980A Precision LCR Meter (Agilent Technologies, Santa Rosa, USA). The sample dimensions were prepared with an ML-W1290 (Millaser, Pont-à-Mousson, FRA) into disks of 25 mm in diameter and 0,5 mm in thickness. BDS tests were conducted in an isothermal setup from 0 °C to 160 °C with a 5 °C heating level. The frequency range was between 20 and 2 MHz. The laboratory BDS gave the capacitance (C_p) and the loss tangent ($\tan \delta$). So, the dielectric constant (ϵ') and dielectric loss (ϵ'') were determined according to **Équation 1** and **Équation 2**. Only the results for 20 °C temperature and the 100 Hz frequency are presented for illustration purposes. Examples of the variation in dielectric properties over the temperature and frequency ranges studied are shown in **Figure A 5** to **Figure A 7** (**Annexe 4**).

- *Rheological analysis*

Rheology tests were performed with a plane rheometer MCR 302 (Anton Paar, Graz, AUT) with a sample diameter of 25 mm. According to the preliminary tests, a gap of 1,5 mm was considered the best compromise. The tests were performed in the Linear Viscoelastic Range (LVE) at 180 °C. The rheological study of the LVE region allows a valid study without degrading the structure of the macromolecular chains. The amplitude sweeps are presented in **Figure A 4a**) (**Annexe 3**). All samples were tested in a nitrogen atmosphere, between 0,1 and 563 $\text{rads}\cdot\text{s}^{-1}$.

- *Scanning electron microscopy (SEM) analysis*

SEM analysis was performed with a JSM IT200 (Jeol, Akishima, JAP). SEM analysis was carried out to observe the morphology of polymeric blends' liquid nitrogen broken surface. Liquid nitrogen was used to prepare a clean surface. Tests were performed at 5 kV with a magnification ranging from x40 to x200. All samples were carbon coated.

- *Fourier Transform Infrared (FTIR) analysis*

FTIR analysis was performed on a Nicolet iS10 IR-TF spectrometer (ThermoFisher Scientific, Waltham, USA) at a frequency range of 500 cm^{-1} to 4000 cm^{-1} . to characterize the chemical composition of the samples. Measurements were made in Attenuated Total Reflectance (ATR) mode.

4.2.5. Results

4.2.5.a. Surface chemistry and morphology properties

Figure 4.3 presents PLA, PHBV, and CA FTIR spectra. All biobased polymers showed a C=O carbonyl vibration at 1749, 1719, and 1736 cm^{-1} for PLA, PHBV, and CA, respectively.

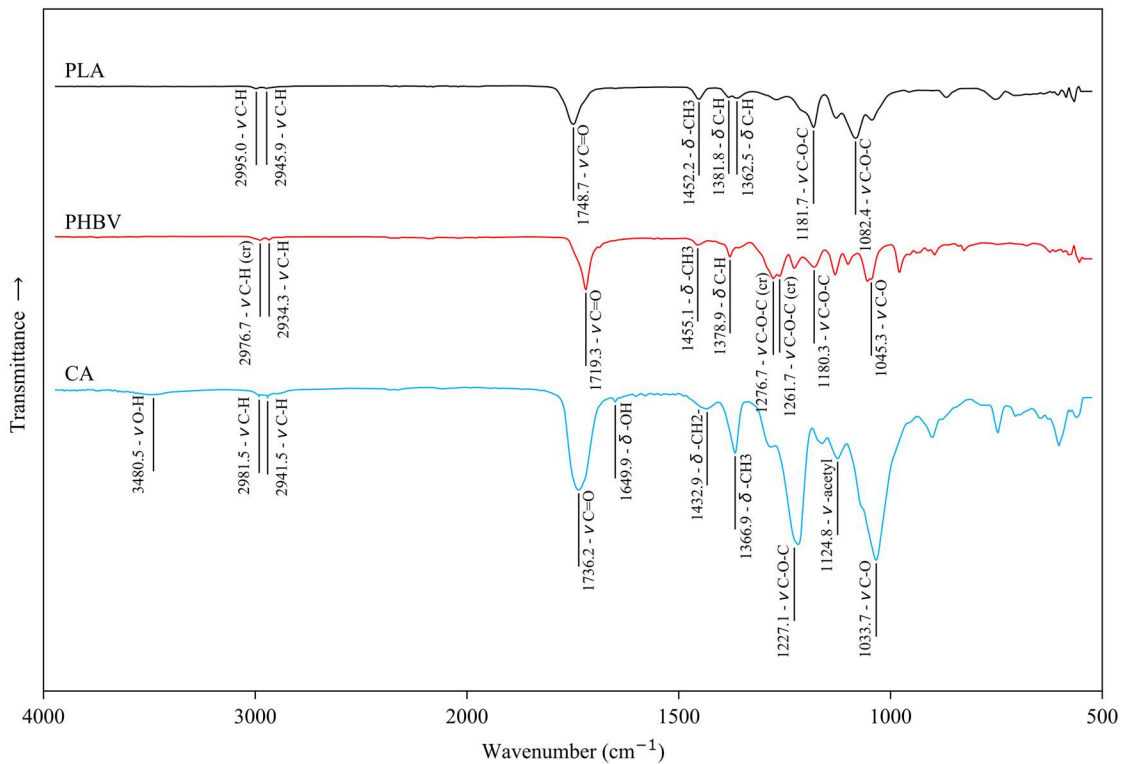


Figure 4.3 : FTIR analysis of PLA, PHBV, and CA

The strongest carbonyl vibration was obtained for CA, which is logical considering that CA contains up to 6 acetate functional groups per monomer unit, depending on their degree of substitution (Wsoo et al., 2020). Furthermore, all biobased polymers showed

C–O–C deformation between $1300\text{--}1180\text{ cm}^{-1}$, assigned to the ester and acetate groups. CA also showed a very intense peak for C–O–C deformation at 1125 cm^{-1} , which also refers to the oxygen atoms in the ring structure of its monomer, increasing the intensity of the observed peak. Moreover, as expected, all neat biobased polymers contained –CH vibration, and –CH₃ and –CH deformations. PHBV showed peaks at 1277 and 1261 cm^{-1} attributed to the C–O–C stretching of the crystal phase (Mazur et al., 2020). Among the studied neat biobased polymers, only CA showed the presence of –OH functional groups in the absorption region of 3481 cm^{-1} and 1649 cm^{-1} . These hydroxyl groups indicated that the CA had a degree of substitution < 3 and can be considered as cellulose diacetate (Wsoo et al., 2020), the most commercially available CA. Finally, CA had no absorption bands around 1800 cm^{-1} or 1700 cm^{-1} . According to Jilal et al. (2018), this observation proved that CA appeared to be free of unreacted acetic acid and of acetic acid byproducts.

The FTIR analysis of the blends revealed molecular interactions, illustrated in **Figure 4.4**. In the PLA:CA blends, the carbonyl vibration peaks were narrow, intense and underwent a shift at a higher wave number than expected, up to a wave number of 1754 cm^{-1} for PLA₁_CA₂.

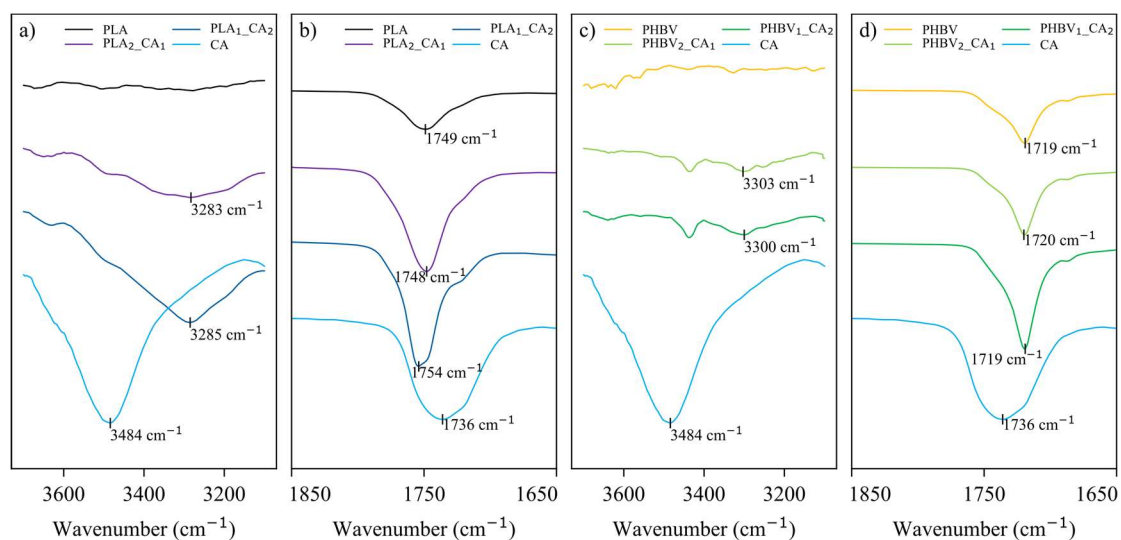


Figure 4.4 : Zoomed FTIR a) PLA:CA blends at 3500 cm^{-1} , b) PLA:CA blends at 1750 cm^{-1} , c) PHBV:CA blends at 1750 cm^{-1} , d) PHBV:CA blends at 1750 cm^{-1}

Moreover, a zoom in the 3400 cm^{-1} area showed that the hydroxyl vibration also shifted to a lower wavenumber, from 3484 to 3300 cm^{-1} . This behavior could be related to specific interactions between PLA and CA (Xing et al., 2013). This interaction occurred

between the PLA carbonyl groups and the CA hydroxyl groups. Therefore, a certain blend compatibility or strong blend interface can be expected. The PHBV:CA blends also showed a weaker shift of C=O vibrations and –OH vibrations (**Figure 4.4c**) and **Figure 4.4d**), which would imply that the interaction between the PHBV carbonyl groups and the CA hydroxyl groups was weaker than inside the PLA:CA blends. Moreover, a narrow and weak peak still existed at 3400 cm^{-1} for PHBV:CA blends. It is an indication that not all the hydroxyl functions have interacted with the carbonyl functions of CA. Concerning the PLA:PHBV blends, no interaction phenomena have been observed.

SEM analyses were carried out to better understand the blend morphologies (**Figure 4.5**). SEM pictures of neat biobased polymers showed, as expected, a coherent structural homogeneity with a relatively clean surface.

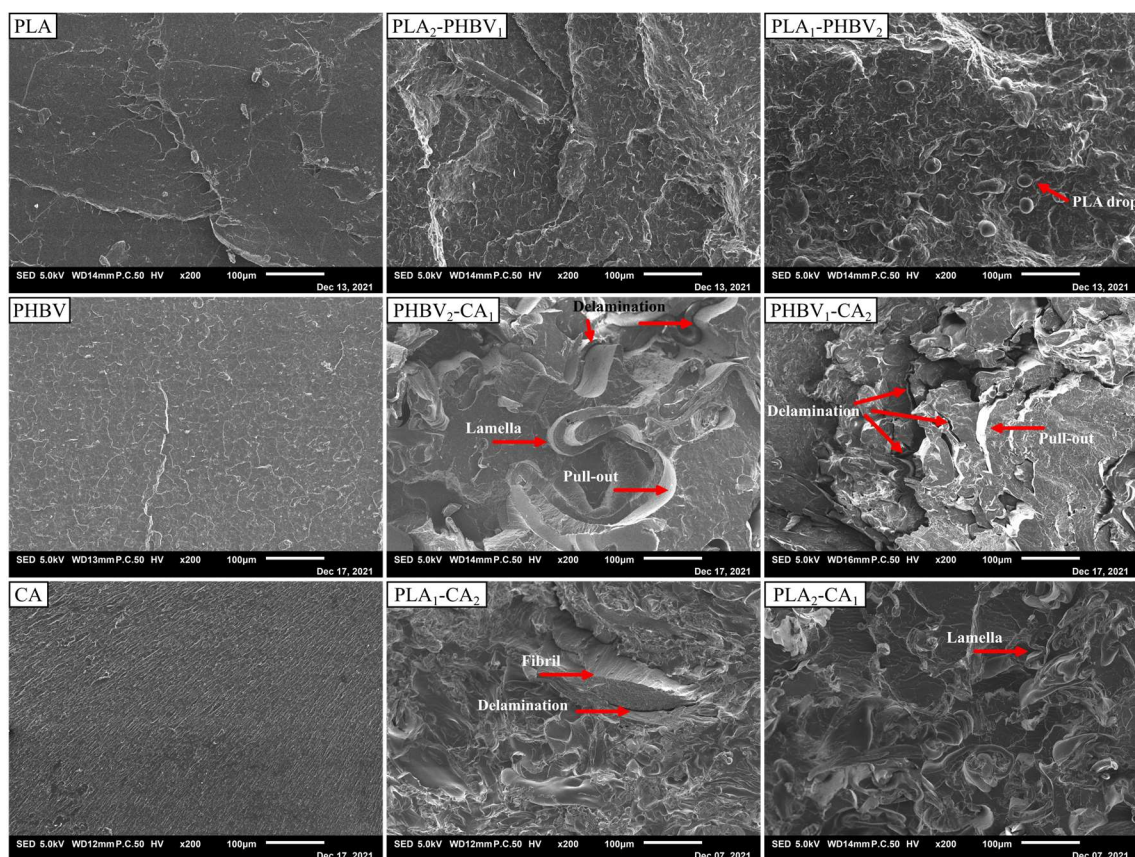


Figure 4.5 : SEM pictures of neat biobased polymers and binary blends

The components of PLA:PHBV blends were difficult to identify separately. No “pulling-out” phenomenon seemed visible, and the interface showed no porosity. They had a sea-island morphology, with droplets of the minor component into the main component.

Gérard and Budtova (2011) also observed a sea-island morphology, but with a pronounced decohesion between the different phases. A dual fibrillar and lamellae morphology was visible for CA-based blends, more pronounced for PHBV:CA blends. Meereboer et al. (2020) also observed this fibrillar form for PHBV:CA blends. This morphology could explain the relatively weak interaction observed by FTIR for PHBV:CA blends: the interactions between the carbonyl and hydroxyl groups could only occur at the PHBV:CA interface. Despite this immiscibility, the interface showed less delamination, in good agreement with a previous report supporting the occurrence of interaction between the phases (Souza et al., 2012). PLA:CA blends also had well-visible phases, but the fibrillar morphology seemed more dispersed. Coltelli et al. (2021) also observed this fibrillar morphology and associated the visible fibrils with CA. This more dispersed fibrillar morphology partly explained the FTIR results. The enhanced dispersion increased the interface and, therefore, more interactions between the carbonyl groups of PLA and the hydroxyl groups of CA were possible.

Table 4.2 presents the water angle contact of PLA, PHBV, and CA observed in the literature to investigate morphological observations further.

Table 4.2 : Water angle contact of PLA, PHBV, and CA

Biobased polymer	Water contact angle (°)	References
PLA	85,2	(Tejada-Oliveros et al., 2021)
PLA	70	(Jariyasakoolroj, 2014)
PLA	77,5	(Laput et al., 2019)
PLA	81	(Paragkumar N et al., 2006)
PHBV (8 % HV)	87,9	(Santos et al., 2011)
PHBV (12 % HV)	86,8 ± 2,0	(Santos et al., 2011)
PHBV (14 % HV)	88,8 ± 2,1	(Santos et al., 2011)
PHBV	97,1	(Shuai et al., 2020)
CA	56	(Ali, 2020)
CA 22	54,7	(Guezguez et al., 2013)
CA 25	56,5	(Guezguez et al., 2013)
CA	37,6 ± 1,2	(Iqhrammullah et al., 2020)

Wettability provides information on a surface's hydrophilic or hydrophobic behavior by measuring the angle that a drop (mostly water) makes on the surface of the tested material. The smaller the angle that a drop of water makes on the material, the greater the surface energy of this material and the more hydrophilic the material is. Moreover, the more the

surface energy between the two materials is identical, the more likely they are to be miscible. **Table 4.2** shows that CA surface energy was much higher than PLA surface energy, which was higher than PHBV surface energy. These findings confirmed the observations of a partial miscibility of the PLA:PHBV blends. Similar surface energies between PLA and PHBV could explain the partial miscibility. The large surface energy difference between CA and PLA:PHBV could explain the relative immiscibility observed by SEM. The more dispersed morphology of PLA:CA blends could be due to a lower surface energy difference between PLA:CA compared to PHBV:CA.

4.2.5.b. Dielectric properties

Figure 4.6a) shows the dielectric constant of PLA:PHBV blends as a function of frequency at 20 °C.

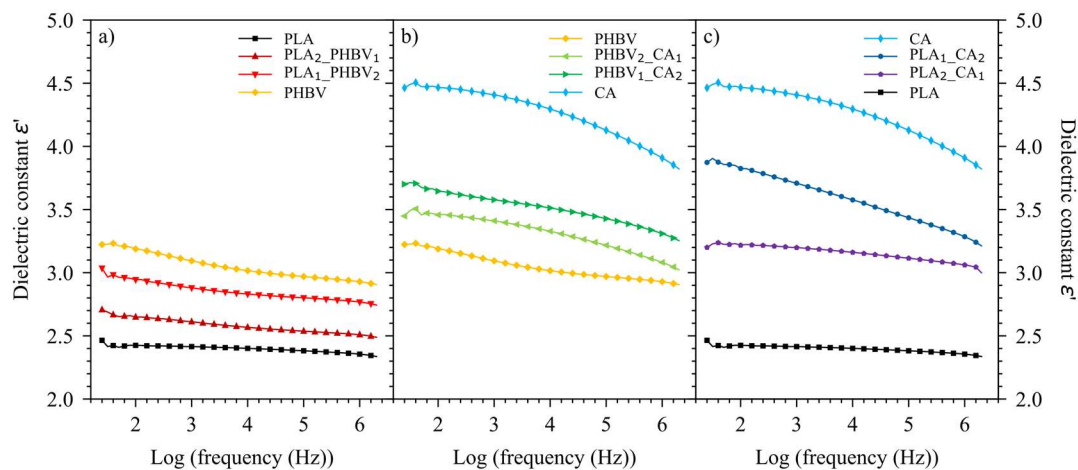


Figure 4.6 : Dielectric constant ϵ' of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends @ 20 °C

In good agreement with previous findings, increasing the frequency decreased the ϵ' (Ciuprina et al., 2020; Gallot-Lavallee and Heux, 2013; Khouaja et al., 2021). This phenomenon was due to poor dipolar polarization with the frequency increasing, synonyms of limited molecular mobility between the electric field and the polar groups (Khouaja et al., 2021). At 100 Hz and 20 °C, a ϵ' of 2,42 and 3,19 for PLA and PHBV, respectively, was measured. The observed behaviors were coherent with those reported in the literature (Ciuprina et al., 2020; Gallot-Lavallee and Heux, 2013; Larguech et al.,

2021). The addition of PHBV into PLA slightly increased the ϵ' . At any frequency, the dielectric constant of the PLA:PHBV blends followed the rule of mixtures and the frequency affected only slightly the dielectric constant of PHBV:PLA blends. **Figure 4.6b)** and **Figure 4.6c)** present the dielectric constant of CA-based blends. At 100 Hz and 20 °C, a ϵ' of 4,47 was observed for CA, 84 % and 40 % higher than PLA and PHBV, respectively. This higher dielectric constant was associated with the hydroxyl groups of CA (as shown in **Figure 4.3**). This presence of polar groups increased the possible interaction of the biobased polymer with the presence of the applied electric field, thereby increasing its permittivity (Khouaja et al., 2021). A similar improvement of the dielectric constant by adding a polar component into an apolar material was observed by Larguech et al. (2021) for jute fibers in a thermoplastic matrix, and by Johns and Nakason (2011) and Larguech et al. (2021) for a nonpolar natural rubber and polar chitosan blends. The variation of ϵ' as a function of the tested blends seemed to follow a rule of mixtures for all frequencies.

Figure 4.7 shows the dielectric constant of all the produced blends as a function of temperature at 100 Hz.

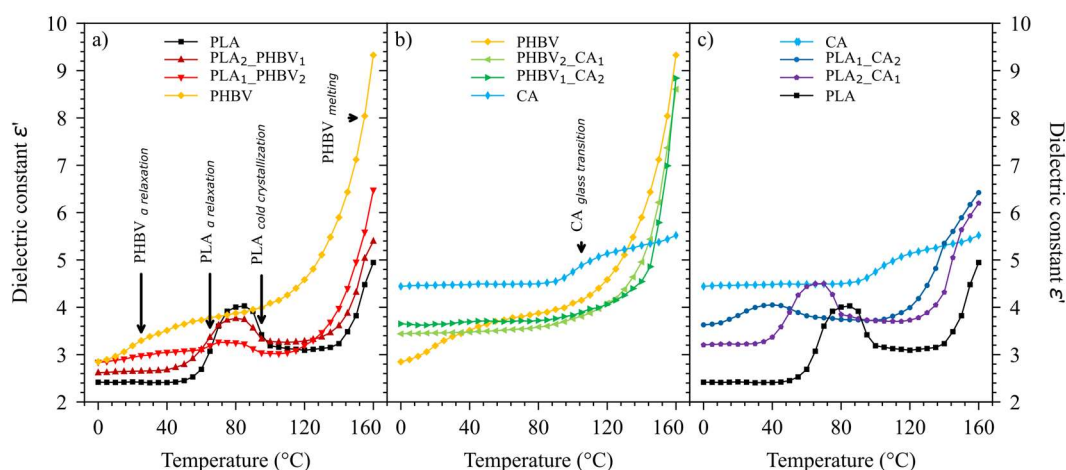


Figure 4.7 : Dielectric constant ϵ' of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends versus temperature @ 100 Hz

The temperature increase enhanced the dielectric constant for the neat biobased polymers and all tested blends. The ϵ'_{PLA} , ϵ'_{PHBV} , and ϵ'_{CA} increased from 2,42, 2,85, and 4,44 at 0 °C to 4,95, 9,33, and 5,52 at 160 °C, respectively. This phenomenon could be attributed

to the polymers' thermal softening, allowing the macromolecular chains to follow more easily the electric field switching (Deshmukh et al., 2017). The ϵ'_{PHBV} was very thermal sensitive beyond 140 °C, increasing from 5,9 to 9,3 between 140 and 160 °C measured at 100 Hz. Despite its higher ϵ' , CA possessed the most stable dielectric constant as a function of temperature compared to the other two biobased polymers. The ϵ'_{CA} between 0 and 160 °C increased by only 24 % compared to ϵ'_{PLA} and ϵ'_{PHBV} , which increased by 104 and 227 %, respectively. This demonstrated the low ϵ' variability of CA as a function of temperature, encouraging its use in dielectric applications over a wide temperature range. **Figure 4.7a)** also shows that the α -relaxation of the PLA and PHBV was associated with a strong increase in the dielectric constant (Badia et al., 2017; Gallot-Lavallee and Heux, 2013). $T_{\text{g PHBV}}$ and $T_{\text{g PLA}}$ were found at 11 °C and 61 °C at 100 Hz, determined from the T_{onset} of the real part (Hsiao, 2013). The ϵ' increase associated with the α -relaxation was due to the transition between the glassy and rubbery state of the polymers, which increases the mobility of the macromolecular chains and thus their polarity. Badia et al. (2017) also reported an increase in the dielectric constant of PLA at 60 °C at low frequencies, associated with an increase of ionic mobility after the glass transition of PLA. Above 80 °C, ϵ'_{PLA} decreased due to a cold crystallization phenomenon, decreasing the softening by a crystalline structure and increasing the mechanical performances (Beg et al., 2023; Chai et al., 2022). **Figure 4.7b)** also showed an α -relaxation of CA at 89 °C at a frequency of 100 Hz with the T_{onset} of the real part. The cold crystallization and α -relaxation of PLA in the PLA:CA blends were also visible but at a lower temperature due to the presence of CA plasticizer (**Figure 4.7c)**).

Figure 4.8a) to Figure 4.8c) shows the dielectric loss of all blends as a function of frequency at 20 °C, which represents the electromagnetic energy converted into heat. The high PLA-content blends had the lowest dielectric losses of all tested biobased blends. This could be due to the amorphous structure of the used PLA (confirmed by DSC tests). In contrast, PHBV gave a higher value of ϵ'' than PLA. This may be due to the presence of the α -relaxation of PHBV, as presented in **Figure 4.7a)**. In addition, preliminary DSC analyses confirmed the highly crystalline character of PHBV ($X_{\text{cr}} = 64 \%$). The literature also gave an X_{cr} of about 60 % for PHBV (Carli et al., 2011). The high crystalline content could generate dielectric loss regions (Khouaja et al., 2021), increasing the ϵ'' . At high frequencies ($> 100 \text{ kHz}$), CA possessed the highest ϵ'' . This could be due to the higher presence of hydroxyl groups contributed by CA that can polarize and then induce losses

in the material (Khouaja et al., 2021). At low frequencies, PLA₁_CA₂ showed the highest ϵ'' . This could be due to the plasticizer present in CA, which reduces the temperature associated with the α -relaxation phenomenon of PLA. **Figure 4.7c)** showed that the α -relaxation of PLA in PLA₁_CA₂ was present around 20 °C, which was the main reason for this increase at low frequency.

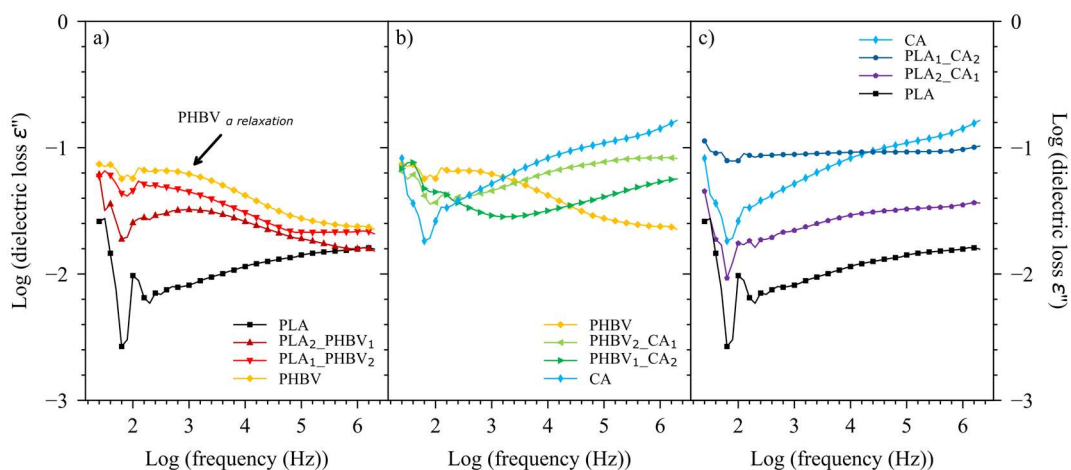


Figure 4.8 : Log (dielectric loss ϵ'') of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends @ 20 °C

4.2.5.c. Rheological properties

Figure 4.9 and **Figure 4.10** show the viscoelastic properties of the different blends. All the blends showed a shear-thinning behavior, with increased loss modulus (G'') and a steady decrease in complex viscosity (η^*) with increasing frequencies. For the neat PLA, the complex viscosity was stable at low frequencies and decreased after $f > 10 \text{ rad}\cdot\text{s}^{-1}$. PLA, PLA₂_PHBV₁, PLA₁_PHBV₂, and PHBV possessed a Newtonian plateau at $f < 10 \text{ rads}\cdot\text{s}^{-1}$, where the viscosity is independent of the shear rate, and also named zero shear viscosity (η_0). By applying the Cross equation (Volpe et al., 2018), the η_0 PLA, η_0 PLA₂_PHBV₁, η_0 PLA₁_PHBV₂, and η_0 PHBV was found at 463, 392, 217, and 83 Pa·s, respectively.

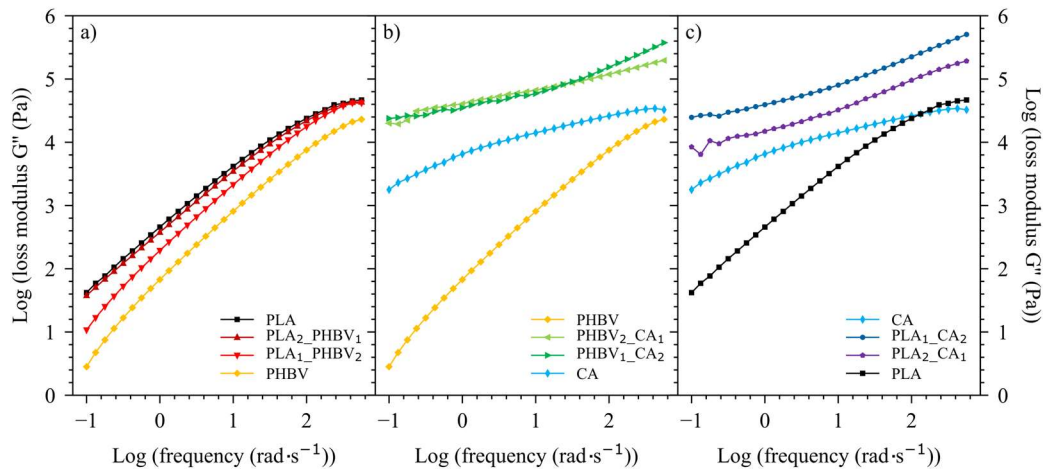


Figure 4.9 : Log (loss modulus G'') of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends versus frequency

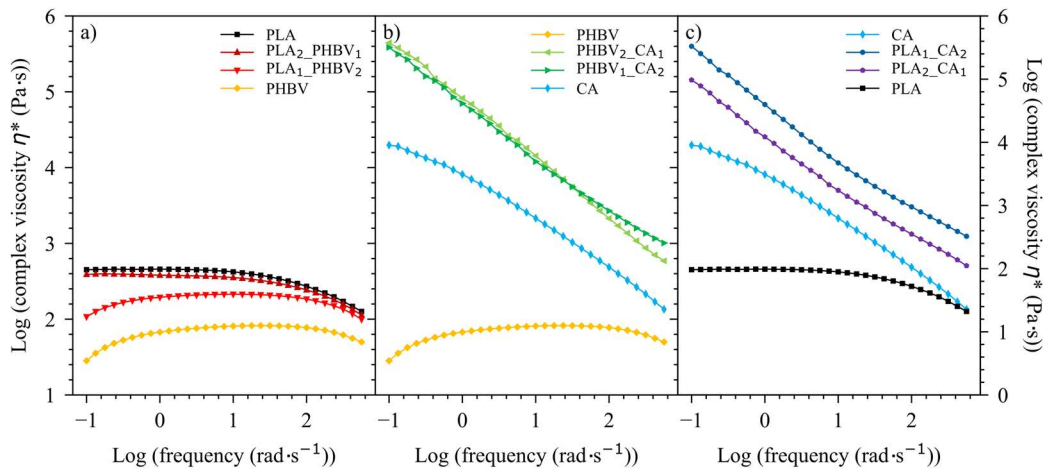


Figure 4.10 : Log (complex viscosity η^*) of a) PLA:PHBV blends, b) PHBV:CA blends, c) PLA:CA blends versus frequency

This steady variation was also observed by Gonzalez-Garzon et al. (2018). Thus, PLA:PHBV blends were considered as partially miscible (Yu and Zhou, 2012). The PHBV content also reduced the viscoelastic behavior and decreased the G'' of PLA blends. The higher viscoelastic behavior of PLA compared to PHBV may be related to the polymer grades. The PLA used was an extrusion grade, while the PHBV was an injection grade. For the same polymer, an injection grade often possesses a shorter chain length than an extrusion grade. As the chain length is directly linked to the complex viscosity (Noroozi et al., 2012), the viscosity difference can be explained by a higher polymerization degree of PLA. At low frequencies, η^*_{PHBV} and $\eta^*_{\text{PLA1_PHBV2}}$ decreased.

This result was due to the degradation of PHBV associated with a too-long application of temperature, which caused scissions in the macromolecular chains and thus decreased η^* (Lajewski et al., 2021).

Furthermore, **Figure 4.10** shows CA-based blends' complex viscosity. The investigation showed that CA was much more viscous than PLA and PHBV. At 180 °C and 1 rad·s⁻¹, CA had a complex viscosity of 8129 Pa·s, and a Newtonian plateau can be extrapolated at 3,53*10⁴ Pa·s using the Cross equation, which is 425 and 76 times higher than PHBV and PLA respectively. The high stiffness of the cellulosic chain (J. Zhang et al., 2023), the high bulking effect of the CA monomer unit due to the acetyl functions, and the hydroxyl groups creating hydrogen bonds between the CA macromolecular chains are factors that can increase the entanglement of the system. It gave a higher complex viscosity than PHBV and PLA (Ma et al., 2018). This higher measured viscosity could be the reason for the low thermal variability of the dielectric constant of CA. The very limited mobility of the chains limits the polarization potential. Concerning the blends, PLA:PHBV followed the viscosity and complex modulus rule of mixtures, confirming the FTIR observations that no specific interactions occurred between PLA and PHBV. However, the CA-based blends had a viscosity and a complex modulus much higher than their constituents, indicating of specific interactions between the hydroxyl groups of CA and the carbonyl groups of PLA and PHBV.

4.2.6. Conclusions

This study investigated the dielectric and rheological properties of cellulose acetate (CA), polylactic acid (PLA), and polyhydroxybutyrate-co-valerate (PHBV) biobased polymeric blends. The incorporation of CA into PLA and PHBV significantly enhanced their dielectric behavior. At 100 Hz and 20 °C, ϵ'_{CA} was 41 and 83 % higher than ϵ'_{PLA} and ϵ'_{PHBV} , respectively. The fact that CA favored high dielectric polarization has been associated with the hydroxyl groups of CA. The influence of temperature was an important key parameter for all the tested blends. However, the CA-based blends were the least sensitive to temperature variation. The dielectric constant of CA between 0 and 160 °C increased by only 24 %, compared to PLA and PHBV, which increased by 95 and 228 %, respectively. These results showed that PLA-based blends are preferred for low-

temperature dielectric insulation applications, and CA-based blends are preferred for high-temperature dielectric insulation applications. Regarding the rheological properties, results showed that all tested materials have a shear-thinning behavior. The neat polymers and the PLA:PHV blends possessed a Newtonian plateau at the tested measuring conditions. However, the PHBV:CA and PLA:CA blends were much more viscous due to molecular interaction between the hydroxyl groups of CA and the carbonyl groups of PLA and PHBV. They did not have a predictable Newtonian plateau at the measurement condition tested. The SEM and rheological results showed that the blends do not have the same morphology. PLA:PHBV was partially miscible, and PLA:CA and PHBV were immiscible. The compatibility of the blends could be related to the dual hydrophobic:hydrophilic character of the neat polymers used. A classification of the compatibility of the blends would give the compatibility of PLA:PHBV blends >>> compatibility of PLA:CA blends > compatibility of PHBV:CA blends. Molecular interactions were present in the interface of PLA:CA and PHBV:CA. The PLA:CA blends had a more dispersed phase than PHBV:CA, the higher interaction for PLA:CA observed by FTIR explain this finding. Future studies will include mechanical analyses to provide a better understanding of the performance of these new biobased polymeric blends.

4.3. Discussions et bilan du Chapitre 4

Les objectifs évoqués pour ce chapitre ont pu être atteints avec succès durant cette phase. Six différents mélanges binaires, ainsi que les trois polymères purs, ont pu être mis en œuvre par thermocompression et testés. Les résultats diélectriques ont bien confirmé que les mélanges binaires gardaient les performances diélectriques de leurs constituants, mais avec quelques variations en fonction de leur nature. Des analyses de conductivité électrique proposées en **Table A 1 (Annexe 4)** et des analyses de constante diélectrique à haute fréquence avec un spectromètre Keysight E4991A (**Table A 2 et Figure A 8**) ont aussi confirmé les observations réalisées dans l'article publié. Le CA possède une permittivité plus importante que le PLA et le PHBV. Selon la classification de Dubois (2001), le PLA et le PHBV peuvent être considérés comme des polymères apolaires et le CA comme polymère faiblement polaire, en accord avec les observations de la synthèse bibliographique. Ces résultats ont pu aussi être mis en corrélation avec les résultats FTIR, où seul le CA possédait bien des groupes hydroxyles polaires. Il a aussi été remarqué que les mélanges à base de CA augmentaient fortement la viscosité des mélanges et donc altèreraient potentiellement l'imprimabilité des mélanges si le CA représente une part trop importante du mélange. Ce phénomène, selon la littérature, serait associé à des interactions hydrogène entre les groupes hydroxyles du CA et les groupes carbonyles du PLA et/ou du PHBV.

Concernant les résultats thermiques des mélanges présentés en **Annexe 5**, les résultats DSC ont montré que le PLA et le CA présentaient une morphologie amorphe par rapport au PHBV, hautement cristallin (**Figure A 9 et Table A 3**). Le plastifiant du CA a comme prévu impacté les températures de relaxation du PLA et PHBV en diminuant l'énergie nécessaire à leur apparition. Les résultats ATG ont montré que le PLA était le polymère le plus stable par rapport au PHBV et au CA (**Figure A 10 et Table A 4**). Ce dernier a la plus faible T_{95} %, en raison de la dégradation des groupes acétyles. Les analyses DMA complémentaires (**Annexe 6**) et BDS ont aussi montré que les polymères n'ont pas le même comportement en fonction de la température. Le PHBV, semi-cristallin, n'a vu ses propriétés mécaniques altérées qu'uniquement vers sa T_m (**Figure A 11**). Le CA est resté relativement stable et le PLA a subi un phénomène de T_{cc} important vers les 80-100 °C. La présence d'interactions hydrogène et la présence du plastifiant expliqueraient pourquoi

le comportement thermomécanique des mélanges PLA:CA et PHBV:CA ne sont pas linéaires.

Pour le choix du mélange à sélectionner pour la production par impression 3D, la **Figure 4.11** présente les propriétés clés des différents mélanges dans un graphique radar. Les résultats ont montré que les mélanges PLA/PHBV, malgré leurs propriétés mécaniques (**Annexe 6**) et diélectriques pertinentes pour une utilisation en isolant électrique rigide, ont leurs propriétés sévèrement impactées par la température. De plus, la tenue du mélange à 180 °C est médiocre. Pour rappel, l'impression 3D nécessite un minimum de trois mises en œuvre successives, ce qui risque de faire accumuler rapidement de la dégradation thermique dans le PHBV, limitant grandement son potentiel. Malgré de plus faibles propriétés mécaniques et diélectriques, les mélanges PLA:CA possèdent une bonne stabilité thermodiélectrique, une bonne tenue à 180 °C, et avec un potentiel fort d'innovation, car aucun article à notre connaissance ne l'a utilisé par impression 3D, ou pour une application en isolation électrique. Ce mélange a donc été choisi pour l'application en impression 3D, avec cependant une viscosité, un effet plastifiant et de dégradation des groupes acétyles à surveiller.

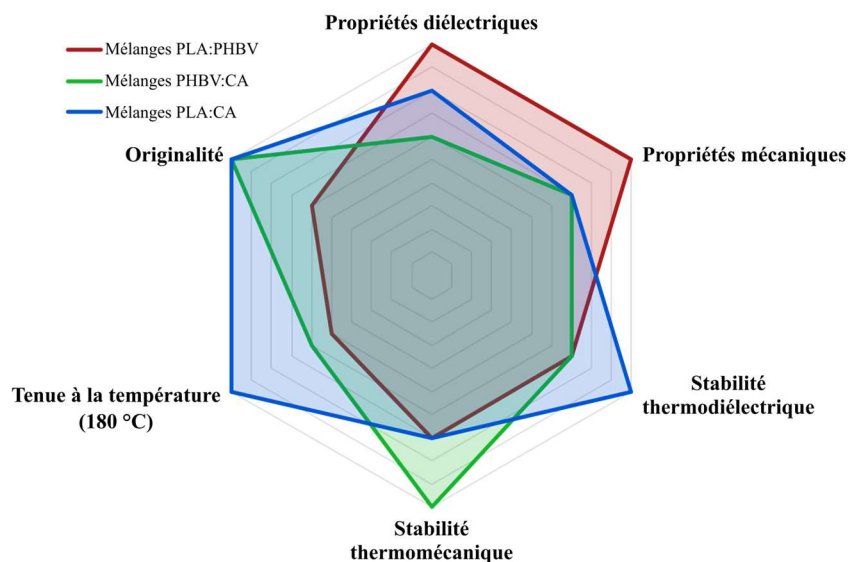


Figure 4.11 : Graphique radar des performances diélectriques et mécaniques, la stabilité de ces dernières en température, la tenue à la température à 180 °C et de l'originalité scientifique du projet des mélanges caractérisés en **Chapitre 4**.

**Chapitre 5) Conception et
caractérisation de mélanges
polymériques PLA:CA pour
impression 3D**

5.1. Introduction

Ce cinquième chapitre vise à utiliser la stratégie de conception de mélanges polymériques évoqués en synthèse bibliographique pour produire des matériaux visant une application en isolation électrique grâce à l'impression 3D. Les observations du **Chapitre 4** ont montré que le mélange PLA:CA serait approprié pour une étude approfondie. Le choix d'un tel mélange est aussi pertinent à plus d'un titre. Incorporer le PLA dans le mélange pour impression 3D est intéressant, car le PLA est un polymère historique dans ce procédé, donc déjà très démocratisé et donc bien maîtrisé. De plus, utiliser le CA comme constituant du mélange est intéressant afin de favoriser l'utilisation de biomasse cellulosique dans à la fois le domaine diélectrique et dans le domaine de l'impression 3D. Pour finir, très peu de littérature et donc de retour d'expérience existe à l'heure actuelle sur la faisabilité d'utiliser de la cellulose sous forme thermoplastique en impression 3D par FFF. Il serait donc à la fois pertinent et innovant d'étudier de près de tels mélanges. Ainsi, les objectifs visés durant cette campagne seront de :

- Étudier l'imprimabilité des mélanges PLA:CA et évaluer le potentiel du CA dans le domaine diélectrique par impression 3D.
- Étudier comment le CA influencera les propriétés diélectriques, mécaniques et viscoélastiques des mélanges PLA:CA.
- Optimiser les propriétés mécaniques et diélectriques de tels matériaux pour une application en isolation électrique par l'utilisation d'un plan d'expérience.

Compte tenu des connaissances générales et accumulées durant la synthèse bibliographique, les hypothèses ci-contre sont proposées :

- L'ajout de CA augmentera les propriétés diélectriques et de conductivité des mélanges, tout augmentant la viscoélasticité des mélanges en état fondu, risquant de complexifier l'imprimabilité des mélanges à haut taux de CA.
- L'ajout de CA diminuera les propriétés mécaniques et les températures de relaxation du PLA, par la présence du plastifiant du CA.

- L'impression 3D améliorera le potentiel d'application en basse permittivité de tels mélanges par ajout de porosité interne inhérente au procédé d'impression, mais ces porosités réduiront leurs potentiels mécaniques.
- L'amélioration des propriétés d'isolation électrique de l'impression 3D compensera l'ajout de CA.
- Un plan de Taguchi serait pertinent pour faire varier les paramètres d'impression et pour faire diminuer le temps de caractérisation.
- Selon le plan de Taguchi, le taux de remplissage diminuera la constante diélectrique, la conductivité électrique, mais aussi diminuera le module de stockage, et l'épaisseur de couche augmentera la constante diélectrique, la conductivité électrique et aussi le module de stockage de tels mélanges.

Ce chapitre se divise en trois parties. La première partie consiste en un article présentant une étude détaillée des propriétés diélectriques et viscoélastiques des mélanges PLA:CA imprimés en 3D. La deuxième partie consiste en un article visant à optimiser les propriétés diélectriques et de mécanique dynamique des mélanges PLA:CA au travers d'un plan de Taguchi. Le troisième article propose une étude synthétique des matériaux développés durant ce chapitre. Pour finir, une partie discussion sera proposée.

5.2. Dielectric and viscoelastic properties of 3D-printed biobased materials *

Morgan Lecoublet^{1,2}, Mohamed Ragoubi¹, Nathalie Leblanc¹ and Ahmed Koubaa²

¹ UniLaSalle, Unité de Recherche Transformations et Agro-Ressources (ULR 7519 UniLaSalle -Université d'Artois), Mont-Saint-Aignan, France

² UQAT, Campus de Rouyn-Noranda, 445, boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

* Article accepté et publié dans *Industrial Crops and Products*, Volume 212, n° 118354, Juin 2024. DOI : 10.1016/j.indcrop.2024.118354

5.2.1. Abstract

This study aimed to develop new biobased materials containing plasticized cellulose acetate (CA) by fused filament fabrication (FFF). We investigated the influence of CA on the viscoelastic/dielectric properties and the influence of 3D printing on the dielectric properties of the polymer blends. A microstructural analysis showed that the blends had a strong heterogeneous morphology, as the two phases formed a fibrillar and lamellar structure. CA strongly increased the blend viscosity at 175 °C, multiplying by 100 times the complex viscosity between neat PLA and the blend containing 40 % of CA by weight (CA-40). The addition of CA to the blends increased the dielectric constant (ϵ'), dielectric loss (ϵ''), as well as the alternative current electrical conductivity (σ_{AC}). The dielectric constant of CA (ϵ'_{CA}) was proportional to its percentage in the blend, showing a behavior analogous to a rule of mixture. Moreover, the activation energy of the electrical conductivity (σ_{DC}) measured at $T > 124$ °C decreased with increasing CA content and was associated with the enhancement of the ionic conductivity provided by the CA and its plasticizer. A decrease in the α -relaxation temperature and the associated activation energy of the PLA was also linked to the presence of the CA plasticizer. Finally, 3D printing greatly decreased both ϵ' , ϵ'' , and σ_{AC} due to the internal voids induced by the 3D printing process. The porosity was measured at 12 % for neat PLA and between 20 and 25 % for the blends. These results showed the advantage provided by FFF technology in the production of PLA:CA blends with controlled dielectric properties, thereby favoring the use of these new materials in key dielectric areas.

5.2.2. Résumé en français

Cette étude avait pour objectif le développement de nouveaux matériaux biosourcés à base d'acétate de cellulose plastifié (CA) par impression 3D de dépôt de fils fondus (FFF). Nous avons étudié l'influence de l'acétate de cellulose sur les propriétés viscoélastiques et diélectriques ainsi que l'influence du procédé d'impression 3D. Une analyse microstructurale a montré que les mélanges avaient une morphologie hétérogène, les deux phases formant une structure fibrillaire et lamellaire. Le CA a fortement augmenté la viscosité du mélange à 175 °C, avec une multiplication par 100 de la viscosité complexe entre le PLA pur et le mélange contenant 40 % de CA en masse (CA-40). L'ajout de CA dans le PLA a augmenté la constante diélectrique (ϵ'), la perte diélectrique (ϵ''), ainsi que la conductivité électrique en courant alternatif (σ_{AC}). La constante diélectrique du CA (ϵ'_{CA}) était proportionnelle à son pourcentage dans le mélange, montrant un comportement analogue à une loi des mélanges. De plus, l'énergie d'activation de la conductivité électrique en courant continu (σ_{DC}) mesurée à $T > 124$ °C a diminué avec l'augmentation de la teneur en CA, associable à l'amélioration de la conductivité ionique grâce au CA et à son plastifiant. Une diminution de la température et de l'énergie d'activation de relaxation α du PLA a également été liée à la présence du plastifiant du CA. Enfin, l'impression 3D a fortement diminué l' ϵ' , l' ϵ'' et la σ_{AC} en raison de vides induits par le processus d'impression 3D. La porosité a été mesurée à 12 % pour le PLA pur et entre 20 et 25 % pour les mélanges. Ces résultats ont montré l'avantage de la technologie FFF dans la production de mélanges PLA:CA avec des propriétés diélectriques contrôlées, favorisant ainsi l'utilisation de ces nouveaux matériaux dans des domaines diélectriques clés.

5.2.3. Introduction

The dielectric field is vital in our daily lives, usually occupied by glass, wood, ceramics, and synthetic polymer-based composites (Khouaja et al., 2021; Yuan et al., 2022). Polymer-based composites, such as PVC, PE, and PP, with their excellent dielectric and electrical properties and processability, are indispensable in today's world. However, due to their harmful ecological impacts and the increasing scarcity of fossil resources, it is necessary to find replacements to ensure sustainable development. Recent reports aim to

promote new biobased polymers (Jin et al., 2022; Pei et al., 2020; Spinelli et al., 2020). One of the most promising biobased polymers is cellulose acetate (CA).

CA is a cellulose ester derived from cellulose (Deshmukh et al., 2017), the largest available polymer stock in the world, with an estimated annual production of $1,5 \cdot 10^{12}$ tons (Liu and Sun, 2010). This family is defined by the substitution degree (DS) of the hydroxyl groups of the D-glucose unit of cellulose by acetyl groups (Assis et al., 2020). The DS ranges from 0 (cellulose) to 3 (cellulose triacetate) and can be tuned to adjust the multiphysical properties of CA (de Freitas et al., 2017; Rubio-Valle et al., 2022). Once associated with a plasticizer, its simplicity of processing makes it suitable for many applications such as medical products, packaging, membranes, and synthetic fibers (Assis et al., 2020; Deshmukh et al., 2017). Deshmukh et al. (2017) proposed using CA:alumina (Al_2O_3)-based bionanocomposites for the manufacturing of electronic devices, such as embedded passives. They obtained a dielectric constant (ϵ') of 27,5 with a weight content of Al_2O_3 ($W_{\text{Al}_2\text{O}_3}$) of 25 % in CA film matrix, measured at 30 °C and 50 Hz. In addition, this material had a low dielectric loss (ϵ''), which makes it perfectly suited for applications in passive embedded printed circuit boards (PCB) requiring such performance levels.

The necessity of replacing synthetic matrices is an invaluable vector of innovation for material processing. 3D printing processes would be perfectly suited in this case. Fused filament fabrication (FFF) is the most common 3D printing technology. It is a promising and perfectly adapted technology for the fast development of customizable, cheap, and thermoplastic structures for numerous applications (Bajwa et al., 2021; Zhou et al., 2022). During the FFF processing, the material filaments are fused in a heated nozzle, extruded, and deposited layer-by-layer to build physical models previously designed in CAD software (Bajwa et al., 2021; Bi et al., 2018). Spinelli et al. (2020) produced PLA nanocomposites filled with carbon nanotubes (CNT) and graphene nanoplatelets (GNP) using FFF technology to increase both electrical and thermal conductivity properties. At 100 Hz and a $W_f = 6$ %, the electrical conductivity of PLA was around 3 decades higher for CNT-based nanocomposites than for GNP-based ones, which was made possible by the CNT form factor, favoring the percolation point of CNT-based nanocomposites. Kuzmanić et al (2023) evaluated the dielectric properties of 3D-printed PLA parts and the processing parameters influencing the dielectric properties. They showed that the

infill ratio plays a key role in the dielectric constant, going from 1,78 to 2,81 for an infill ratio of 33 and 100 %, respectively. This result shows the possibility of controlling the dielectric constant using keen material design. Concerning the use of cellulose acetate through the 3D printing process, the majority of literature relies on inkjet technology. By using the FFF technology, plasticized cellulose acetate propionate (CAP) samples, a cellulose ester, have been successfully produced (Immonen et al., 2021). The research team noted the potential of cellulose esters for 3D processing, while also pointing out the problems of layer adhesion in the case of an excessive plasticizer content. For applications in electronics, cellulose acetate has been used in conjunction with acrylonitrile butadiene styrene (ABS) and graphite for electrode design using FFF technology (Amorim et al., 2022). The authors reported that the addition of CA enhanced the electroactive surface area and heterogeneous electron transfer rate constant of the electrodes, demonstrating the potential of combining cellulose acetate and 3D printing for electronic devices.

Even if CA is a promising biobased polymer for electronic applications, its application by FFF technology is still largely undeveloped. To further investigate such materials, this study proposes the dielectric and viscoelastic investigation of CA-based materials produced by FFF technology. To facilitate the processing, PLA was chosen as a co-matrix for 3D printing because of its wide availability and good 3D printing capacity. The originality of this work is multiple, as it proposes to study the influence of CA content and the 3D printing process on the dielectric, dynamic mechanical and rheological properties of CA-based polymer blends, which has not yet been performed as far as we know. This combined properties study will help to investigate the potential of such 3D-printed materials to promote the integration of biobased materials in the dielectric field.

5.2.4. Materials & Methods

5.2.4.a. Raw materials and sample preparation

Natureplast (FRA) and EURL BBFil (Heiligenberg, FRA) supplied the ACI 002 plasticized cellulose acetate (CA) and the Ingeo 2003D polylactic acid (PLA), respectively. The PLA presented a D-lactic acid content of 4,5 %. All biobased polymers

were 4 mm diameter in 25 kg bags. According to the suppliers, the CA had a plasticizer content of 29 % and the PLA had a Melt Flow Index of $7 \text{ g} \cdot 10\text{min}^{-1}$ at $190 \text{ }^\circ\text{C}$ and 2,16 kg.

A total of 4 different blends were produced with different CA content by mass (W_{CA}). The 4 blends were named CA-10, CA-20, CA-30, and CA-40 and possessed a W_{CA} of respectively 10 , 20, 30 and 40 %. Neat PLA was also added and used as a reference. The first processing step was the blending via extrusion. Pellets were dried in an oven at $60 \text{ }^\circ\text{C}$ overnight to ensure a perfectly dry state to avoid the effect of high moisture on CA processing. A SCAMEX 25-20D (SCAMEX, Isques, FRA) single screw extruder was used, with a temperature profile of 160-170-180 $^\circ\text{C}$ and a screw speed of 30 rounds per minute (RPM), as determined by preliminary tests. The filament-making step was carried out with a 3DEVO filament maker (3DEVO, Utrecht, NL) with a temperature profile of 170-180-180-170 $^\circ\text{C}$ and a screw speed of 5 RPM. The resulting filaments had a $2,85 \pm 0,1 \text{ mm}$ diameter. This diameter was a compromise between size stability and filament quality. Filaments were stored at $60 \text{ }^\circ\text{C}$ in an oven before being processed by a SIGMAX R19 3D printer (BCN3D, Gavà, ESP). The UltiMaker Cura slicer was used, and the printing parameters are shown in **Table 5.1**. All produced conditions used the same printing parameters with the exception of the infill pattern. The **Figure 5.1** presents the produced samples for BDS and DMA samples. Overall, all samples achieved good quality, with no warping or cracking effects. Only CA-30 and CA-40 required the use of glue stick on the glass bed to increase adhesion.

Table 5.1 : 3D printing parameters

Nozzle temperature	215 $^\circ\text{C}$
Nozzle diameter	0,6 mm
Printing speed	30 $\text{mm} \cdot \text{s}^{-1}$
Bed temperature	60 $^\circ\text{C}$
Sample thickness	$\sim 2 \text{ mm}$
Layers	14
Layer thickness	0,15 mm
Infill density	100 %
Infill pattern (BDS)	Concentric
Infill pattern (DMA)	± 45

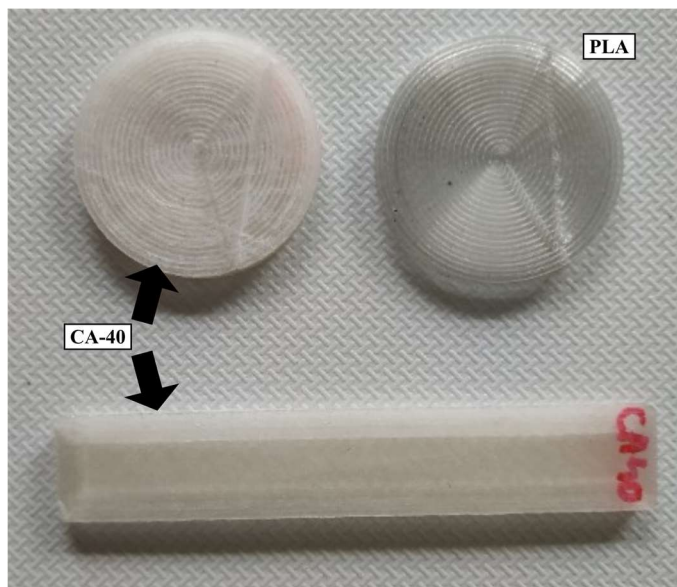


Figure 5.1 : 3D-printed PLA and CA-40 samples. Disk-shaped specimens are used for BDS analysis and rectangular shaped specimens are used for DMA analysis

Reference specimens were produced by hot-pressing with a Scamex 20 T 300*300 press (SCAMEX, Isques, FRA) at 180 °C, with a processing time of 2 minutes, and a mold pressure of 2,5 bars. The hot-pressed samples were cut with an ML-W1290 150 W laser cutter (MLlaser, Pont-à-Mousson, FRA). A laser power of 30 % at 30 mm·s⁻¹ was sufficient to cut the samples without degradation nor distortion. Moreover, for the dielectric analysis, a neat CA, named CA-100, was also prepared by hot-press. All samples were stored in a desiccator during 3h before being characterised.

5.2.4.b. *Methods used*

- *Scanning electron microscopy (SEM) analysis*

SEM analysis was performed with a Jeol JSM IT200 (Jeol, Akishima, JAP) to characterize the microstructure of the blends. Tests were carried out on specimens obtained by hot-press. A cryofracture with liquid nitrogen was carried out to obtain a clean cross-section, and the selected specimens were all carbon-coated. Tests were made at 15 kV with a magnification of x200.

- *Rheological analysis*

The dynamic rheological tests were conducted on an MCR 102 plane rheometer (Anton Paar, Graz, AUT) to characterize the viscoelastic behavior of the hot-pressed samples in the melt state. Disk samples with a diameter of 25 mm and a thickness of 1,5 mm were subjected to a temperature of 175 °C under nitrogen. All tests were performed in the Linear Viscoelastic Range (LVE) and with a shear rate range between 0,1-631 rad·s⁻¹. The amplitude sweeps are presented in **Figure A 4b)** (**Annexe 3**).

- *Broadband dielectric spectroscopy (BDS) analysis*

Two BDS tests were conducted with an E4980A Precision LCR Meter (Keysight, Santa Rosa, USA) on the hot-pressed samples and 3D-printed samples. An isothermal test at 20 °C with a frequency ranging from 100 Hz to 2 MHz with 20 measurements per decade was used to get the dielectric properties at room temperature. A test from 0 °C to 160 °C with 4 °C steps and a frequency ranging 100 Hz to 1 MHz with 10 measurements per decade were conducted to get the dielectric behavior vs temperature of the samples. All samples, 3D-printed or hot-pressed, were disk-shaped with a 25 mm diameter and 2 mm thickness. The dielectric constant (ϵ'), dielectric loss (ϵ'') and AC conductivity (σ_{AC}) were determined according to **Équation 1**, **Équation 2** and **Équation 5** respectively. The DC conductivity (σ_{DC}) was determined according to the work of Benabed and Seghier (2015). The activation energy E_a of the conductivity was calculated by applying an Arrhenius model proposed by Ziemath et al. (2017). The T_g determined by BDS was based on the research of Dichtl et al. (2017), with an application of the Havrilak-Negami (HN) model, followed by a Vogel-Fulcher-Tamman (VFT) fit to obtain the final relaxation temperature associated with the α -relaxation of PLA. Complementary BDS results versus temperature are presented in the **Annexe 7**.

- *Dynamic mechanical analysis*

Hot-pressed samples and 3D-printed samples of 60*10*2mm were tested on a DMA 242 E Artemis (Netsch, Selb, DEU) in double cantilever mode to obtain the viscoelastic behavior of the blends in the solid state. The dual cantilever mode was chosen instead of the 3-point bending mode because of the very low stiffness of PLA once its glass

transition temperature is reached ($T > 60$ °C). The tests were conducted in ramp mode between 30 and 140 °C with a heating rate of 5 °C·min⁻¹, a monitored force of 1 N and a frequency of 1 Hz.

- *Determination of the porosity content of the samples*

To determine the porosity in the samples, a method derived from the measured permittivity was used (**Équation 24**):

$$Porosity(\varepsilon) (\%) = 100 - \left(\frac{\varepsilon_{xp} - \varepsilon_{air}}{\varepsilon_{th} - \varepsilon_{air}} \right) * 100 \quad \text{Équation 24}$$

Where ε_{xp} corresponds to the measured dielectric constant of the sample; ε_{th} corresponds to the theoretical dielectric constant; ε_{air} corresponds to the permittivity of the air filling the voids. In this case, ε_{air} was assumed to be equal to 1. Moreover, since a first-order model between dielectric constant and CA content has been demonstrated, ε_{th} can be derived from a rule of mixture (**Équation 25**):

$$\varepsilon_{th} = \varepsilon_{PLA} * \frac{(100 - W_{CA})}{100} + \varepsilon_{CA} * \frac{W_{CA}}{100} \quad \text{Équation 25}$$

Where W_{CA} corresponds to the weight content of CA; ε_{PLA} corresponds to the dielectric constant of hot-pressed PLA (found at 2,92); ε_{CA} corresponds to the dielectric constant of hot-pressed CA (found at 4,20). This method of determining the porosity will be compared to the method derived from the density and given by **Équation 26**:

$$Porosity(d) (\%) = 100 - \frac{w}{d_{th}} * 100 \quad \text{Équation 26}$$

Where w is the mass of the sample (in grams), V is the volume of the sample (in cm³), and d_{th} is the theoretical density. The specimens being disks of 25 mm in diameter, the porosity can be simplified (**Équation 27**):

$$Porosity(d) (\%) = 100 - \frac{w}{d_{pyc}} * 100 \quad \text{Équation 27}$$

Where l is the thickness of the sample (in cm) and d_{pyc} is the density of the blends and was calculated by a pycnometer analysis of the 3D-printing filaments. Densities were found between 1,2605 and 1,2877 (**Table 5.2**).

Table 5.2 : Densities measured by pycnometer analysis for the hot-pressed samples

	PLA	CA-10	CA-20	CA-30	CA-40
Density	1,2605	1,2689	1,2742	1,2848	1,2877

5.2.5. Results and discussion

5.2.5.a. Microstructural properties

Figure 5.2 shows the SEM images of all tested samples. As expected, PLA had a smooth surface. However, the incorporation of CA into PLA dramatically increased the system's heterogeneity. The roughness of the cryo-fractured cross-sections also increased with the addition of CA. The two phases are visible, as the blends were incompatible. Moreover, the system presents a lamellar and fibrillar-like morphology.

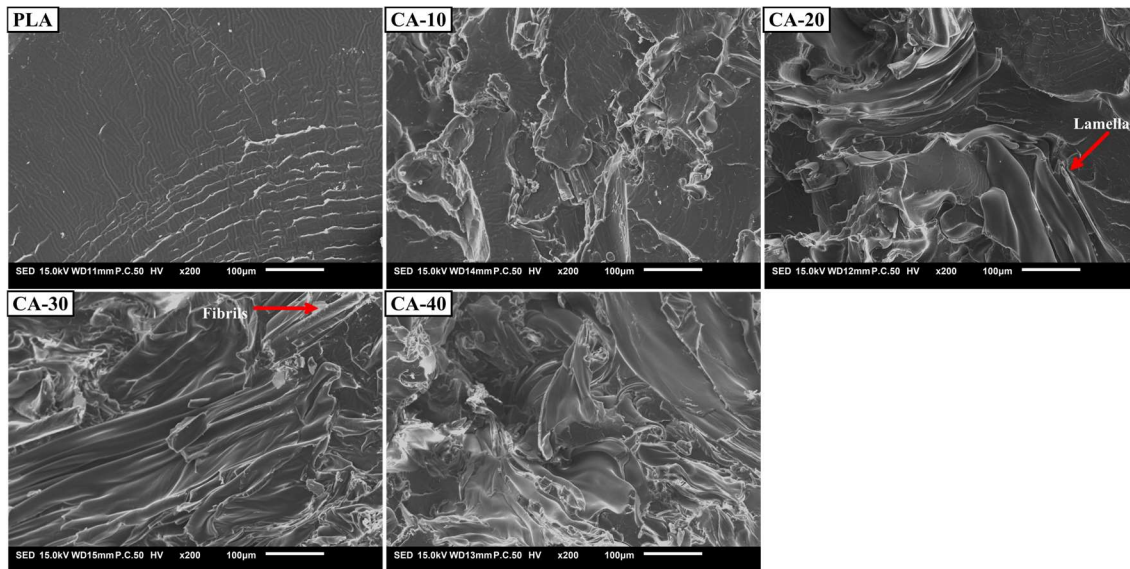


Figure 5.2 : SEM analysis of a) PLA, b) CA-10, c) CA-20, d) CA-30, e) CA-40 at x200

Figure 5.3a) presents the variation in complex viscosity of hot-pressed PLA and PLA:CA blends as a function of frequency.

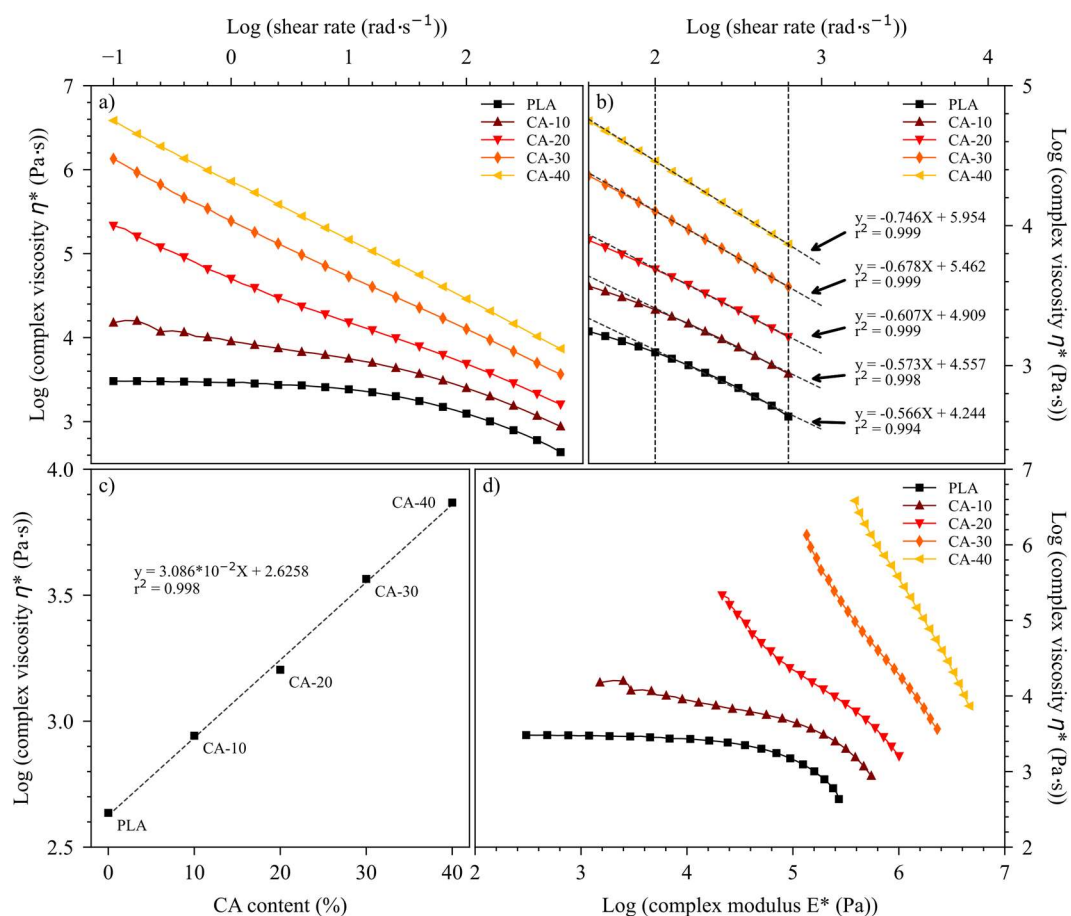


Figure 5.3 : a) Log (complex viscosity η^*) versus frequency of hot-pressed samples of PLA and CA:PLA blends, b) Zoom on high shear rate and their associated power law fit, c) log(complex viscosity η^*) versus CA content measured at 631 rad·s⁻¹ and the associated first-order fit, d) Log (complex viscosity η^*) versus log (complex modulus G^*)

Neat PLA and all the blends tested had a shear-thinning behavior. When the complex viscosity decreased, the shear rate increased. Neat PLA presented a Newtonian plateau at $f < 1$ rad·s⁻¹, where the viscosity is independent of shear rate and named zero-shear viscosity (η_0). By applying a Cross model (Volpe et al., 2018), the shear-independent viscosity η_0 was determined for PLA at 3060 Pa·s. Increasing the CA content from 0 % to 40 % at a 1 rad·s⁻¹ shear rate increased the complex viscosity by 248 times. CA-10 and CA-20, as for PLA, had a flattening shoulder in their curves around 100 rad·s⁻¹, tending

towards a Newtonian plateau. Another shoulder was observed around $5 \text{ rad}\cdot\text{s}^{-1}$ and the viscosity increased exponentially towards low frequencies. The complex viscosity of CA-30 and CA-40 blends were very frequency dependent as they did not exhibit inflections in the tested frequency range. A simple power law curve was perfectly fitted for CA-30 and CA-40, $2,51\cdot 10^5 X^{-0,656}$ and $7,31\cdot 10^5 X^{-0,706}$, respectively, with X being the shear rate in $\text{rads}\cdot\text{s}^{-1}$. Their respective coefficients of determination (r^2) were 0,997 and 0,999. **Figure 5.3b**) shows a close-up at high frequency of the previously mentioned curves and their associated power law. This zoom was performed at frequencies $f > 100 \text{ s}^{-1}$, a shear rate range similar to the 3D processing. It is important to know the material behavior under a high shear rate to predict its printability (Ding et al., 2023; Gunduz et al., 2018). The five blends clearly showed a perfect power law fit with a good coefficient of determination ($r^2 > 0,995$). Both models' exponents and coefficients increased as expected with the addition of CA. Moreover, at $631 \text{ rad}\cdot\text{s}^{-1}$, the addition of CA increased under a first-order fit to the complex viscosity of the blends (**Figure 5.3c**)). This behavior permitted the reliable prediction of the viscosity of all blends at $175 \text{ }^\circ\text{C}$. **Figure 5.3d**) shows the complex modulus G^* as a function of the complex viscosity η^* . According to Wang et al. (2017), this curve provides information about the flow behavior of fluids. The PLA showed a well-defined Newtonian plateau and present at low G^* . The addition of CA, however, made the Newtonian plateau disappear, and the ensuing curve became steeper, a complex viscosity trend also observed by Coltelli et al. (2021). This increase in viscosity may be due to the rigidity of the cellulosic unit of the CA (J. Zhang et al., 2023), thereby restricting the mobility of PLA and, therefore, of the associated blends. Moreover, in a previously published work, we demonstrated that the PLA and CA blends showed interactions between the hydroxyl functions of CA and the carbonyl functions of PLA (Lecoublet et al., 2023). These interactions also hindered and increased the viscosity of the associated blends. These types of interactions between PLA and CA were also reported by El Assimi et al. (2021). This higher viscosity could explain the need to use adhesives to improve adhesion, since a viscous material, combined with a lower PLA content in the blends, does not adhere properly on the glass bed. Another hypothesis suggested by Immonen et al. (2021), suggested an excessive plasticizer content in the blend. However, despite a complex viscosity between 20 and 1000 times higher than neat PLA, CA-40 was successfully produced by 3D printing. This may be due to the combined effect of the shear-thinning properties of the blends and the high shear rate process induced by the 3D printing process, which mitigates the high viscosity of PLA:CA blends.

5.2.5.b. Dielectric properties

Figure 5.4 presents the dielectric constant ϵ' of hot-pressed and 3D-printed blends at 20 °C.

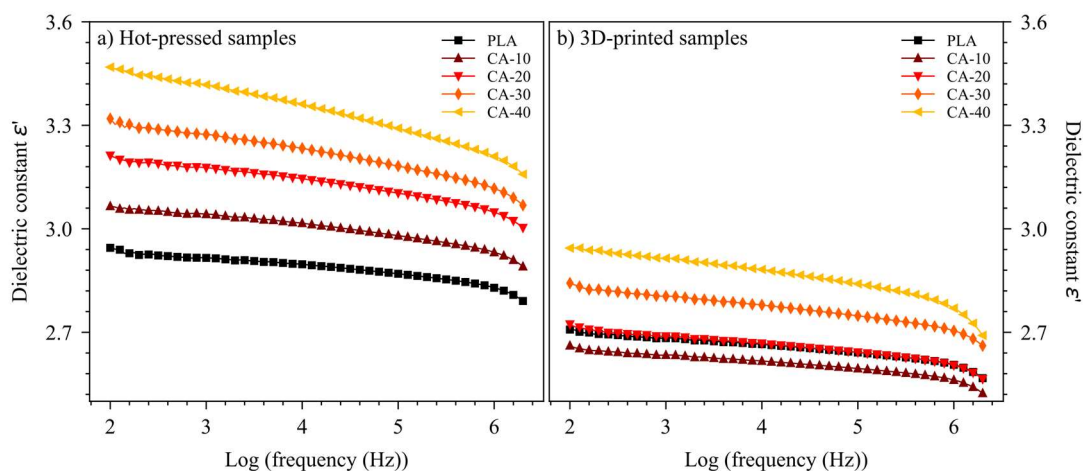


Figure 5.4 : Dielectric constant ϵ' versus frequency of a) hot-pressed samples, b) 3D-printed samples. 3D-printed PLA and CA-20 curves are overlapping

All the specimens had ϵ' between 2,5 and 3,5, which corresponds to the expected behavior of a low-permittive polymer. The highest ϵ' was observed for the hot-pressed CA-40 and the lowest for the 3D-printed CA-10. However, all the curves had the same decreasing trend in their dielectric constant with increasing frequency. For example, at 100 Hz, ϵ' of the hot-pressed PLA was 3,32 and decreased to 3,16 at a frequency of 2 MHz, representing a 5 % decrease in the material response to the applied electric field. Wang and Yang (2023) argued that dipolar polarization cannot follow the AC voltage shift, which leads to a continuous decrease in the dielectric constant. All the tested samples showed a larger decrease at $f > 10^6$ Hz, which could be due to the upper measuring limit of the equipment used. A linear-like increase in the dielectric constant with the addition of CA was observed for the hot-pressed specimens due to the higher polar aspect of CA. However, for the 3D-printed specimens, CA-10 had a lower ϵ' than PLA and CA-40 had higher values than CA-10, showing that an interference phenomenon hindered the linear increase in the dielectric constant with the addition of CA in hot-pressed samples. Moreover, a 20 % decrease in the dielectric constant was observed for the 3D-printed blends compared to the hot-pressed blends.

Figure 5.5 presents the dielectric loss (ϵ'') of hot-pressed and 3D-printed blends at 20 °C.

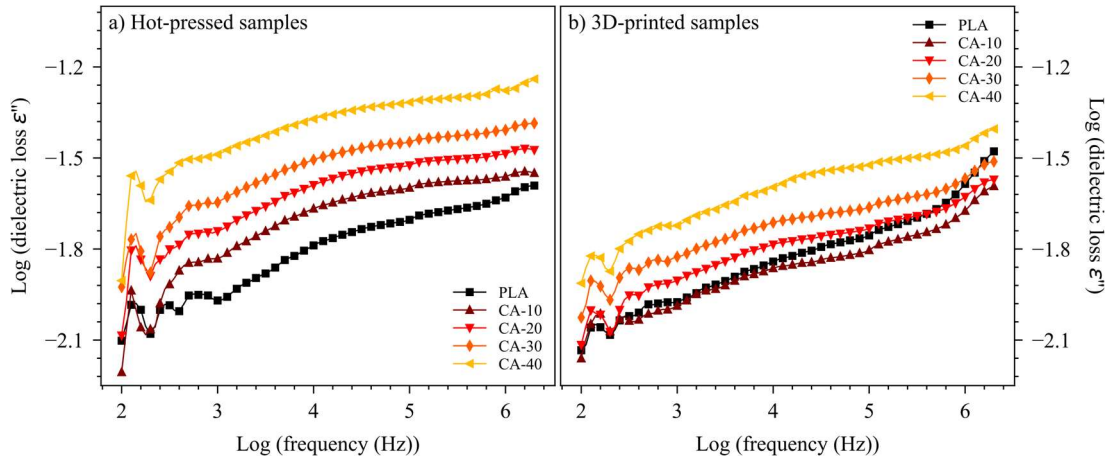


Figure 5.5 : Log (dielectric loss ϵ'') versus frequency of a) hot-pressed samples, b) 3D-printed samples

The dielectric loss represents the part of the electromagnetic energy absorbed by the material and converted into heat. It is a physical quantity that must be kept low to improve the durability of thermally sensitive biobased materials for use in the field of dielectrics. For the tested samples, the lowest dielectric losses were obtained for the hot-pressed PLA and the 3D-printed CA-10, and the highest dielectric loss was observed for the hot-pressed CA-40. At 1 kHz, the 3D-printed PLA presented an ϵ'' of $1,06 \cdot 10^{-2}$ and the 3D-printed CA-40 presented an ϵ'' of $1,83 \cdot 10^{-2}$. The dielectric loss increased with increasing frequency for all blends, which can be associated with the presence of the β -relaxation of PLA (Badia et al., 2014). The 3D-printed specimens showed a significant increase in ϵ'' toward frequencies $> 10^6$ Hz, with a more pronounced behavior for the PLA-rich specimens. Here again, 3D printing decreased the dielectric loss and the addition of CA increased this dielectric loss for all blends.

Table 5.3 presents the calculated conductivity σ_{AC} of hot-pressed and 3D-printed blends at 20 °C. The highest σ_{AC} was measured for hot-pressed CA-40 at $1,38 \cdot 10^{-12}$ S·cm⁻¹ and the lowest for 3D-printed PLA at $4,37 \cdot 10^{-13}$ S·cm⁻¹, both measured at 100 Hz. At 20 °C, the σ_{AC} conductivity values of PLA were consistent with those reported by Fal et al. (2021). We found that, overall, conductivity increased with increasing frequency. This increase was steady for all the tested blends and processes.

Table 5.3 : Electrical conductivity σ_{AC} of hot-pressed and 3D-printed samples @ 20 °C

Frequency (Hz)		100	1 k	10 k	100 k	1 M
Conductivity (S·cm ⁻¹) Hot-pressed samples	PLA	7,59*10 ⁻¹³	6,17*10 ⁻¹²	8,71*10 ⁻¹¹	1,02*10 ⁻⁹	1,07*10 ⁻⁸
	CA-10	9,55*10 ⁻¹³	8,51*10 ⁻¹²	1,17*10 ⁻¹⁰	1,38*10 ⁻⁹	1,51*10 ⁻⁸
	CA-20	9,12*10 ⁻¹³	1,00*10 ⁻¹¹	1,35*10 ⁻¹⁰	1,55*10 ⁻⁹	1,62*10 ⁻⁸
	CA-30	7,24*10 ⁻¹³	1,07*10 ⁻¹¹	1,51*10 ⁻¹⁰	1,78*10 ⁻⁹	2,24*10 ⁻⁸
	CA-40	1,38*10 ⁻¹²	1,70*10 ⁻¹¹	2,24*10 ⁻¹⁰	2,75*10 ⁻⁹	4,37*10 ⁻⁸
Conductivity (S·cm ⁻¹) 3D-printed samples	PLA	4,37*10 ⁻¹³	5,62*10 ⁻¹²	7,59*10 ⁻¹¹	8,91*10 ⁻¹⁰	1,12*10 ⁻⁸
	CA-10	5,25*10 ⁻¹³	5,13*10 ⁻¹²	6,92*10 ⁻¹¹	7,94*10 ⁻¹⁰	1,00*10 ⁻⁸
	CA-20	6,03*10 ⁻¹³	6,46*10 ⁻¹²	8,71*10 ⁻¹¹	9,77*10 ⁻¹⁰	1,17*10 ⁻⁸
	CA-30	5,75*10 ⁻¹³	7,76*10 ⁻¹²	1,00*10 ⁻¹⁰	1,12*10 ⁻⁹	1,35*10 ⁻⁸
	CA-40	7,41*10 ⁻¹³	1,15*10 ⁻¹¹	1,48*10 ⁻¹⁰	1,70*10 ⁻⁹	2,00*10 ⁻⁸

For example, the 3D-printed PLA's conductivity increased by 25600 between 100 Hz and 1 MHz. The frequency increase favors the hopping carrier phenomenon, conveying the electrical current in the insulating materials. This purely frequency-dependent behavior has been associated with an insulating material's behavior (Wu et al., 2019). An improvement in the electrical insulation behavior of 3D-printed samples has been observed. This phenomenon may be associated with the presence of interfaces between layers, which can generate boundary zones for electron flow and, consequently, limit electrical conductivity (Yang et al., 2019). An increase in the electrical sensitivity of the blends with the addition of CA were also observed. Blends with CA showed a slightly more conductive character than neat PLA. This behavior could be associated with the more polar nature of CA and the plasticizer improving the mobility of the carrier charges (Bandara et al., 2011). Moreover, **Table 5.3** shows that no electrical percolation point was present, even at $W_{CA} = 40\%$, attesting to the electrical insulating nature of these materials. The conductivity values were in the electrically insulating range noted by Solazzo et al. (2019), which also suggests that the proposed materials are suitable for the electrical insulation field.

To better understand the effect of CA on the dielectric constants of blends, **Figure 5.6a**) shows the dielectric constant of the hot-pressed samples at 20 °C and 100 Hz vs CA content.

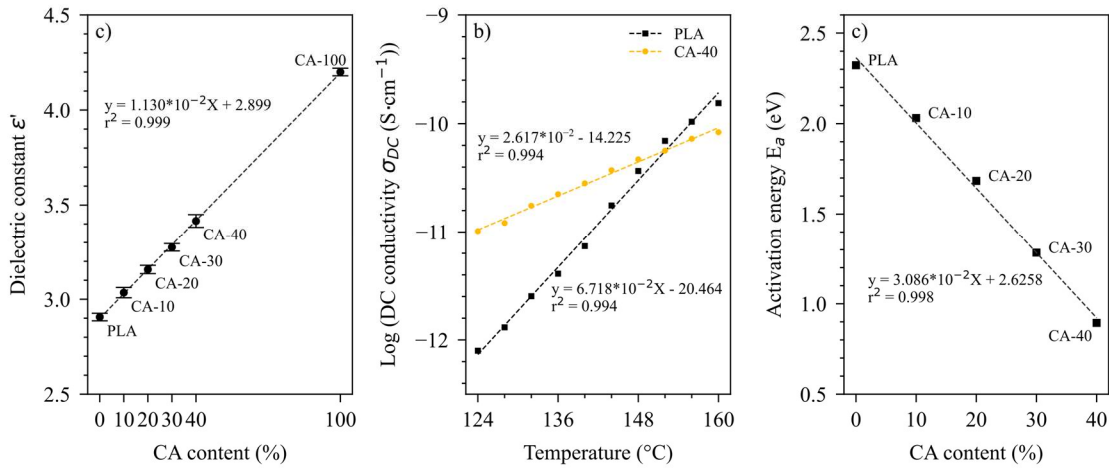


Figure 5.6 : a) Dielectric constant VS CA content at 100 Hz. Error bars represent the standard deviation. b) log (DC conductivity) versus temperature and c) activation energy of electrical conductivity VS CA content. First-order fits are shown in all figures

The dielectric constant of CA-100 was added to the graph to improve the fitting of the associated model. At 100 Hz and 20 $^{\circ}\text{C}$, CA-100 had a dielectric constant of 4,21, a similar value to those observed by Saad et al. (1992). Furthermore, under these measurement conditions, the PLA possessed a ϵ' of 2,91, a value also reported in the literature (Badia et al., 2017; Cao et al., 2014). The variation of ϵ' when CA was incorporated perfectly matched a first-order fit with an associated equation of $0,01296 X + 2,8994$, with X being the percent W_{CA} . With the R^2 being higher than 0,995, we can assume that the PLA:CA blends followed the rule of mixtures. The isothermal-step BDS analysis also provided the direct current (DC) conductivity σ_{DC} of the blends between 124 and 160 $^{\circ}\text{C}$. **Figure 5.6b)** shows the σ_{DC} of PLA and CA-40 as a function of temperature. As expected, $\sigma_{DC \text{ PLA}}$ and $\sigma_{DC \text{ CA-40}}$ increased with temperature. This increase in temperature was directly linked to the free volume of the polymers caused by an increase in the segmental chain motion and to the thermal expansion of polymers, which facilitates ionic mobility and the mobility of the polymers (AlFannakh and Ibrahim, 2022). At 124 $^{\circ}\text{C}$, the $\sigma_{DC \text{ PLA}}$ and $\sigma_{DC \text{ CA-40}}$ was $7,95 \cdot 10^{-13}$ and $1,02 \cdot 10^{-11}$ S $\cdot \text{cm}^{-1}$, respectively. The $\sigma_{DC \text{ CA-40}}$ was 13 times higher than for neat PLA, which is consistent with the observed behavior of σ_{AC} at 20 $^{\circ}\text{C}$. However, at 160 $^{\circ}\text{C}$, the behavior changed, and the $\sigma_{DC \text{ PLA}}$ was 85 % higher than $\sigma_{DC \text{ CA-40}}$. The σ_{DC} was less temperature dependent for CA-40 than for PLA. This observation could be related to the rheological observations; the addition of CA greatly restricted PLA mobility and thus limited the

creation of free volumes. **Figure 5.6c**) shows the activation energy (E_a) of conductivity as a function of the blends. Activation energy decreased linearly from 2,32 to 0,87 eV with increasing amounts of CA. This activation energy decrease could also be linked to the more polar nature of CA and with the plasticizer improving the mobility of the carrier charges.

5.2.5.c. Relationship between porosity and permittivity

To quantify the dielectric properties variation observed, **Table 5.4** presents the dielectric constants (ϵ'), dielectric losses (ϵ''), and AC conductivity (σ_{AC}) measured at 20 °C and 1 kHz for hot-pressed and 3D-printed specimens, as well as the observed decrease between the two. The dielectric constants of 3D-printed PLA were similar to that observed in the literature (Dichtl et al., 2017; Kuzmanić et al., 2023). The smallest decrease was observed for the PLA ϵ'' at -1,2 %, and the largest was observed for the CA-40 ϵ'' at -41,7 %. The ϵ'' and σ_{AC} quantities were very sensitive to the printing process compared to the ϵ' . PLA showed only small variations in its values, under 10 %, while all blends showed much higher property decreases. Finally, no clear relationship between CA content and observed decreases was noted.

Table 5.4 : Dielectric and electrical variation between hot-pressing and 3D-printing processing @ 100 Hz

	ϵ'			ϵ''			σ_{AC}		
	Hot-pressed	3D-printed	$\Delta\epsilon$ (%)	Hot-pressed	3D-printed	$\Delta\epsilon''$ (%)	Hot-pressed	3D-printed	$\Delta\sigma_{AC}$ (%)
PLA	2,92	2,68	-8,0	$1,07*10^{-2}$	$1,06*10^{-2}$	-1,2	$6,19*10^{-12}$	$5,64*10^{-12}$	-8,7
CA-10	3,04	2,63	-13,4	$1,47*10^{-2}$	$1,03*10^{-2}$	-30,1	$8,54*10^{-12}$	$5,11*10^{-12}$	-40,1
CA-20	3,18	2,69	-15,4	$1,82*10^{-2}$	$1,25*10^{-2}$	-31,3	$1,06*10^{-11}$	$6,41*10^{-12}$	-39,6
CA-30	3,27	2,80	-14,3	$2,26*10^{-2}$	$1,50*10^{-2}$	-33,8	$1,27*10^{-11}$	$7,82*10^{-12}$	-38,4
CA-40	3,42	2,91	-14,7	$3,25*10^{-2}$	$1,89*10^{-2}$	-41,7	$1,94*10^{-11}$	$1,15*10^{-11}$	-40,7

A key notion to consider in 3D printing is the creation of internal defects in the printed specimens, called voids. These defects occur as a result of an inability of the filament to fill its given space which causes a triangle-shaped void between two deposited filaments (**Figure 5.7a**)).

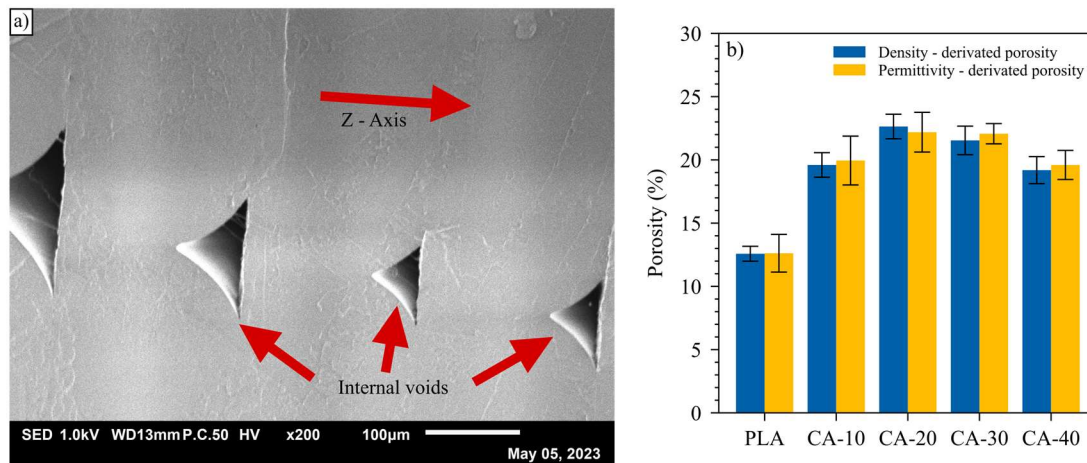


Figure 5.7 : a) SEM analysis of a cross-section of 3D-printed PLA, b) Comparison of porosities of 3D-printed specimens with a 100 % infill density, determined by density and permittivity derived methods. Error bars represent the standard deviation

A direct link has already been established between the porosity and permittivity (Goulas et al., 2019; Kuzmanić et al., 2023). The calculated porosities of the 3D-printed samples are presented in **Figure 5.7b**). All measured porosities of the samples were globally between 12 and 23 %. The lowest porosity observed, 12,5 %, was for PLA, which is logical for a neat material and agreed with the results obtained by Liao et al. (2019) for 3D-printed PLA. CA-20 had the highest porosities at approximately 23 %. Adding CA up to a $W_{CA} = 20$ % greatly increased the porosity, with a P-Value for the density-derived porosity and the permittivity-derived porosity of respectively $1,12 \cdot 10^{-9}$ and $4,13 \cdot 10^{-6}$. The increase in porosity observed with CA content up to 20 % can be linked to the complex viscosity results presented. A less viscous material can better fit and fill the free space than a more viscous material. After peaking for CA-20 blends, the porosity of 3D-printed samples decreased slightly for higher CA contents, with P-Values of $5,82 \cdot 10^{-4}$ and $1,17 \cdot 10^{-2}$ for the derived density measurement and derived permittivity measurement, respectively. Note, also, that the two methods gave comparable porosity measurements, with P-Values above 0,4. This observation validated the use of BDS analysis to determine the porosity of 3D printed samples. It also showed that it is possible to control the permittivity of the 3D-printed system by controlling the internal porosity. This parameter can easily be tuned by varying the infill ratio. The much higher porosity of CA-10 compared to PLA seemed to be the reason for the lower dielectric properties shown in **Figure 5.4** and **Figure 5.5**.

5.2.5.d. *Dynamic mechanical properties*

Figure 5.8 and **Figure 5.9** present, respectively, the storage modulus (E') and the loss modulus (E'') of hot-pressed and 3D-printed blends.

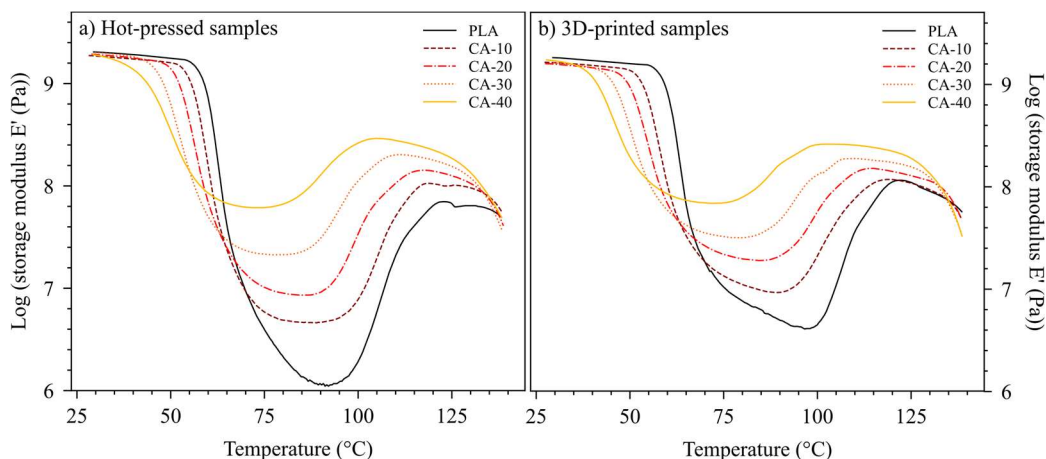


Figure 5.8 : Storage modulus E' versus temperature of a) hot-pressed samples, b) 3D-printed samples

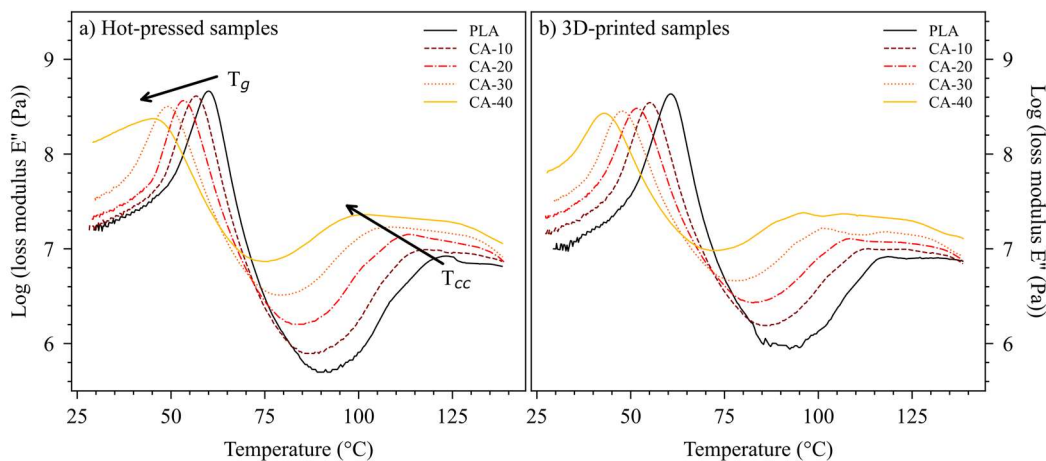


Figure 5.9 : Loss modulus E'' versus temperature of a) hot-pressed samples, b) 3D-printed samples

At 30 °C, the highest moduli were reported for neat PLA and the lowest for CA-40. At 30 °C, the 3D-printed PLA presented a storage modulus of 1,81 GPa. All blends showed the same general behavior as a function of temperature. At low temperatures (< 40 °C), all the samples showed a storage modulus > 1 GPa and a relatively low loss modulus. This behavior is typical of the glassy state, where the mobility-limited macromolecules

produced good stiffness properties and low-temperature dependencies. A sharp drop of E' and a E'' peak were observed for all blends, between 40 and 70 °C, depending on the blend. This behavior is typical of the α -relaxation of PLA, shifting from a glassy state to a rubbery state (Ding et al., 2023). The incorporation of CA tended to decrease the modulus drop and the E'' peak, as well as widening the peak. A collective drop of storage and loss moduli was observed between 60 and 90 °C, depending on the blend. This can be attributed to the rubbery state of PLA. It is also worth noting that the E' and E'' drop was lower for the high CA content specimens. An increase in both storage and loss moduli was visible between 80 and 100 °C, depending on the blend. This behavior is well reported in the literature and is associated with the cold crystallization relaxation of PLA. The thermal energy was high enough for PLA to rearrange into a crystalline network. This decreases the entropy by forming a crystalline network, logically increasing the material stiffness. Between 100 and 130 °C, depending on the blend, a second rubbery state was observed, characterized, however, by a more rigid state than the first rubbery state due to the newly formed crystalline network. Finally, towards temperatures > 130 °C, a last inflection of E' and E'' was observed, which was associated with the beginning of fusion of the previously formed crystal lattice of PLA. This drop was more pronounced for high-CA content blends. The effect of 3D printing on mechanical properties was less clear than for the dielectric properties. However, the 3D-printed specimens showed higher storage moduli in the first rubbery state than the hot-pressed specimens. This observation was even more pronounced for low CA-content blends. This could be due to the 3D-printing process, which induced a greater macromolecular orientation on the deposition axis (Park et al., 2022) and could decrease the stiffness drop in the rubbery state. The addition of CA to PLA decreased the energy required for the relaxations (T_g , T_{cc} , and T_m) and decreased their respective temperature. This probably comes from the presence of the plasticizer in CA, which also impacts PLA. Also, once the T_g is reached, the CA acts as a stiffener for the PLA in the rubbery state. For the 3D-printed specimens in the first rubbery state ($60 < T < 90$ °C), the minimum E'_{PLA} was 4,1 MPa, and the E'_{CA-40} was 68,3 MPa, i.e., 12 times higher.

CA influenced blend structure and modified their viscoelastic properties. **Figure 5.10** shows the Cole-Cole plot of the moduli determined by DMA. Cole-Cole plots are useful for determining the homogeneity of the blend by interpreting the shape of the given curve. The more homogeneous the material, the more its curve is shaped like a half-sphere (Sahu

and Gupta, 2021). PLA had a quasi-circular curve, which was expected for a homogeneous material. The observed viscoelastic behavior is coherent with the values observed by Bajwa et al. (2021) and Eichers et al. (2022). As the CA content of the blend increases, the curve steepens and deflects, demonstrating that heterogeneity increases with the addition of CA. The SEM analysis supports these results, as the roughness increased with the incorporation of CA. A previous study also reported this roughness increase for PLA-starch blends (Yang et al., 2023). The special fibrillar and lamellar morphology was also observed for PLA:CA blends (Coltelli et al., 2021). The Cole-Cole curve also highlighted the cold crystallization phenomenon at high temperatures.

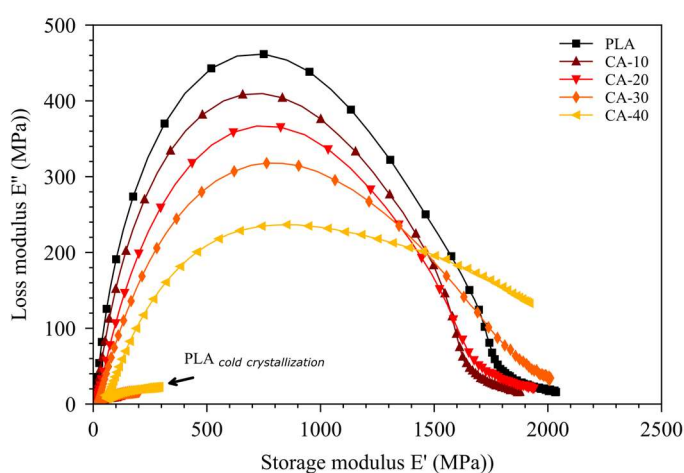


Figure 5.10 : a) Cole-Cole plot E'' VS E'

5.2.5.e. *Glass transition determination by BDS and DMA analysis*

BDS and DMA measurements both showed that the addition of CA impacted the α -relaxation of PLA. To better understand this phenomenon, **Figure 5.11** presents the $T_{g, PLA}$ for the hot-pressed and 3D-printed blends obtained by DMA and BDS measurements. The determination of $T_{g, PLA}$ by DMA was based on calculating the E'' peak (Yang et al., 2009) to better correlate with the $T_{g, PLA}$ values determined by BDS. BDS measurements gave glass transition temperatures of 52,3 and 53,5 °C for hot-pressed and 3D-printed PLA, respectively. These values were coherent with those observed by Dichtl et al. (2017) using the same method.

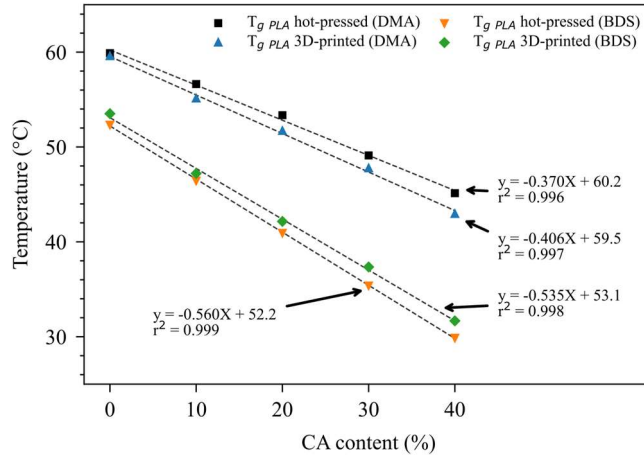


Figure 5.11 : Glass transition temperature of PLA measured by DMA and BDS and their associate first-order fits

DMA measurements gave glass transition temperatures of 59,9 and 59,6 °C for hot-pressed and 3D-printed PLA, respectively, which is also in agreement with previous findings (Pluta and Galeski, 2007; Yang et al., 2009). The $T_{g, PLA}$ determined by DMA had higher values than those observed for BDS. This result can be explained by the nature of the measurement, but these results are also consistent with the preliminary results from the DSC analysis. Regardless of the blends and $T_{g, PLA}$ determination methods, an overall decreasing $T_{g, PLA}$ trend with increasing CA content was observed. This decrease followed a first-order fit (**Figure 5.11**). The $T_{g, PLA}$ determined by BDS seemed more sensitive to adding CA, with a slope of approximately $-0,54$ compared to the $-0,39$ for DMA. These results allowed accurate prediction of blend glass transition temperatures. Finally, the processing method does not have a clear influence on the response of the CA to the α -relaxation.

All fittings VFT parameters from the BDS results are given in **Table 5.5**. The data showed that 3D-printed and hot-pressed PLA had an activation energy of the α -relaxation at $960 \text{ kJ}\cdot\text{mol}^{-1}$. A decrease in the activation energy was observed with the addition of CA. According to Delpouve et al. (2018), this decrease could be due to the rupture of the macromolecular interaction caused by the intercalation of the CA and plasticizer molecules. The parameter m is the Fragility Index, useful for quantifying the deviation of the temperature-dependence of relaxation times from an Arrhenius behavior (Delpouve et al., 2018). A high m reflects a high deviation, indicating a "fragile" polymer behavior.

A low m , on the other hand, reflects a good correlation with an Arrhenius behavior, giving the polymer a "strong" behavior. The hot-pressed PLA presented a m index of 154, which is in good agreement with previous reports (Delpouve et al., 2018, 2014; Pascual-Jose et al., 2021). Moreover, the decrease in the Fragility Index of the blends could indicate that the CA and the plasticizer produced a "stronger" PLA behavior, the temperature dependence deviating from a VFT-like behavior and moving closer to an Arrhenius-like behavior (Delpouve et al., 2018).

Table 5.5 : Calculated parameters for the VFT model. The Fragility Index m and activation energy of the α -relaxation E_a were added

		log (f_0) (log (Hz))	B (K)	T_0 (K)	T_g (K)	m (S.U.)	E_a (kJ·mol ⁻¹)
3D-printed samples	PLA	12,12	1093	294,8	326,7	153,1	957,5
	CA-10	13,11	1382	282,6	320,4	135,0	828,2
	CA-20	12,63	1258	279,9	315,3	137,5	829,7
	CA-30	13,67	1514	270,6	310,5	128,1	761,3
	CA-40	15,42	2015	257,8	304,8	116,0	703,8
Hot-pressed samples	PLA	12,14	1073	294,3	325,5	155,7	970,3
	CA-10	13,41	1413	281,7	319,6	136,8	836,9
	CA-20	14,43	1729	270,5	314,1	124,1	746,1
	CA-30	14,90	1867	262,8	308,6	119,2	704,3
	CA-40	14,87	1804	258,7	303,0	120,7	700,5

5.2.6. Conclusion

In this study, biobased polymer blends made from PLA and CA were successfully prepared using a 3D-printing process. Samples with a CA weight content (W_{CA}) up to 40 % were produced and tested with Broadband Dielectric Spectroscopy (BDS), Dynamic Mechanical Analysis (DMA), and dynamic rheology. BDS and DMA measurements showed that the plasticizer in CA decreased the α -relaxation temperature and behavior of PLA. The complex viscosity increased with the addition of CA, following a power law, associated with an increasingly constrained system limiting the fluidity of PLA. The dielectric properties were also influenced by the addition of CA. CA increased the dielectric constant and the dielectric loss, as well as the AC conductivity at 20 °C. Moreover, the activation energy of the DC conductivity decreased with the addition of CA. The dielectric constant of the PLA:CA blends followed a rule of mixture. 3D-printed biobased blends had lower permittivities and conductivities than the hot-pressed ones.

These lower values have been associated with the addition of voids during the 3D-printing process. It would, therefore, be possible to control the dielectric performance of PLA:CA blends by controlling the porosity. Furthermore, this study showed that 3D-printing is a viable method for the use of CA in innovative electronic fields requiring low permittivity and conductivity, such as electrical insulation.

5.3. How can 3D printing parameters affect the dielectric and mechanical performance of PLA:CA polymer blends ? *

Morgan Lecoublet^{1,2}, Mohamed Ragoubi¹, Léonel Billy Kenfack¹, Nathalie Leblanc¹ and Ahmed Koubaa²

¹ UniLaSalle, Unité de Recherche Transformations et Agro-Ressources (ULR 7519 UniLaSalle -Université d'Artois), Mont-Saint-Aignan, France

² UQAT, Campus de Rouyn-Noranda, 445, boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

* Article accepté et publié dans *Journal of Composite Science*, Volume 7, issue 12, 28 Novembre 2023. DOI : 10.3390/jcs7120492

5.3.1. Abstract

Three-dimensional printing is a prototyping technique widely used in various fields, such as the electrical sector, to produce specific dielectric objects. Our study explores the mechanical and dielectric behavior of polylactic acid (PLA), and plasticized cellulose acetate (CA) blends manufactured via fused filament fabrication (FFF). A preliminary optimization of 3D printing parameters showed that a print speed of $30 \text{ mm} \cdot \text{s}^{-1}$ and a print temperature of $215 \text{ }^\circ\text{C}$ provided the best compromise between printing quality and processing time. The dielectric properties were very sensitive to the three main parameters (CA content W_{CA} , infill ratio, and layer thickness). A Taguchi L9 3^3 experimental design revealed that the infill ratio and W_{CA} were the main parameters influencing dielectric properties. Increasing the infill ratio and W_{CA} increased the dielectric constant ϵ' and electrical conductivity σ_{AC} . It would, therefore, be possible to promote the integration of CA in the dielectric domain through 3D printing while counterbalancing its greater polarity by reducing the infill ratio. The dielectric findings are promising for an electrical insulation application. Furthermore, the mechanical findings obtained through dynamic mechanical analysis were discussed.

5.3.2. Résumé en français

L'impression 3D est une technique de prototypage largement utilisée dans divers domaines, comme le secteur électrique, pour produire des objets diélectriques spécifiques. Notre étude explore le comportement mécanique et diélectrique de mélanges

d'acide polylactique (PLA) et d'acétate de cellulose plastifié (CA) obtenus par fabrication de filaments fondus (FFF). Une optimisation préliminaire des paramètres d'impression 3D a montré qu'une vitesse d'impression de $30 \text{ mm} \cdot \text{s}^{-1}$ et une température d'impression de $215 \text{ }^\circ\text{C}$ offraient le meilleur compromis entre la qualité d'impression et le temps de traitement. Les propriétés diélectriques étaient très sensibles aux trois paramètres principaux (teneur en CA W_{CA} , taux de remplissage et épaisseur de la couche). Un plan expérimental Taguchi $L_9 3^3$ a révélé que le taux de remplissage et le W_{CA} étaient les principaux paramètres influençant les propriétés diélectriques. L'augmentation du taux de remplissage et du W_{CA} a accru la constante diélectrique ϵ' et la conductivité électrique σ_{AC} . Il serait donc possible de favoriser l'intégration du CA dans le domaine diélectrique par l'impression 3D, tout en contrebalançant sa plus grande polarité en réduisant le taux de remplissage. Les résultats diélectriques sont prometteurs pour une application d'isolation électrique. En outre, les résultats mécaniques obtenus grâce à l'analyse mécanique dynamique ont été discutés.

5.3.3. Introduction

Considering the challenges of sustainable development initiatives, designing dielectric materials based on biobased polymers would be a crucial solution to replacing synthetic polymers derived from petroleum (Masarra et al., 2022; Rezvani Ghomi et al., 2021). It is, therefore, essential to promote biobased materials with properties similar to those of traditional polymers. Among biobased polymers, polylactic acid (PLA) was produced in the greatest quantities in 2023, according to European Bioplastics (2023). It is synthesized from renewable biomass sources such as corn starch and is a potent candidate to replace petroleum-based polymers such as polystyrene, polyethylene terephthalate, or polypropylene (Hamad et al., 2016). It shows excellent biocompatibility, compostability properties, and straightforward processability (Hamad et al., 2016; Rezvani Ghomi et al., 2021). PLA is simple to formulate, making it a desirable polymer for additive manufacturing, with a broad range of applications in the biomedical, electronics, textile, agriculture, and packaging industries (Quintana et al., 2013). Cellulose is the most abundant polymer on Earth, with attractive potential for use as a raw material in biobased materials with advanced applications ranging from matrix filler for engineering applications to biomedical and electronic applications (Aziz et al., 2023; Z. Chen et al., 2023). Cellulose is naturally present in plant biomass in both crystalline and amorphous

forms. By processing cellulose through the acetylation of hydroxyl groups with acetyl groups, it is possible to obtain cellulose acetate, a cellulose-derived ester. According to the hydroxyl groups' degree of substitution (DS), different CA grades can be produced with tunable properties. Increasing the DS of a CA can reduce the biodegradation rate, glass transition and melting temperature, while improving film transparency and mechanical properties (Dreux, 2019; Phuong et al., 2014). CA also exhibits excellent optical, insulating, and flame-retardant properties and good UV stability (Quintana et al., 2014). CA was among the first plastics developed in the late 19th century and is now widely used, including in commercial applications and pharmacological research (Aziz et al., 2023). However, to process it as a conventional thermoplastic, the addition of a plasticizer is needed. Various enhancement strategies can be applied to encourage the application of these new materials in the field of dielectrics and advanced electronics. An industrially viable application approach consists of the production of polymer blends. A blend's properties are dependent on the choice of components. Concerning electrical insulator/conductor blends, Ebrahim et al. (2007). studied the impact of adding polyaniline (PAni) to cellulose triacetate (tCA). They also showed an immiscible morphology via optical microscopy. They noted that the electrical conductivity of CA can be multiplied by $2 \cdot 10^7$, from $1 \cdot 10^{-13}$ to $2 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$, by adding only 15 % by weight of PAni (W_{PAni}). The electrical percolation threshold was observed for $W_{\text{PAni}} = 10 \%$. They pointed out that although the percolation point was reached at higher W_{PAni} values than those reported in the literature, this addition was still low enough to maintain the mechanical properties of CA while increasing its electrical conductivity. This improvement brings the material produced into the semiconductor range. Concerning electrical insulator/insulator blends, Gasmi et al. (2019) focused on PLA and PHBV blends. They noted that the dielectric loss ϵ'' followed the rule of mixture, varying proportionally with the polymer ratio. Furthermore, the blend did not affect the glass transition temperatures of the polymers, as measured with BDS, indicating that PLA and PHBV are immiscible. However, mechanical properties did not follow the rule of mixture, probably because of the specific morphology observed.

Another strategy for improving the possible applications of these new materials is to capitalize on the democratization of the 3D printing process, rethinking material architecture and products. Three-dimensional printing allows complex three-dimensional

shapes to be produced using computer-assisted technology (Dichtl et al., 2017). Three main technologies exist for 3D printing: Selective Laser Sintering (SLS), stereolithography (SLA), and fused filament fabrication (FFF). Regarding the FFF method, a heated nozzle deposits material (mainly polymers) in successive layers to obtain a final shape previously defined using 3D technology (Dichtl et al., 2017; Veselý et al., 2018). Three-dimensional printing is currently used in key applications, such as fast industrial prototyping, robotics, electronics, and the biomedical industry (Mullaveetil et al., 2021). Electronics and sensors could fully benefit from this process via the design of electrical conductor and insulator prototypes, further favors the integration of biopolymers into new applications (Junpha et al., 2020; Lin et al., 2021; Vivaldi et al., 2022). Recently, Kuzmanić et al. (2023) conducted a study on the influence of the infill ratio and infill shape on the dielectric constant of 3D-printed PLA and ABS specimens. They showed that the infill ratio had a clear influence on the dielectric properties of these materials. For both polymers, the infill ratio positively affected the dielectric constant, as the more porous specimens contained more voids and, therefore, had weaker polarization potentials. They also found that the form factor played a significant role in the dielectric constant, indicating that it is possible to adjust the dielectric constant of 3D-printed materials according to the chosen 3D architecture. Masarra et al. (2022) showed that the infill shape influenced the electrical resistivity of a 3D-printed PLA-based polymer composite. They demonstrated that the electrical resistivity was greater for a $\pm 45^\circ$ printing angle than a $0-90^\circ$ printing angle due to the PLA printing orientation favoring conductivity. Goulas et al. (2019) have also shown the influence of architecture on dielectric properties, as the dielectric constant of ABS:ceramic composites increased with layer height due to the internal porosity decrease.

Even if CA is a promising biobased polymer for electronic applications, there is a need to investigate its dielectric and mechanical behavior when blended with other biopolymers. Thus, this article compares the dielectric and mechanical properties of PLA:CA blends made via 3D printing. After optimizing the 3D printing process, the influence of CA content, infill ratio, and layer thickness on mechanical and dielectric properties was studied and analyzed using a Taguchi L9 (3^3) experimental design. The originality of this work lies in the dielectric analysis of the PLA:CA blends for a specific application and the concurrent analysis of the dielectric and mechanical properties of these innovative blends using a Taguchi design.

5.3.4. Materials and methods

5.3.4.a. *Raw materials and blend formulation*

Two biobased polymers were used to prepare the different biobased polymeric blends: PLA-20003D (PLA) was purchased from EURL BBFil (Heiligenberg-Vallée, FRA) and ACI-002 plasticized cellulose acetate (CA) was purchased from Natureplast (Caen, FRA). All biobased polymers were received in pellets with a diameter $\phi = 4$ mm in 25 kg bags. According to the supplier, the CA had a plasticizer content of 29 %. The supplier stated the Melt Flow Index (MFI at 190 °C with 2,16 kg) of PLA was $7 \text{ g} \cdot 10 \text{ min}^{-1}$. For the blend formulation, the first step was performed with a single-screw extruder and a SCAMEX 25-20D (SCAMEX, Isques, FRA). Four different PLA:CA blends were obtained with CA contents (W_{CA}) varying up to 40 %. The screw speed was set at 30 RPM, and the extrusion profile temperature was set at 160-170-180 °C. The extruded filaments were water-cooled and immediately pelletized and oven-dried at 60 °C. The second processing step was the filament obtention at the ITHEMM laboratory (Charleville-Mézières, FRA). A 3DEVO filament maker (3DEVO, Utrecht, NLD) produced the final filaments following a temperature profile of 170-180-180-170 °C and a screw speed of 5 RPM. These filaments, with a diameter of $2,85 \pm 0,1$ mm, were then used for the 3D printing of the samples. The last processing step was the FFF process. Two different shapes were proposed (**Figure 5.12**).

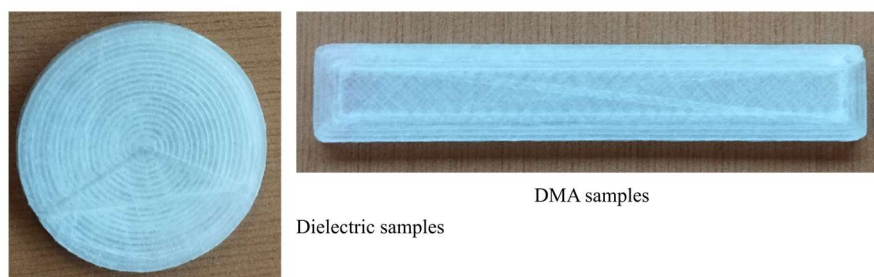


Figure 5.12 : PLA:CA 3D printed samples: rectangular samples with dimensions of 60*10*4 mm for dynamic mechanical analysis and circular samples of 25 mm diameter disks with a thickness of 4 mm for dielectric analysis

These parts were designed using FUSION 360 computer-aided design technology and then exported to CURA SLICER 3D printing technology and printed using a SIGMAX

R19 3D printer (BCN3D, Gavà, ESP). All filaments were conditioned in an oven at 60 °C to remove all internal moisture before printing. The printing bed was set at 60 °C, and the nozzle diameter was set at 0,8 mm. The initial parameters were inspired by the works of Kuzmanić et al. (2023) and Masarra et al. (2022). All samples were stored in a desiccator before being characterised.

5.3.4.b. *Methods used*

- *Scanning electron microscopy (SEM) analysis*

SEM analysis was performed with a JSM IT200 (Jeol, Akishima, JAP). Tests were carried out on cryofractured and carbon-coated specimens. Tests were conducted at 1 kV with a magnification ranging from x40 to x200.

- *Dynamic mechanical analysis (DMA)*

60*10*4 mm samples were tested in dual cantilever mode, on a DMA 242 E Artemis (Netsch, Selb, DEU). The dual cantilever mode was chosen instead of the 3-point bending mode because of the very low stiffness of PLA once its glass transition temperature is reached ($T > 60$ °C). The tests were conducted in a ramp mode between 30 and 140 °C with a heating rate of 5 °C·min⁻¹ and a monitored force of 1 N on bar-shaped specimens. Measurements were taken for 3 different samples at a frequency of 1 Hz.

- *Broadband Dielectric Spectroscopy (BDS) analysis*

BDS tests were conducted with a Keysight E4980A Precision LCR Meter (Agilent Technologies, Santa Rosa, CA, USA). An isothermal test at 20 °C with a frequency ranging from 100 to 2 MHz with 20 measurements per decade was performed to obtain the dielectric properties at room temperature on disk-shaped samples. The dielectric constant (ϵ'), dielectric loss (ϵ'') and AC conductivity (σ_{AC}) were determined according to **Équation 1**, **Équation 2** and **Équation 5** respectively. Measurements were taken for 3 different samples.

- *Thermogravimetric Analysis (TGA)*

TGAs were conducted with a Tg 209 F1 (Netzsch, Selb, DEU). The analyses were conducted with a temperature ramp ranging from 20 to 800 °C and a 10 °C·min⁻¹ speed in an inert gas (argon). For each sample, 20 mg of material was taken and characterized.

5.3.4.c. *Printing process optimization*

Printing process optimization was carried out to ensure good printing conditions. Three parameters were selected: printing temperature, speed, and nozzle diameter. The variable values are summarized in **Table 5.6**. For this step, only the CA-40 blend was selected. Microstructure and mechanical analysis were conducted to assess sample quality via SEM and DMA, respectively.

Table 5.6 : Experimental 3D printing parameters

Print parameters			
T _{nozzle} (°C)	205	215	225
Printing speed (mm·s ⁻¹)	10	20	30

5.3.4.d. *Architectural design*

An architectural characterization step was performed once the printing parameters had been fixed. A Taguchi L9 (3³) experimental design was applied to study the influence of the infill ratio, the W_{CA}, and the layer thickness on dielectric and mechanical properties. These 3 parameters have 3 value levels. This plan required 9 different conditions, which are summarized in **Table 5.7**. All Taguchi analyses were performed with the Minitab 17 Statistical Software. All the additional statistical information is given in **Annexe 8**.

Table 5.7 : L9 (3³) Taguchi experimental design

Condition	W _{CA} (%)	Infill ratio (%)	Thickness (mm)
1	20	40	0,1
2	20	60	0,2
3	20	80	0,3
4	30	40	0,2
5	30	60	0,3
6	30	80	0,1
7	40	40	0,3
8	40	60	0,1
9	40	80	0,2

5.3.5. Results and discussion

5.3.5.a. Optimization of printing parameters

Figure 5.13 shows the storage modulus of PLA:CA blends with a W_{CA} = 40 % at different processing temperatures and printing speeds.

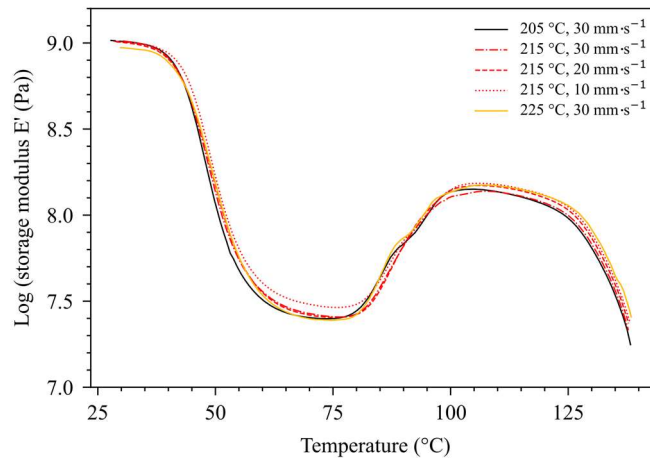


Figure 5.13 : Log (storage modulus E') versus temperature of PLA:CA 3D-printed blends

All blends showed typical plasticized PLA behavior (Cristea et al., 2020). The first phase of the curves before 40 °C corresponds to the glassy state of the PLA component. The sharp drop in the storage modulus E' between 40 and 60 °C corresponds to the glass transition of plasticized PLA. The area between 60 and 80 °C corresponds to the rubbery transition of the PLA component. Cold crystallization could be observed and led to the creation of a crystalline network, improving the blends' mechanical properties (Cristea et

al., 2020). In **Figure 5.13**, no significant change can be seen in the storage modulus with the tested parameters. Furthermore, the SEM analyses presented in **Figure 5.14** showed the morphology of the blends.

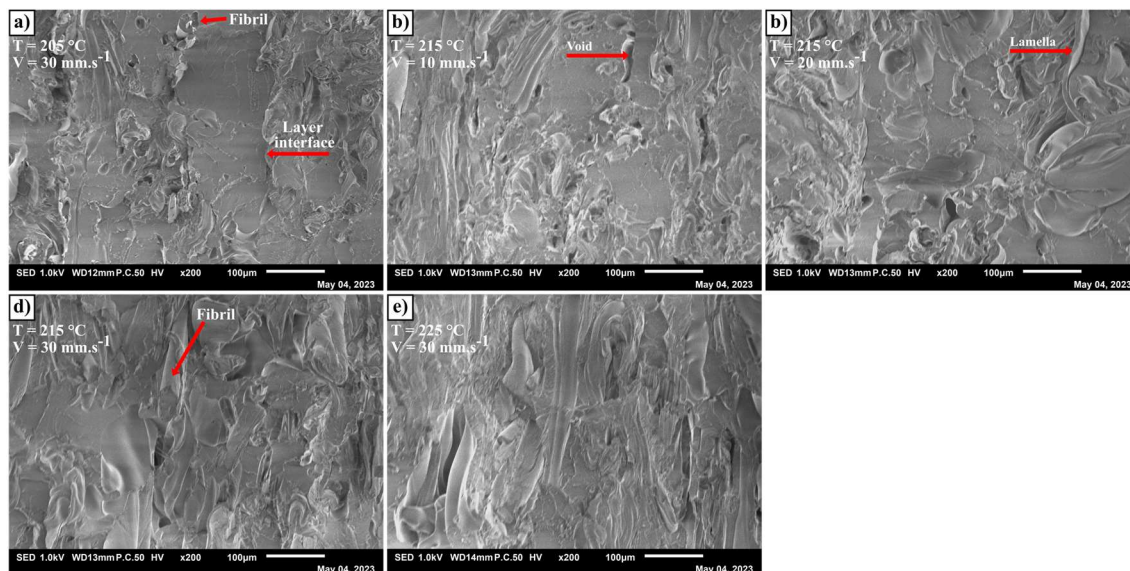


Figure 5.14 : SEM picture of PLA:CA blends at $W_{CA} = 40\%$, $T = 215\text{ °C}$ at a) $10\text{ mm}\cdot\text{s}^{-1}$, b) $20\text{ mm}\cdot\text{s}^{-1}$, c) $30\text{ mm}\cdot\text{s}^{-1}$

As expected and in agreement with the literature, the blend morphology was immiscible, with observable lamellae and fibrils (Coltelli et al., 2021; Lecoublet et al., 2023). Moreover, it was empirically difficult to print samples at 205 °C for a $W_{CA} = 40\%$, as it seems the temperature was too low to achieve good printing quality and replicability. **Figure 5.14a)** shows that the interfaces between the different layers were visible. At 215 and 225 °C , the samples were much simpler to obtain, with an overall better quality, as shown in **Figure 5.14b-e)**. The interfaces between layers were difficult to distinguish. The thermal stability analyses of PLA:CA blends are presented in **Figure 5.15**. The blends showed three distinct degradation peaks. Slow degradation was first visible around 200 °C . This degradation could be attributed to the esterification degradation of CA (Shaikh et al., 2022). Around 300 °C , unstable degradation was also noticeable, which might have corresponded to the plasticizer degradation of CA. It is interesting to note that the degradation of both thermoplastics took place at the same time. So, to limit the degradation of CA during the process, a temperature of 215 °C was chosen for the rest of the study. Regarding the printing speed, $30\text{ mm}\cdot\text{s}^{-1}$ was chosen for the rest of the study

to speed up the printing process. For reference, printing a DMA sample takes 14 and 31 min at print speeds of $30 \text{ mm}\cdot\text{s}^{-1}$ and $10 \text{ mm}\cdot\text{s}^{-1}$.

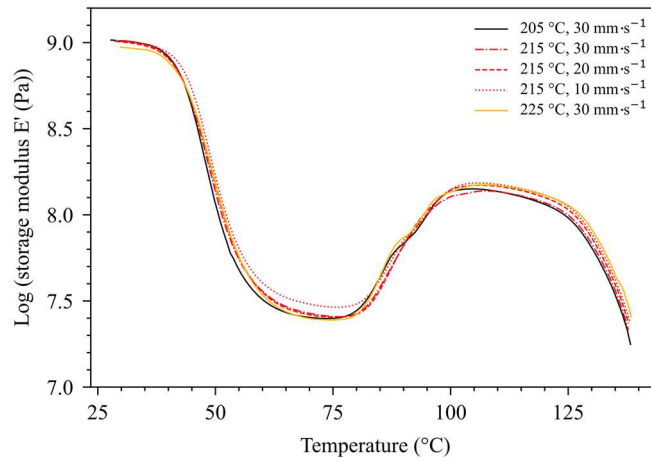


Figure 5.15 : Thermal stability of PLA:CA blends

5.3.5.b. Dielectric properties

Table 5.8 shows the dielectric constants obtained via BDS at room temperature from the 3D-printed PLA:CA biocomposite using different parameters (W_{CA}), infill ratio, and layer thickness).

Table 5.8 : Variation of dielectric constant ϵ' in function of frequency at $20 \text{ }^\circ\text{C}$

Condition	W_{CA} (%)	Infill (%)	Thickness (mm)	ϵ' @ 100 Hz	ϵ' @ 1 kHz	ϵ' @ 10 kHz	ϵ' @ 100 kHz	ϵ' @ 1 MHz
1	20	40	0,1	$1,91 \pm 0,05$	$1,94 \pm 0,06$	$1,93 \pm 0,06$	$1,92 \pm 0,06$	$1,90 \pm 0,06$
2	20	60	0,2	$2,21 \pm 0,02$	$2,24 \pm 0,01$	$2,23 \pm 0,08$	$2,22 \pm 0,01$	$2,20 \pm 0,01$
3	20	80	0,3	$2,32 \pm 0,03$	$2,35 \pm 0,04$	$2,34 \pm 0,04$	$2,32 \pm 0,03$	$2,30 \pm 0,03$
4	30	40	0,2	$2,04 \pm 0,03$	$2,08 \pm 0,01$	$2,06 \pm 0,01$	$2,05 \pm 0,01$	$2,03 \pm 0,01$
5	30	60	0,3	$2,31 \pm 0,02$	$2,33 \pm 0,02$	$2,31 \pm 0,02$	$2,29 \pm 0,01$	$2,27 \pm 0,01$
6	30	80	0,1	$2,36 \pm 0,03$	$2,39 \pm 0,03$	$2,37 \pm 0,04$	$2,35 \pm 0,04$	$2,32 \pm 0,03$
7	40	40	0,3	$2,11 \pm 0,07$	$2,12 \pm 0,07$	$2,11 \pm 0,07$	$2,09 \pm 0,07$	$2,07 \pm 0,07$
8	40	60	0,1	$2,25 \pm 0,04$	$2,26 \pm 0,04$	$2,25 \pm 0,04$	$2,23 \pm 0,03$	$2,20 \pm 0,04$
9	40	80	0,2	$2,46 \pm 0,12$	$2,48 \pm 0,11$	$2,45 \pm 0,11$	$2,42 \pm 0,11$	$2,39 \pm 0,11$

The measured dielectric permittivity ranged from 1,90 to 2,46, increasing gradually with W_{CA} and the infill ratio. The lowest dielectric constants were obtained for condition 1, corresponding to a $W_{CA} = 20 \%$, infill ratio = 40% , and layer thickness = $0,1 \text{ mm}$. The highest dielectric constants were obtained for condition 9, corresponding to a

$W_{CA} = 40\%$, infill ratio = 80 %, and layer thickness = 0,2 mm. Typical dielectric constants for these conditions are summarized in **Figure 5.16**. However, the dielectric constant of PLA:CA biocomposites decreased with increasing frequency, which was associated with the limitation of dipole mobility as the frequency increased.

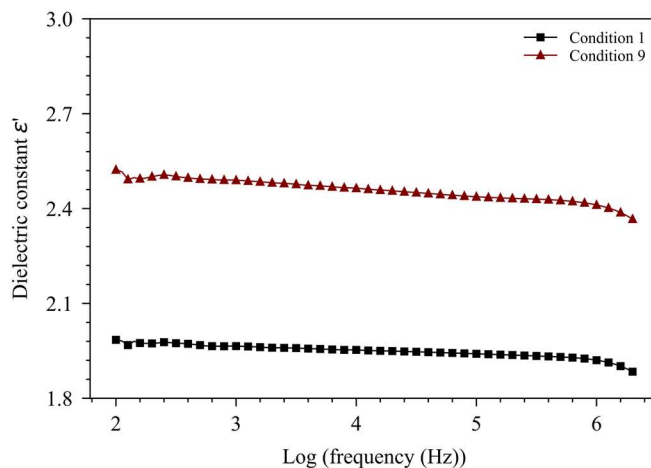


Figure 5.16 : Dielectric constant ϵ' versus frequency. Condition 1 corresponds to a $W_{CA} = 20\%$, infill ratio = 40 %, and layer thickness = 0,1 mm. Condition 9, corresponds to a $W_{CA} = 40\%$, infill ratio = 80 %, and layer thickness = 0,2 mm

Figure 5.17 shows the results of the Taguchi analysis at 1 kHz, which we used to identify the parameters separately.

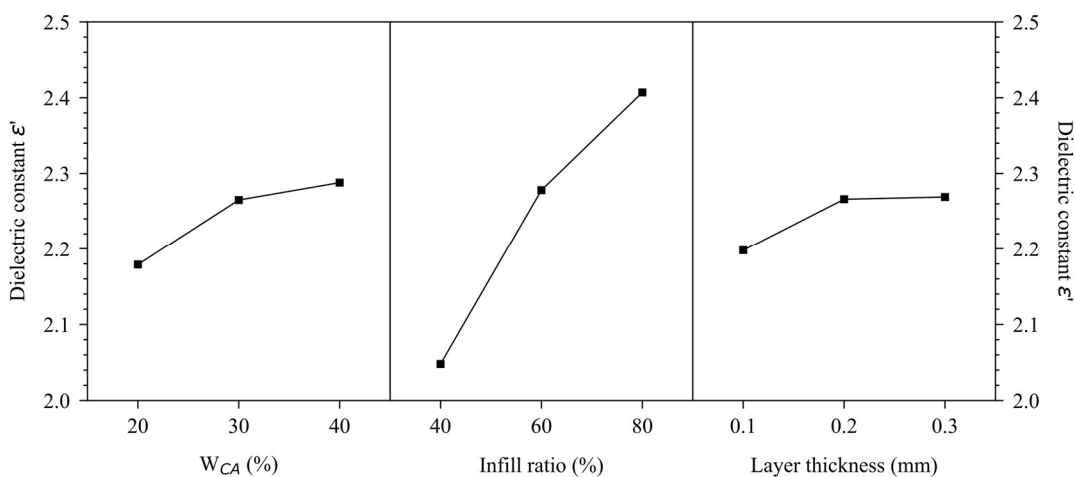


Figure 5.17 : Means dielectric constant ϵ' at room temperature and 100 Hz

All the tested parameters positively influenced the dielectric constant. The P-Value indicated 0,003, 0,032, and 0,064 for the infill ratio, W_{CA} , and layer thickness, respectively. The infill ratio significantly affected the dielectric constant. This observation has already been made by Kuzmanić et al. (2023) and was attributed to the samples' porosity. Reducing the infill ratio resulted in less dense specimens and, therefore, less susceptible to being polarized, as the dielectric constant of air ~ 1 . The impact of W_{CA} on the dielectric constant was also significant, as cellulose acetate had polar hydroxyl functions compared with PLA. On the other hand, the layer thickness had only a slight positive impact (P-Value $> 0,05$) on the dielectric constant. Goulas et al. (2019) also observed a slight influence associated with the diminution in porosities with increasing layer thickness. So, to reduce the dielectric constant, a reduction in the infill ratio needs to be made, followed by a reduction in the W_{CA} , and finally, a reduction in the layer thickness. Interestingly, the dielectric constants of conditions 7, 8, and 9 were between 2,11 and 2,46, values comparable with those of LDPE, HDPE and PP, synthetic polymers commonly used in electrical insulation (presented later in the document in **Table 5.11**). This proves that conditions 7 to 9 would be attractive alternatives to the above-mentioned conventional polymers.

5.3.5.c. *Electrical conductivity properties*

Table 5.9 shows the different electrical conductivities obtained via BDS at room temperature and 1 kHz for the 3D-printed PLA:CA biocomposite when using different parameters (W_{CA} , infill ratio, and layer thickness).

Table 5.9 : Log (electrical conductivity σ_{AC}) at room temperature and 1 kHz

Condition	W_{CA} (%)	Infill (%)	Thickness (mm)	σ_{ac} @ 1 kHz
1	20	40	0,1	$-11,58 \pm 0,03$
2	20	60	0,2	$-11,36 \pm 0,04$
3	20	80	0,3	$-11,32 \pm 0,04$
4	30	40	0,2	$-11,45 \pm 0,05$
5	30	60	0,3	$-11,28 \pm 0,04$
6	30	80	0,1	$-11,30 \pm 0,06$
7	40	40	0,3	$-11,42 \pm 0,06$
8	40	60	0,1	$-11,26 \pm 0,06$
9	40	80	0,2	$-11,14 \pm 0,07$

The measured electrical conductivity ranged from $2,63 \cdot 10^{-12}$ to $7,24 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$. As for the dielectric constant, the lowest electrical conductivity was obtained for condition 1 and the highest for condition 9 (**Figure 5.18**).

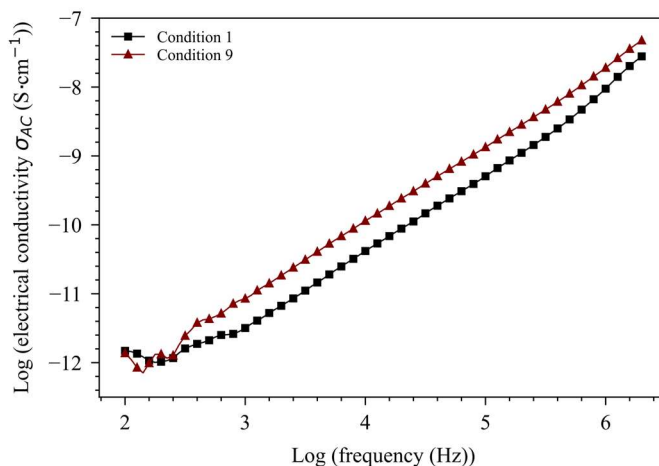


Figure 5.18 : Log (electrical conductivity σ_{AC}) at room temperature versus frequency of condition 1 and 9

The electrical conductivity increased with the applied frequency for all tested conditions (1 to 9). Increasing the frequency favors the hopping carrier phenomenon, conveying the electrical current in the insulating materials. A steady increase in conductivity as a function of frequency was apparent for both conditions. Wu et al. (2019) showed this behavior is typical of an electrical insulator material. Finally, all conditions characterized with electrical frequencies below 100 kHz possessed electrical conductivity values under $10^{-8} \text{ S} \cdot \text{cm}^{-1}$. According to Solazzo et al. (2019), this would also make our materials electrically insulating materials.

Figure 5.19 shows the results of the Taguchi analysis at 1 kHz. The W_{CA} and infill ratio significantly and positively influenced the electrical conductivity (P-Values were 0,013 and 0,032, respectively). Adding CA into PLA increased the electrical conductivity of the latter due to the more polar nature of CA and the plasticizer, improving the carrier charges' mobility (Bandara et al., 2011). Moreover, porosity has already been proven to reduce the electrical conductivity of polymeric materials (Galos et al., 2021). Conversely, the layer thickness had little impact (P-Value = 0,164) on the electrical conductivity. Globally, the effect of the various parameters on electrical conductivity was less

significant than their effect on the dielectric constant. So, to reduce the electrical conductivity, the first step is to reduce the infill ratio, followed by a reduction in the W_{CA} .

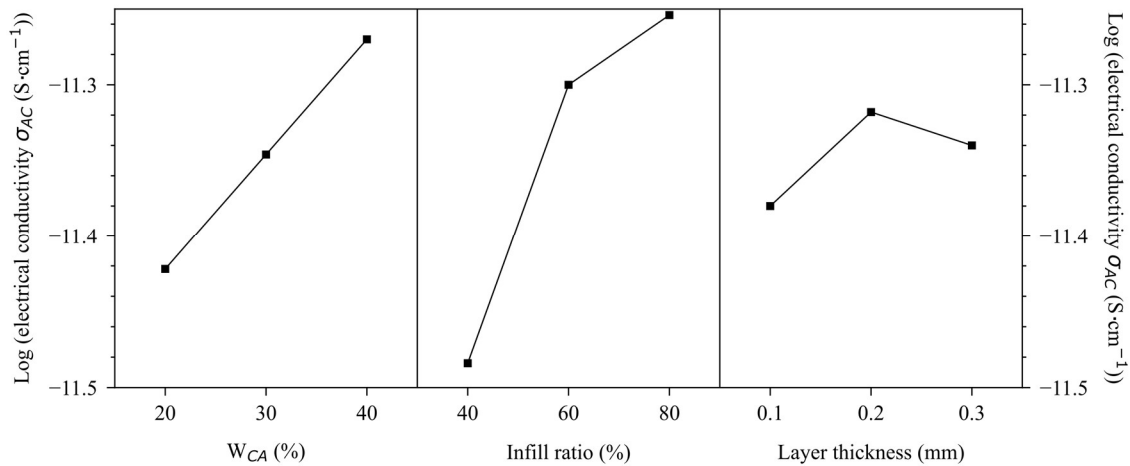


Figure 5.19 : Means for log (electrical conductivity σ_{AC}) at room temperature and 1 kHz

5.3.5.d. Dynamic mechanical properties

Table 5.10 shows the different storage moduli (E') and glass transition temperatures of PLA ($T_{g,PLA}$) obtained via DMA for different parameters.

Table 5.10 : Storage modulus E' @ 1 Hz and 30°C, and glass transition temperature measured by BDS analysis

Condition	W_{CA} (%)	Infill (%)	Thickness (mm)	E' (MPa)	$T_{g,PLA}$ (E'' peak, °C)
1	20	40	0,1	694,4	53,5
2	20	60	0,2	805,8	53,1
3	20	80	0,3	976,8	53,3
4	30	40	0,2	692,2	49,0
5	30	60	0,3	774,6	49,4
6	30	80	0,1	877,4	49,1
7	40	40	0,3	656,2	43,0
8	40	60	0,1	424,6	41,3
9	40	80	0,2	654,1	43,1

At 30 °C and 1 Hz, the storage moduli ranged from 425,6 MPa to 976,8 MPa. The highest E' was measured for condition 3 and the lowest for condition 8. The $T_{g,PLA}$, measured at the loss modulus peak (peak E''), ranged from 41,3 to 53,5 °C. Complementary DSC

measurements (**Annexe 9**) gave very similar values, validating the use of DMA to determine the $T_{g\text{ PLA}}$. Moreover, **Figure 5.20** presents the E' and E'' of the conditions 3 and 8. The curves are typical of plasticized PLA, as already described in **Figure 5.13**.

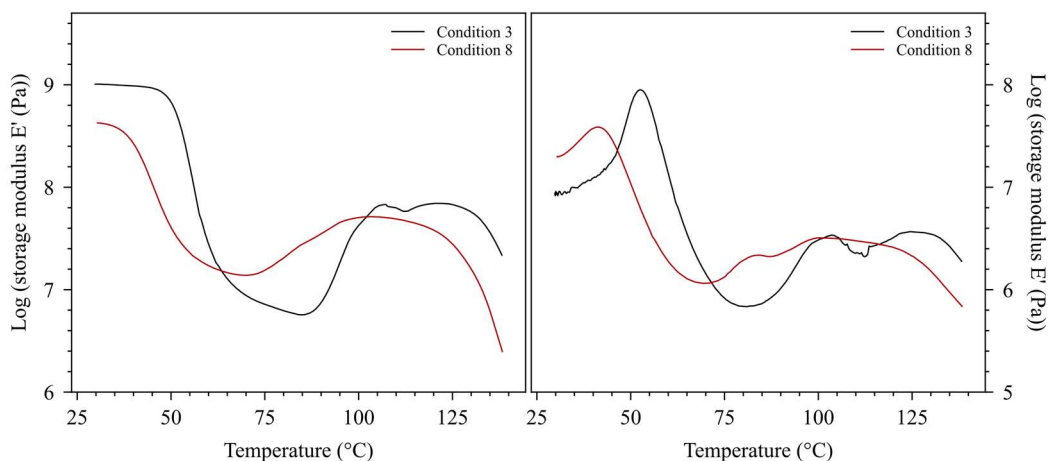


Figure 5.20 : Storage and loss modulus versus temperature of condition 3 and 8

Figure 5.21 shows the results of the Taguchi analysis at 1 Hz. The Taguchi analyses were relatively unclear.

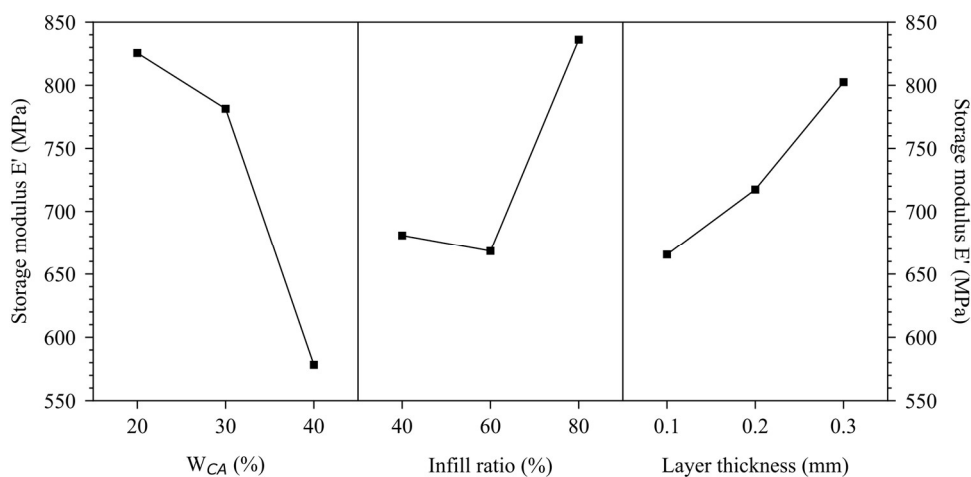


Figure 5.21 : Means for storage modulus E' at 30°C and 1 Hz

The W_{CA} , infill ratio, and layer thickness had P-Values of 0,103, 0,186, and 0,295, respectively (**Annexe 8**). The higher P-Values probably originate from two causes. Firstly, the mechanical tests were not carried out using triplicates due to material and time limitations. Secondly, the condition 8 DMA specimens exhibited an unusually poor print

quality with many surface defects, resulting in mechanical properties that were well below expectations. It can be argued that immiscible PLA:CA blends had great printing difficulty at high CA content levels when small amounts of material were extruded (corresponding to a layer thickness of 0,1 mm). Furthermore, previous analyses have shown that the viscosity of PLA was greatly increased by adding CA (Lecoublet et al., 2023), which can reduce the effectiveness of layer adhesion, especially when combined with a low infill ratio. Further tests were carried out by changing the layer thickness to 0,2 mm, and the print quality improved significantly. Condition 8 may have biased the Taguchi analysis results. However, given the literature and the observed trends, we can deduce that the infill ratio positively affected material stiffness due to a higher porosity content (Abeykoon et al., 2020; Öteyaka et al., 2021; K. Wang et al., 2020), where W_{CA} had a slight negative effect. Layer thickness did not seem to influence the storage modulus. Further analyses are required to confirm the observed trends.

Concerning the storage modulus, a comparative analysis employing synthetic polymers was conducted, as presented in **Table 5.11**.

Table 5.11 : Comparative analysis of the dielectric constant ϵ' and storage modulus E' for synthetic polymers

Polymer	T (°C)	ϵ'	Ref
CA-40	20	2,11	Our study
		2,25	
		2,46	
LDPE	Room T	2,43	(Ahmed Dabbak et al., 2018)
		2,21	(Han et al., 2020)
HDPE	Room T	2,48	(Ahmed Dabbak et al., 2018)
		2,5	(Xu et al., 2021)
PP	Room T	2,3	(Ahmed Dabbak et al., 2018)
		2,1	(Uyor et al., 2022)
Polymer	T (°C)	E' (MPa)	Ref
CA-40	30	656	Our study
		425	
		654	
LDPE	Room T	380	(Chen et al., 2020)
		390	(Molefi et al., 2010)
HDPE	30	1710	(Molefi et al., 2010)
PP	30	1800	(Chen et al., 2020)
		1816	(Yeole et al., 2021)

It showed that the storage moduli obtained for PLA:CA for conditions 7, 8, and 9 were comparable with those of LDPE. It also proved once again that these materials could be relevant alternatives for replacing synthetic polymers in an electrical insulation application.

Finally, **Figure 5.22** present the Taguchi analysis results for the PLA glass transition temperature as determined via DMA.

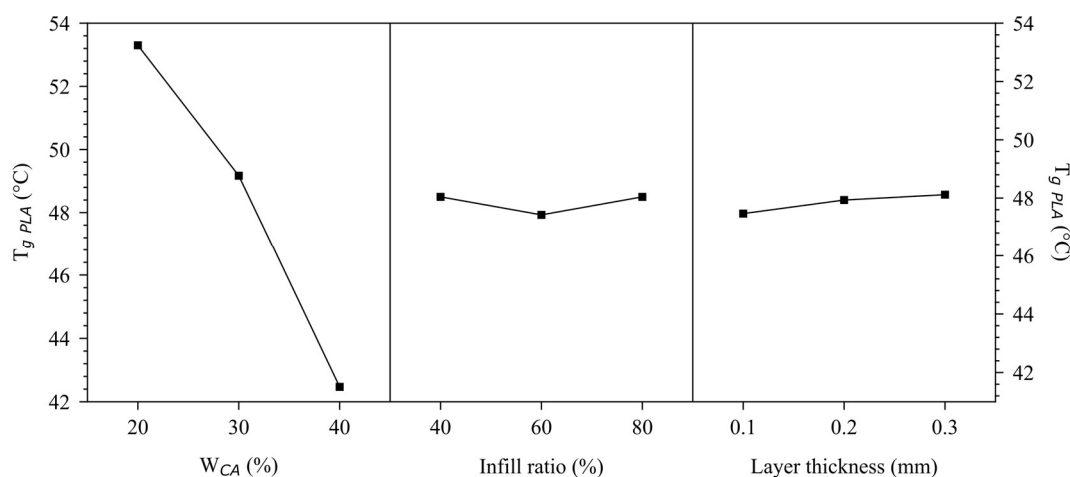


Figure 5.22 : Means for glass transition temperature measured by DMA analysis

It can be seen that the infill ratio and layer height had no significant influence on $T_{g,PLA}$. On the contrary, W_{CA} strongly influenced the $T_{g,PLA}$ (P-Value = 0,006). This decrease can be attributed to the presence of the CA plasticizer, reducing the energy required for the α -relaxation of PLA.

5.3.6. Conclusion

Cellulose acetate is a biobased polymer with great potential for applications in the electronics industry, but there is a lack of research on its application via 3D printing. This study investigated the dielectric and mechanical properties of PLA:CA blends obtained through 3D printing. A printing optimization phase was firstly conducted to find the appropriate printing temperature and speed. The best compromise was found at 215 °C and 30 mm·s⁻¹. A Taguchi L9 3³ experiment was successfully performed to observe the

influence of the CA content, infill ratio, and layer thickness on dielectric properties, mechanical properties, and glass temperature transition. The findings are:

- The infill ratio strongly decreased the dielectric and mechanical properties of 3D-printed PLA:CA blend samples. These observations can be linked to the more porous structure induced by the lack of infill.
- The W_{CA} positively influenced the dielectric constant and electrical conductivity due to the higher polar aspect of CA. The CA's plasticizer could have caused the decrease in the storage modulus and T_g_{PLA} induced by the W_{CA} . These observations show that it would be possible to counterbalance the higher dielectric properties of CA by reducing the infill ratio to obtain a material with the best electrical insulating properties.
- The layer thickness had little influence on the tested properties. However, it has been proven to cause critical failures at a high CA content. Therefore, it would be desirable to print PLA:CA blends with a layer thickness of 0,3 μm to accelerate printing speed and improve the printing quality of high-CA-content blends.

From an industrial point of view, this work is particularly promising, as it demonstrates that it is possible to manufacture and control the dielectric and mechanical properties of CA-based polymeric blends for electrical insulation applications, with the products having dielectric and mechanical properties close to those of polyethylene, a polymer commonly used in this field. In addition, it would be interesting to investigate the influence of the infill pattern on mechanical and dielectric properties to pursue architectural optimization. Furthermore, a focus on the mechanical properties of blends is needed in order to create a material able to rival the synthetic polymer commonly used in electrical insulation.

5.4. What are the limitations of 3D-printed biobased materials for dielectric applications ?

Lecoublet Morgan^{1,2}, Ragoubi Mohamed¹, Leblanc Nathalie¹ and Koubaa Ahmed²

¹ UniLaSalle, Unité de Recherche Transformations et Agro-Ressources (ULR 7519 UniLaSalle–Université d'Artois), 76130 Mont-Saint-Aignan, France

² Laboratoire de Biomatériaux, Campus de Rouyn-Noranda, Université du Québec at Abitibi-Témiscamingue (UQAT), 445, Boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

5.4.1. Abstract

Renewable dielectric materials attract the attention of industrial and stakeholders, but such materials possess limited properties. This research focused on studying polylactic acid (PLA): cellulose acetate (CA) blends produced by 3D printing to facilitate their integration into the electrical insulation field. Dielectric findings showed that a blend containing 40 % of CA by mass had a dielectric constant (ϵ') of 2,9 and an electrical conductivity (σ_{AC}) of $1,26 \cdot 10^{-11} \text{ S} \cdot \text{cm}^{-1}$ at 100 Hz and 20 °C while exhibiting better mechanical rigidity in the rubbery state than neat PLA. In addition, it was possible to increase the electrical insulating effect by reducing the infill ratio at the cost of reduced mechanical properties. Differential scanning calorimetry (DSC), broadband dielectric spectroscopy (BDS), and dynamic mechanical analysis (DMA) results showed that the PLA plasticizer reduced the energy required for PLA relaxations. These preliminary results demonstrated the benefits of using a combination of PLA, CA, and 3D printing for electrical insulation applications.

5.4.2. Résumé en français

Les matériaux diélectriques renouvelables attirent l'attention des industriels et des acteurs concernés, mais ces matériaux possèdent des propriétés limitées. Pour faciliter leur intégration, cette recherche s'est concentrée sur l'étude de mélanges d'acide polylactique (PLA) et d'acétate de cellulose (CA) produits par impression 3D pour l'isolation électrique. Les résultats diélectriques ont montré qu'un mélange contenant 40 % en masse de CA avait une constante diélectrique (ϵ') de 2,9 et une conductivité électrique (σ_{AC}) de $1,26 \cdot 10^{-11} \text{ S} \cdot \text{cm}^{-1}$ à 100 Hz et 20 °C, tout en présentant une meilleure rigidité mécanique à l'état caoutchouteux que le PLA pur. En outre, il a été possible d'augmenter l'effet d'isolation électrique en réduisant le taux de remplissage, au prix d'une réduction des

propriétés mécaniques. Les résultats de la calorimétrie différentielle à balayage (DSC), de la spectroscopie diélectrique à large bande (BDS) et de l'analyse mécanique dynamique (DMA) ont montré que le plastifiant du PLA réduisait l'énergie nécessaire à la relaxation du PLA. Ces résultats préliminaires ont démontré les avantages de l'utilisation d'une combinaison de PLA, de CA et d'impression 3D pour les applications d'isolation électrique.

5.4.3. Introduction

Dielectric materials are increasingly needed and produced for electronic applications in an increasingly connected world. The global electronic materials market has been estimated at USD 65,7 billion in 2022, with a 6 % increase over the next 5 years (TechSci Research, 2023). This fast-paced production also raises issues such as the end-of-life of such materials. According to Ankit et al. (2021), 54 Mt of electronic waste have been produced in 2019, with a forecasted 75 Mt production by 2030. Current e-waste management solutions are still inadequate, mainly based on landfill and incineration processes, with the associated pollution problems. Biobased materials would be highly desirable to mitigate such problems. These materials are more environmentally friendly than their synthetic counterparts in their manufacture, renewability, and biodegradability properties. According to The European Association, 87 kT of biobased materials was used in 2023 the electronics industry and, with an exponential increase (European Bioplastics, 2023b).

Concerning the use of biobased materials in electronics, Nakatsuka (2011) produced plasticized PLA-coated electrical cables. The plasticized PLA showed an electrical conductivity of $10^{-12} \text{ S} \cdot \text{cm}^{-1}$, and the cable presented a dielectric strength (E_{BR}) of around 45 kV with good flexural properties. Still, the authors pointed out the plasticizer's temporal stability issues. By controlling the alignment of electrospun cellulose acetate (CA) fibers, Meng et al. (2020) controlled the CA:aluminum bimetal deformation. These devices were used as actuators in a non-contact sensor for detecting the moisture content of a human hand, without showing any degradation in the electrical resistance of the aluminum part. This showed high potential in wearable health monitors and advanced non-contact human-machine interactions. The polymer blending strategy could be envisaged to obtain a final material combining the properties of its constituents to

overcome the limitations of biobased polymers. Henning et al. (2019) proposed a PLA:CA blend filled with zinc pyrophosphate (ZnPP) as a biobased alternative to conventional printed circuit board (PCB). PLA:CA and PLA:CA blended with $W_{\text{ZnPP}} = 5\%$ presented comparable dielectric properties to FR4 and FR2 glass:epoxy laminates, except for a significative lower dielectric constant and higher surface resistivity. They have been successfully used for PCB demonstrators, but issues remain unsolved, such as a warping effect during the soldering of components on its surface. 3D printing is a recent technology that both facilitates the prototyping of industrial parts and controls the internal design of the product. (Barbosa et al., 2018) developed a PLA-based 3D-printed electrical insulator for smart grid electrical insulator application. The produced insulators have endured voltages of 35 kV, with no observed degradation, which validates the interest in integrating these new biobased smart isolators for 13,8 kV applications.

Even if PLA:CA is a promising biobased polymeric for electronic applications, its application by fused filament fabrication (FFF) technology is still largely undeveloped for electrical insulation applications. Their dielectric and thermomechanical performances should be optimized. To pursue the work aimed at promoting the use of biobased materials, this study proposes to investigate the use of PLA: plasticized CA blends by 3D printing for electrical insulation applications, to understand the advantages of such materials and their noted limitations.

5.4.4. Material and methods

PLA-20003D (PLA) and ACI-002 plasticized cellulose acetate (CA) were supplied by respectively Natureplast (Caen, FRA) and EURL BBFil (Heiligenberg-Vallée, FRA). The supplier gave the $W_{\text{plasticizer}}$ at 29 %. All materials were oven-dried for at least 4 hours at 60 °C for all the processing steps to avoid internal moisture. A first extrusion processing was performed with a SCAMEX 25-20D (SCAMEX, Isques, FRA). Five different conditions were produced, resumed in **Table 5.12**. A screw speed of 30 RPM and an extrusion profile temperature of 160-170-180 °C were used.

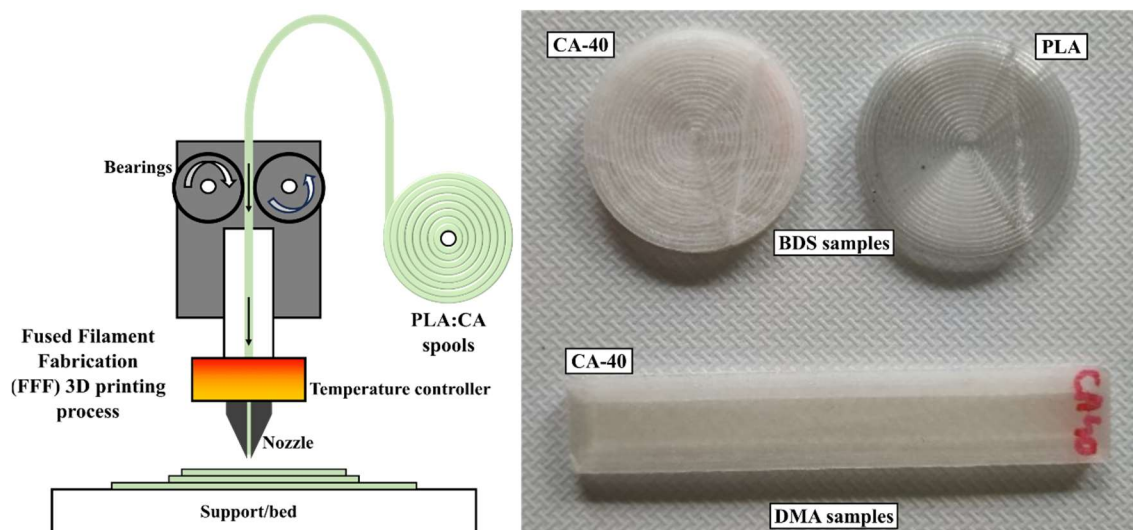
Table 5.12 : Produced conditions

Conditions	W _{PLA} (%)	W _{CA} (%)
PLA	100	0
CA-10	90	10
CA-20	80	20
CA-30	70	30
CA-40	60	40

The 3D filaments were produced with a 3DEVO filament maker (3DEVO, Utrecht, NDL) at the ITHEMM laboratory (Charleville-Mézières, FRA), with a screw speed of 5 RPM and an extrusion profile of 170-180-180-170 °C. The fused filament fabrication (FFF) was performed with a SIGMAX R19 3D printing device (BCN3D, Gavà, Spain). The parameters used were resumed in **Table 5.13**, and the produced samples were presented in **Figure 5.23**

Table 5.13 : 3D parameters conditions

Nozzle temperature	215 °C
Printing speed	30 mm·s ⁻¹
Bed temperature	60 °C
Sample thickness	2 and 4 mm
Infill pattern (BDS)	Concentric
Infill pattern (DMA)	± 45

**Figure 5.23 : Fused filament fabrication (FFF) 3D printing process and produced samples**

In this study, the thermal behavior of the various blends was determined with a DSC Q20 (TA Instruments, New Castle, US) with a dynamic ramp rate of 10 °C·min⁻¹. Dynamic mechanical analysis (DMA) was carried out on 60*10*2 mm and 60*10*4 mm samples

in double cantilever mode with an Artemis DMA 242 E (Netsch, Selb, Germany) and a ramp between 30 and 140 °C at 5 °C·min⁻¹ and a controlled force of 1 N. Finally, BDS tests were carried out using a Keysight E4980A Precision LCR Meter (Agilent Technologies, Santa Rosa, CA, USA) on 25 mm-disks samples. The heating program consisted of an isothermal rise between 0 and 160 °C with 4°C per step and measured at 100 Hz. All the figures presented below were produced with the Python 3.10.11 programming language, using Pandas' module to read the dataset and Matplotlib to produce the graphs.

5.4.5. Results and discussions

Table 5.14 shows the thermal properties of PLA and PLA:CA blends.

Table 5.14 : Thermal temperature of PLA:CA blends

	T _g PLA (heat)	T _{cc} PLA	T _m PLA
PLA	61,7 ± 0,4	127,6 ± 0,1	154,2 ± 0,6
CA-10	56,4 ± 0,7	122,9 ± 1,1	152,4 ± 0,5
CA-20	51,6 ± 0,4	120,6 ± 0,6	150,2 ± 0,2
CA-30	47,1 ± 1,2	117,3 ± 1,2	148,9 ± 1,0
CA-40	41,1 ± 1,5	110,8 ± 1,4	145,9 ± 0,4

Neat PLA exhibited all the expected relaxations for a PLA: a glass temperature (T_g) of 62 °C, a cold crystallization temperature (T_{cc}) of 128 °C and a melting temperature (T_m) of 154 °C (Kang et al., 2018). Adding CA decreased all the observed relaxations. At W_{CA} = 40 %, the T_g, T_{CC}, and T_m of PLA decreased respectively by 20,6, 16,8, and 8,3 °C. Kang et al. (2018) have also observed a decrease in T_g by adding plasticizers into PLA. According to the latter, adding plasticizers, generally small molecules, increased the free volume of macromolecular chains, thereby improving the polymer's mobility. It is also worth noting that the supplied PLA was amorphous, with a measured X_{cr} below 0,5 %. Furthermore, while adding plasticizer improved the mobility of the macromolecular chains, it did not significantly change the crystallinity of the blends, with X_{cr} still below 0,5 %.

As the DSC findings demonstrated, the addition of CA varied the thermal properties of PLA by lowering the relaxation energies. Dielectric materials are subjected to various

temperature fluctuations due to electric current, which alters their dielectric properties. Knowing this thermal dielectric stability would be important to qualify the presented materials. **Figure 5.24** presents the dielectric constant (ϵ') and electrical conductivity (σ_{AC}) of the 3D-printed neat PLA and CA-40 with an infill ratio of 100 % versus temperature.

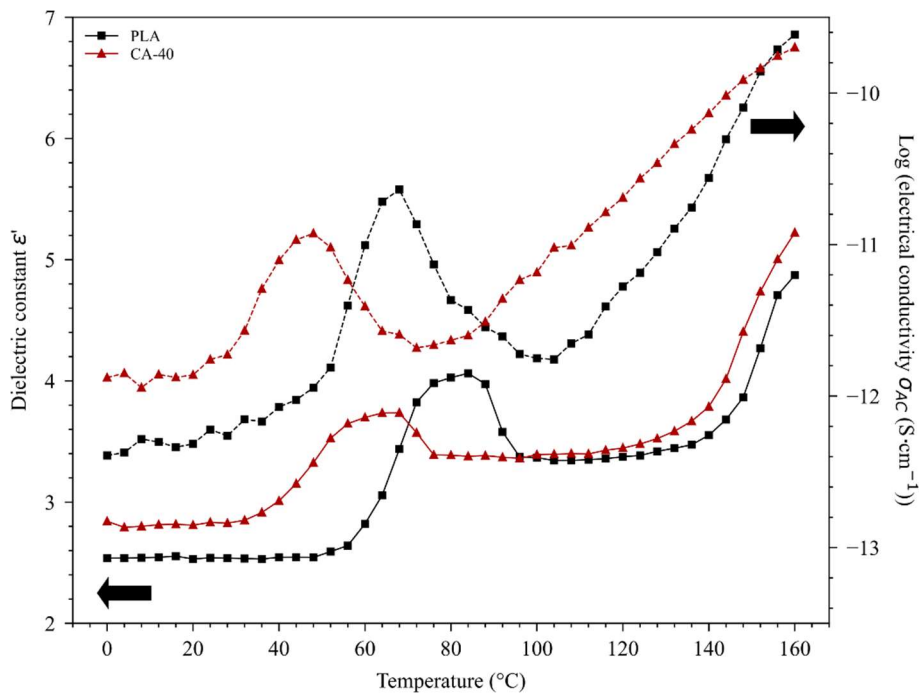


Figure 5.24 : Dielectric constant ϵ' and electrical conductivity σ_{AC} of PLA and CA-40 versus temperature, measured at 100 Hz

At 20 °C, PLA and CA-40 presented a ϵ' of 2,53 and 2,81 respectively, and a σ_{AC} of $4,8 \cdot 10^{-13}$ and $1,4 \cdot 10^{-12} \text{ S} \cdot \text{cm}^{-1}$ respectively. The global measured increase in dielectric properties was attributed to the polar nature of CA, which contains hydroxyl functions as opposed to PLA (Lecoublet et al., 2023). Peaks are present between 40 and 80 °C, representing two PLA relaxations. The sharp increase around 40-60°C is due to the transition to a post- α -relaxation rubbery state, increasing macromolecular mobility and facilitating their following of the AC shift, thus increasing overall permittivity. The noted drop between 60-80°C comes from the cold crystallization of PLA, reducing macromolecular mobility by the formation of a new rigid phase in PLA.

Although the addition of CA increased the conductivity of the blends, the measured properties at 100 Hz for all materials were still in the electrically insulating range (Solazzo

et al., 2019), validating their use for dielectric applications. The produced materials showed notable temperature sensitivity. At 160 °C, PLA exhibited a ϵ' and σ_{AC} respectively 1,92 and 503 times greater, and CA-40 exhibited a ϵ' and σ_{AC} respectively 1,85 and 145 times greater than measured at 20 °C. The observations for neat PLA are in perfect agreement with the literature (Badia et al., 2017; Lecoublet et al., 2023). Badia et al. (2017) have already noticed that measured at 100 Hz, the dielectric constant of neat PLA increased from 3,05 to 3,95 when the temperature shifted from 20 to 130 °C. The temperature-dependent behavior observed of both electrical conductivity and dielectric constant can be associated with the increased ionic mobility of macromolecular chains, as mentioned in the literature (Lecoublet et al., 2023). As the melting temperature approached, the σ_{AC} increased faster for CA-40 than neat PLA. This could also be due to the increased free volume, greatly improving the mobility of the carrier charges (Bandara et al., 2011). CA reduced the energy required for α -relaxation measured by BDS, as observed in the literature when a plasticizer is added to a plastic matrix. CA-40 showed an α -relaxation shift of -20 °C. While the constant and conductivity were slightly higher for CA-40 than for PLA in the measurement range tested, these results remained comparable and low enough to be suitable for electrical insulation applications.

As the field of dielectric materials covers applications requiring high flexibility or high rigidity, it is also important to know the thermomechanical behavior of the proposed materials. PLA suffers from an important loss of mechanical properties beyond its T_g due to its rubbery state. As the incorporation of plasticized CA into PLA will result in complex behavior, it is important to understand its behavior (Lecoublet et al., 2023). **Figure 5.25** presents the storage modulus (E') and loss factor ($\tan \delta$) of the 3D-printed neat PLA and CA-40 with an infill ratio of 100 % versus temperature. At 30 °C, PLA and CA-40 showed an E' of 1,81 and 1,69 GPa respectively. Although the addition of CA in the glassy state decreased the E' and increased the $\tan \delta$, the CA addition appeared attractive from a mechanical point of view, as it seems to greatly limit the loss of mechanical properties when PLA reached the rubbery state. This improvement effect can be directly linked to the CA and not to an improvement in the blend's crystallinity, as demonstrated by DSC. Moreover, the $\tan \delta$ is much lower in the rubbery state, so less electromagnetic energy is converted into heat. It is also worth noting that for both DMA and BDS measurements,

the addition of CA decreased the T_g and T_{cc} of the blends, according to DSC measurements.

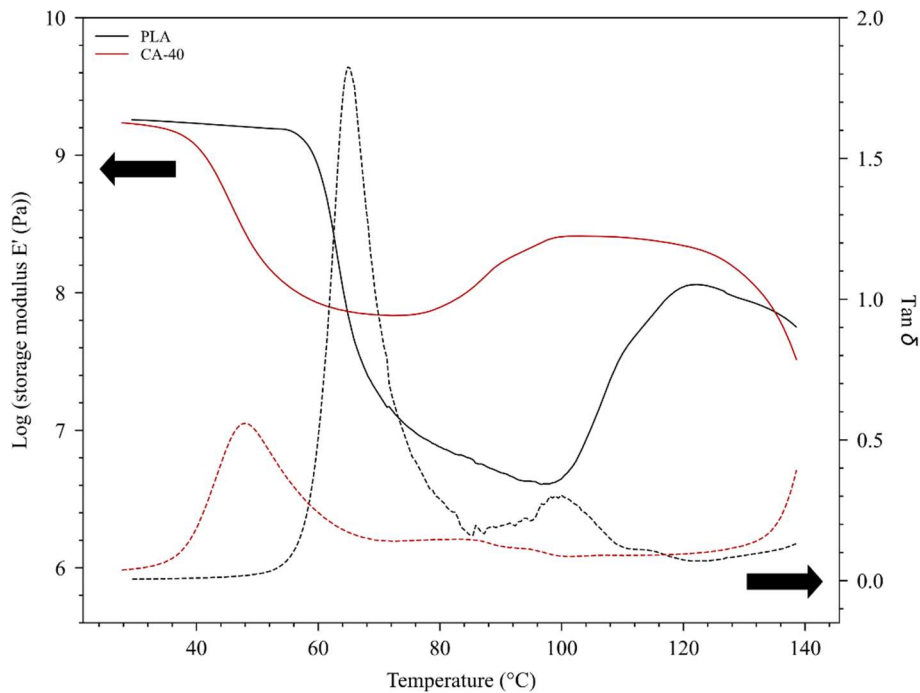


Figure 5.25 : Log (storage modulus E') and loss tangent $\tan \delta$ of PLA and CA-40 specimens versus temperature

One of the main benefits of 3D printing is the ability to control the infill ratio of 3D specimens. Zhang et al. (2016) demonstrated that the dielectric constant was proportionally related to the infill ratio, which can be valuable for producing materials with controlled dielectric properties. To investigate this effect on the mechanical and dielectric properties of PLA:CA blends, **Figure 5.26** shows the ϵ' , σ_{AC} and E' of CA-20, CA-30 and CA-40 blends. The ϵ' and E' decreased with a decreasing infill ratio, while the σ_{AC} increased with decreasing infill ratio. In the case of CA-40, shifting from 100 % to 40 %, the infill ratio decreased the dielectric constant and storage modulus by 29 % and 61 % respectively. The σ_{AC} was however increased by 216 %. The decrease in ϵ' and E' with a decreasing infill ratio can be directly related to the porosity rate of the samples (Öteyaka et al., 2021; Zhang et al., 2016). The increase in electrical insulating properties associated with the reduction in the infill ratio can be linked to more conductive paths, enabling the electrical current to bypass areas of high local resistance due to greater local heterogeneity. These results demonstrate that improving the insulating properties of

PLA:CA blends would be possible by reducing the infill ratio at the cost of lower mechanical stiffness.

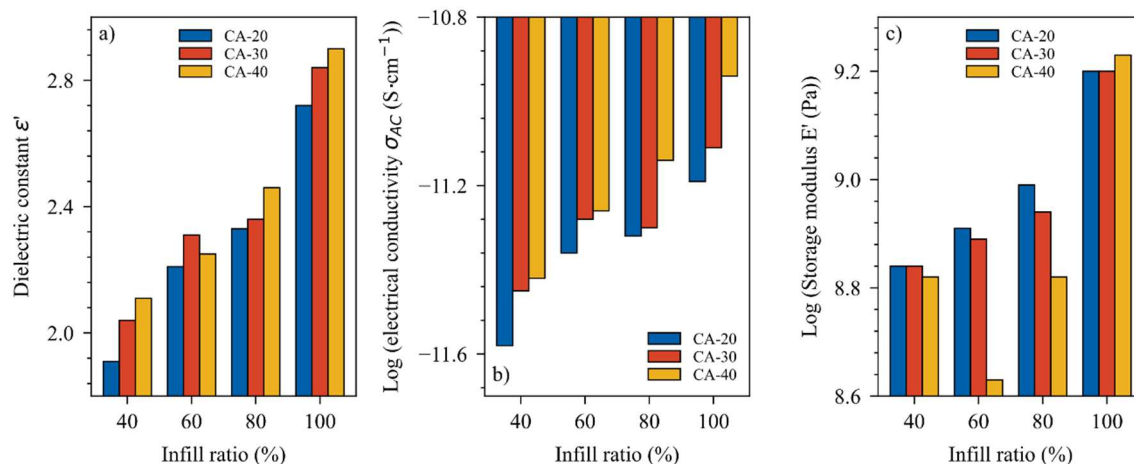


Figure 5.26 : Dielectric constant, electrical conductivity, and storage modulus as a function of infill ratio measured on 4 mm – thick samples. Dielectric constant and electrical conductivity are measured at 100 Hz and 20 °C, and storage modulus is measured at 30 °C and 1 Hz

To compare these new materials with their synthetic counterparts, **Table 5.15** presents a comparative analysis of the tested properties of CA-40 and LDPE as reported in the literature. These results show that CA-40 with 40 % infill has a storage modulus and electrical conductivity equivalent to LDPE, with a lower dielectric constant than LDPE. This would prove that 3D printing of PLA:CA blends is relevant to replace dielectric applications usually dominated by LDPE.

Table 5.15 : Comparative analysis of the tested properties of CA-40 and LDPE as reported in the literature

Dielectric constant ϵ'			
Material	T (°C)	Value	Ref
CA-40	20	2,11	Our study
LDPE	Room T	2,43	(Ahmed Dabbak et al., 2018)
LDPE	Room T	2,21	(Han et al., 2020)
LDPE	Room T	2,46	(Kemari et al., 2020)
Electrical conductivity σ_{AC} (S·cm ⁻¹)			
Material	T (°C)	Value	Ref
CA-40	20	4*10 ⁻¹²	Our study
LDPE	20	8*10 ⁻¹²	(Liang and Tjong, 2006)
LDPE	27	3*10 ⁻¹²	(Ciuprina and Plesa, 2011)
LDPE	30	1*10 ⁻¹²	(Stancu et al., 2013)
Storage modulus E' (MPa)			
Material	T (°C)	Value	Ref
CA-40	30	656	Our study
LDPE	30	380	(Chen et al., 2020)
LDPE	30	230	(Poh et al., 2022)
LDPE	30	205	(Poh et al., 2022)

5.4.6. Conclusion

In this study, we investigated the dielectric and mechanical properties of 3D-printed PLA:CA blends to determine the benefits and limitations of such materials for electrical insulation applications. The CA content and infill ratio were the main criteria in the dielectric and mechanical response of PLA:CA blends. We highlighted that adding of CA improved the thermomechanical stability of PLA in the rubbery state. Moreover, electric insulation performances were improved by reducing the infill ratio of the 3D-printed samples. Under the conditions chosen, the infill ratio had a greater effect on mechanical and dielectric properties than the effect of CA, showing that adjusting the dielectric properties of PLA:CA blends by adjusting these crucial parameters is possible. Our results show that these PLA:CA blends are promising for insulation electrical applications, at the cost of a decrease in mechanical properties in the glassy state and a slight decrease in electrical insulating properties. To go further, it would be possible to analyze in depth the influence of a post-crystallization on the mechanical stability. Furthermore, to limit the plasticizing effect of CA, we can reduce the plasticizer content to fully benefit from the insulating effect of PLA and the reinforcing effect of CA.

5.5. Discussions et bilan du Chapitre 5

Tous les objectifs évoqués ont pu être atteints avec succès durant ce chapitre. Quatre différents mélanges de PLA:CA allant jusqu'à un W_{CA} de 40 % ont été produits par impression 3D et caractérisés. Ces travaux ont pu donner des éclaircissements concernant l'imprimabilité des mélanges PLA:CA. Comme les résultats rhéologiques l'ont montré, les éprouvettes possédant un haut taux de CA ont nécessité un soin particulier pour l'impression. Premièrement, des tests préliminaires ont démontré l'importance de réaliser un étuvage des bobines avant l'impression. Sans cette étape, les éprouvettes n'ont pas pu être imprimées correctement, présentant de nombreuses déchirures et des porosités ouvertes (**Figure 5.27**). Pour enlever l'humidité des filaments avant l'impression, il a aussi été noté qu'il était plus adapté d'utiliser un dessiccateur plutôt que d'étuver à 60 °C. En effet, l'étape d'étuvage a favorisé une recristallisation des filaments, les rendant très cassants et a augmenté drastiquement les probabilités d'échec d'impression par casse du filament.



Figure 5.27 : Éprouvettes de CA-40 imprimé en 3D. Le filament a été étuvé à 60 °C durant 3h pour l'éprouvette de gauche tandis que celle de droite n'a pas été étuvée

Une autre remarque fut le besoin d'augmenter l'adhérence du plateau avec l'utilisation de colles à bâton pour les impressions des conditions CA-30 et CA-40. Cela pourrait venir de l'effet combiné de la diminution de la part de PLA pouvant adhérer et par la présence du plastifiant. Concernant l'effet observé du CA sur les propriétés des mélanges PLA:CA, ces derniers sont en accord avec le précédent chapitre. Le CA, par ses groupes hydroxyles,

a augmenté la viscosité complexe et diminué le pouvoir isolant électrique du PLA ainsi que sa stabilité thermique associée à la dégradation des groupes acétyles (**Annexe 9**). Cependant, les résultats DMA ont montré que l'ajout de CA a été positif sur la stabilité mécanique du PLA durant son état caoutchoutique. Le plastifiant du CA a fortement réduit les phénomènes de relaxation du PLA en diminuant la température de transition vitreuse de cristallisation et de fusion du PLA observée en DMA, BDS et DSC (**Annexe 9**). L'effet de l'impression 3D a amélioré le pouvoir isolant par ajout de porosité interne. Cette amélioration de l'effet 3D a pu être observée plus en détail avec l'application du plan de Taguchi, le taux de remplissage a été un facteur important. La partie optimisation a aussi montré qu'il faut éviter la combinaison d'une faible épaisseur de couche, d'un faible taux de remplissage et d'un haut taux de CA. La condition 8 (à savoir un taux de W_{CA} de 40 % un taux de remplissage de 60 % et une épaisseur de couche de 0,1 mm) a présenté de nombreux défauts de structure, expliquant pourquoi les résultats DMA de cette dernière soient en deçà des résultats prévus. Comme l'épaisseur de couche n'a été que peu impactante sur les propriétés diélectriques, il serait ainsi plus adapté d'imprimer à des épaisseurs de 0,3 mm pour éviter les défauts notés.

Ainsi, durant ce chapitre, nous avons démontré l'intérêt des mélanges PLA:CA imprimés en 3D pour le domaine diélectrique. Après une étape d'optimisation, les matériaux ont présenté des résultats mécaniques et diélectriques comparables au PEBD. Cela rend de tels matériaux intéressants pour remplacer le PEBD pour des applications d'isolation électrique. Pour aller plus loin dans l'utilisation de ce matériau proposé, de nombreuses possibilités existent. Premièrement, il pourrait être envisageable de réaliser une étape de compatibilisation du PLA:CA afin d'améliorer davantage la morphologie des mélanges. Ensuite, il pourrait être envisageable d'améliorer leurs propriétés mécaniques en réalisant une étape de post-cristallisation, ou de renforcement mécanique par ajout de charges. Par ailleurs, pour limiter l'effet du plastifiant contenu dans le CA, il serait possible de réduire la teneur en plastifiant, voire de l'éliminer pour produire des matériaux PLA:CA bénéficiant pleinement de l'effet isolant du PLA et de l'effet renforçant du CA.

**Chapitre 6) Conception et
caractérisation de biocomposites et
bionanocomposites à base de cellulose
pour impression 3D**

6.1. Introduction

Le sixième chapitre de ce manuscrit vise à explorer la stratégie de conception de biocomposites à base de cellulose pour produire des matériaux pour une application en isolation électrique. Un des points soulevés durant les deux précédents chapitres fut la relativement faible rigidité du PLA une fois passée la température de transition vitreuse. Cette barrière limite les applications du PLA à des températures au-delà de 60 °C, ce qui peut être critique pour des applications proches de champs électriques importants, pouvant chauffer le matériau par effet Joule. Comme montré dans la synthèse bibliographique, il est envisageable d'ajouter des charges cellulosiques dans le domaine diélectrique, car contrairement à d'autres renforts, elles n'ont qu'un effet modéré sur les propriétés diélectriques des matériaux, contrairement aux nanotubes de carbone ou au graphène (Spinelli et al., 2020), ce qui est recommandé pour des applications en isolation électrique. De plus, il est possible d'utiliser l'impression 3D pour formuler des mélanges à base de nanocharges. Durant notre étude, le choix des charges s'est porté sur la cellulose microcristalline (MCC) et la cellulose nanocristalline (NCC). Ce sont deux fibres très proches chimiquement, composées toutes les deux de cellulose pure cristalline. Cela permettra de comparer l'effet de la taille des charges et voir si l'apport de la NCC compense son surcoût. À cause de problématiques rencontrées dans le laboratoire pour imprimer des matériaux biocomposites, il a été décidé d'utiliser un PLA possédant un MFI important, à savoir le PLI-005 de Natureplast (Mondeville, FRA). Ainsi, les objectifs visés durant cette campagne seront de :

- Caractériser les propriétés diélectriques, mécaniques et viscoélastiques de biocomposites à base de MCC et bionanocomposites à base de NCC obtenues par impression 3D.
- Optimiser les propriétés mécaniques et diélectriques de tels matériaux pour une application en isolation électrique par l'utilisation d'un plan d'expérience.

À la vue des connaissances accumulées durant le projet, les hypothèses ci-contre sont proposées :

- L'utilisation d'un PLA avec un haut indice de fluidité permettra d'imprimer, sans difficulté, toutes les formulations envisagées.
- L'ajout de charges cellulósiques impactera les propriétés multiphysiques (mécaniques, viscoélastiques et diélectriques) des biocomposites à base de MCC et des bionanocomposites à base de NCC.
- Un taux trop important de nanocharges risquera de créer des agrégats et donc de diminuer leur potentiel.
- Le procédé d'impression 3D diminuera les propriétés mécaniques et augmentera les propriétés d'isolation électrique, par ajout de porosité.
- Un plan factoriel incomplet sera pertinent pour faire varier les paramètres d'impression et pour faire diminuer le temps de caractérisation.
- Selon le plan factoriel incomplet, le taux de remplissage diminuera la constante diélectrique, la conductivité électrique, mais aussi diminuera le module de stockage et la température d'impression diminuera la porosité des éprouvettes.

Ce chapitre se divise en trois parties. La première partie consiste en un article présentant les propriétés multiphysiques des biocomposites à base de MCC et des bionanocomposites à base de NCC produits. Un zoom sur les propriétés thermiques, diélectriques ainsi que viscoélastiques sera réalisé. La deuxième partie consiste en un article proposant une optimisation des propriétés diélectriques et de mécanique statique des biocomposites et bionanocomposites précédents au travers d'un plan factoriel incomplet. Pour finir, une partie discussion est présentée.

6.2. Sustainable 3D printed cellulose based biocomposites and bionanocomposites: Evaluation of dielectric and viscoelastic performances

Morgan Lecouplet^{1,2}, Raphaël Lack², Mohamed Ragoubi ¹, Nathalie Leblanc¹ and Ahmed Koubaa²

¹ UniLaSalle, Unité de Recherche Transformations et Agro-Ressources (ULR 7519 UniLaSalle -Université d'Artois), Mont-Saint-Aignan, France

² UQAT, Campus de Rouyn-Noranda, 445, boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

6.2.1. Abstract

The development of cellulose-reinforced biomaterials appears to be an attractive approach for the production of sustainable materials with good mechanical properties. Although 3D printing of cellulose-reinforced biomaterials has become popular, there is very little feedback regarding their use in electrical insulation applications. This study aimed to develop new biomaterials containing polylactic acid (PLA), microcrystalline (MCC) and nanocrystalline (NCC) cellulose by fused filament fabrication (FFF). The influence of the 3D printing process, cellulose content and filler size on thermal, viscoelastic and dielectric properties was investigated. The addition of cellulosic fillers contributes to increase the dynamic mechanical properties and complex viscosity of MCC and NCC based bionanocomposites. Moreover, as the used fillers had polar functions on their surfaces, their integration increased the dielectric constant (ϵ'), dielectric loss (ϵ''), as well as the electrical conductivity in alternative current (σ_{AC}) of composites. The cellulosic fillers intensively increased the crystallization rate of the materials, improving the mechanical stability of PLA in the rubbery state. At equivalent content, the best properties were observed for NCC-based composites and were attributed to the nanofiller's better dispersion and available specific surface area, although a NCC optimum content was found at 3 %. Finally, the 3D printing process affects all the measured properties, due to the combined effect of a lower crystalline content and the presence of voids induced by the 3D printing process. The porosity was measured at 2,5 % for the neat PLA, and between 3,1 and 5,8 % for the cellulose-based composites. These results showed the advantage provided by the FFF technology in the production of cellulose-based biocomposites with good electrical insulation properties, while noting some needed improvements to achieve sufficient stiffness in the rubberized state.

6.2.2. Résumé en français

Le développement de biomatériaux à renfort de cellulose semble être une approche séduisante pour la production de matériaux durables présentant de bonnes propriétés mécaniques. Bien que l'impression 3D de ces biocomposites soit devenue populaire, il y a très peu de retours d'expérience concernant leur utilisation pour des applications dans le domaine de l'isolation électrique. Cette étude vise à développer, par impression 3D, de nouveaux biomatériaux à base d'acide polylactique (PLA), de microcristaux de cellulose (MCC) et nanocristaux de cellulose (NCC). L'influence du processus d'impression 3D, de la teneur en cellulose et de la taille de la charge sur les propriétés multiphysiques (thermiques, viscoélastiques et diélectriques) a été étudiée. L'ajout de charges cellulosiques contribue à l'augmentation des propriétés mécaniques dynamiques et la viscosité complexe des bionanocomposites à base de NCC et MCC. De plus, les charges utilisées présentant des fonctions polaires ont contribué à l'amélioration de la constante diélectrique (ϵ'), la perte diélectrique (ϵ''), ainsi que la conductivité électrique en courant alternatif (σ_{AC}) des composites. Les charges cellulosiques ont fortement augmenté le taux de cristallisation des matériaux, améliorant la stabilité mécanique du PLA à l'état caoutchoutique. À teneur équivalente, les meilleures propriétés ont été observées pour les bionanocomposites à base de NCC et ont été attribuées à la plus grande dispersion de la nanocharge et à la surface spécifique disponible, bien qu'une teneur optimale de NCC ait été trouvée à 3 %. Enfin et d'une manière générale, le processus d'impression 3D a un effet négatif sur toutes les propriétés mesurées, en raison de l'effet combiné d'une faible cristallinité associé à la présence de vides induits par l'impression 3D. En effet, la porosité a été mesurée à 2,5 % pour le PLA pur, et entre 3,1 et 5,8 % pour les composites à base de cellulose.

6.2.3. Introduction

The market for dielectric materials is demanding more and more advanced performances, while requiring the identification of viable alternatives for the oil-based traditional materials used. Biobased materials can represent this alternative, offering numerous advantages in terms of sustainability, compostability and biodegradability. In 2023, the *European Bioplastic* association noted a biobased polymer production for electronic

production of 87,2 kT (European Bioplastics, 2023b). Recent reports aimed to promote the use of biobased polymers in dielectric applications (Jin et al., 2022; Pei et al., 2020; Spinelli et al., 2020), but several limitations still exist. For example, PLA, the most widely produced biobased polymer by 2023 (European Bioplastics, 2023a), significantly loses its mechanical rigidity when the applied temperature exceeds 60 °C. Gregorova et al. (2009) have determined that the PLA's storage modulus between 20 and 80 °C has decreased from 2,9 GPa to 0,1 GPa, due to the transition from a glassy to a rubbery state, which limits its suitability for high temperature applications. Improving mechanical performance could be achieved by incorporating fillers to create a composite. To maintain the philosophy of a 100 % biobased material and preserve the potential biodegradability of the matrix, the addition of biobased fillers into a biopolymer matrix appears suitable. It is also a pertinent way to promote the valorization of cellulosic materials by proposing high value-added alternatives to pulp and paper industry. However, the presence of fillers has been reported in the literature to have a slight negative effect on the electrical insulation performance. Yakubu et al. (2020) filled rice husks in a polycaprolactone (PCL) matrix and tested both dielectric and mechanical properties. In addition to better tensile and impact strength properties, the biobased composites favored the dielectric constant and dielectric loss at the gigahertz (GHz) frequency. Neat PCL and biobased composites with a rice husk size of 200 µm had a dielectric constant of 2,2 and 3,4 respectively, measured at 10 GHz. Badia et al. (2017) also found an increase in the dielectric constant by adding hydrogen bonds to the resulting biocomposites when sisal fillers were added into the PLA matrix. In addition, by hindering chain mobility, an interaction between the hydrogen bonds of sisal and PLA increased the latter's "fragile" behavior. Regarding the use of nano-sized cellulose, Ten et al. (2012) characterized the dielectric and mechanical performances of nanocrystalline cellulose (NCC):PHBV bionanocomposites. The dielectric constant and electrical conductivity increased with the weight content of NCC (W_{NCC}). However, mechanical and dielectric properties showed an optimum NCC content between 2 and 2,3 %. At $W_{NCC} > 2,3$ %, the authors suspected the presence of nanofiller aggregation, which decreased the available specific surface area and thus the benefits provided by the nanofiller.

3D printing process can be an invaluable vector for innovation by the wide range of adjustable parameters. Fused filament fabrication (FFF) is the most common 3D printing technique, a suitable technology to print biobased polymer (Bajwa et al., 2021). The FFF

process consists of the extrusion of molten materials with a heated nozzle and deposited layer-by-layer to obtain a 3D object, previously designed with a CAD software (Bajwa et al., 2021). For 3D printing applications in the dielectric field, Spinelli et al. (2020) improved the electrical conductivity of 3D-printed PLA by adding carbon nanotubes (CNT) and graphene nanoplatelets (GNP). At 100 Hz and a $W_f = 6\%$, the electrical conductivity of PLA was 1000 times higher for CNT-based nanocomposites than for GNP-based nanocomposites, due to the CNT form factor, favoring the percolation point of CNT-based nanocomposites. The dielectric properties of 3D-printed PLA parts and their processing parameters were also evaluated by Kuzmanić et al. (2023). Dielectric constant was strongly influenced by the infill ratio, increased from 1,78 to 2,81 as example for a corrugated infill pattern, and for an infill ratio of 33 % to 100 % respectively. Furthermore, the infill pattern also played a role on the dielectric constant at low electrical frequency. This result demonstrates the possibility of controlling the dielectric constant through keen material design.

Although 3D printing, as well as biocomposites for electrical insulation are becoming increasingly popular, to our knowledge there is no experience of combining these two methods to produce new electrical insulating materials. So, we propose an analysis of the dielectric and viscoelastic properties of 3D-printed cellulose-based biocomposites. PLA was chosen as a matrix for the composite elaboration because of its wide availability and good 3D printing capacity. We also propose a comparative study of microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) to investigate the effect of cellulose filler size on the viscoelastic, mechanical, and dielectric properties of blends, as well as the influence on the filler content. For the study of the influence of the 3D printing process, the results will be compared to a conventional process.

6.2.4. Materials & Methods

6.2.4.a. Raw materials

PLI-005 supplied by Natureplast (Montdeville, FRA) was used. The MFI given by the technical data sheet was $25\text{-}35\text{ g}\cdot 10\text{ min}^{-1}$ (ISO 1133 @ 190 °C). To study the influence of cellulose filler size on dielectric and mechanical properties, microcrystalline and

nanocrystalline cellulose (MCC and NCC respectively) were selected. MCC was supplied by J. Rettenmaier (Fosston, USA), obtained from bleached kraft pulp. The density given by the suppliers was 0,27-0,33 g·cm⁻³. NCC (DextraCel Nano HP) was supplied by Anomera (Montreal, QC, CAN). The given bulk density was 0,3-0,7 g·cm⁻³.

6.2.4.b. *Filler silanization and masterbatch processing*

Silanization was carried out on MCC and NCC fillers, following the protocol proposed by Dammak (2022), by magnetic stirring, at room temperature and in 1 L Erlenmeyer flasks. (3-aminopropyl)triethoxysilane (APTES) was used, supplied by Sigma Aldrich. The protocol consisted of a preliminary hydrolysis of 2 % by mass of APTES in a 1:1 solution of ethanol (95 % by volume) and distilled water for 1h at room temperature. In the second step, acetic acid is added to obtain a pH between 4 and 5. For 1 L of solution, 20-22 ml of acetic acid was found to achieve a pH of 4,5. After 15 minutes, the fillers are added and left in solution for 3 hours. Once the reaction is completed, the fillers were filtered and washed, then dried in an oven at 60 °C for 24 hours. Infrared analysis confirmed the presence of compatibilizer on MCC and NCC, with a decrease in the peak associated with adsorbed water, and the presence of a new peak associated with the Si-O-C binding. TGA analysis showed that silanized fillers demonstrated improved thermal stability, potentially associated with a reduction in the hydroxyl groups, and thus attenuating oxidation phenomena at high temperatures. Once silanized, microscopic analysis of the MCC gave a median and a mean length of 34,1 and 51,9 µm respectively, and a median and a mean width of 16,6 and 22,9 µm respectively.

masterbatch pre-processing was carried out for NCC bionanocomposites before the extrusion processing. The melt route was chosen for industrial purposes and achieved on a Haake Minilab II (Thermo Scientific, Massachusetts, USA). This microcompounder operated by batch extrusion of 5 g of PLA:NCC blend. The raw material was conditioned at 60 °C until the moisture content of the components fell below 1 %. Preliminary tests showed that a temperature of 180 °C was sufficient to fully melt the PLA, while limiting the thermal degradation of the extrudate. The protocol used consisted of a screw speed of 70 RPM at 180 °C for 1 minute. Once obtained, the extrudate was finally granulated.

6.2.4.c. *Extrusion processing*

The Coalia company (Thetford Mines, QC, CAN) extruded and granulated the materials. A twin-screw extruder was used with a temperature of 190 °C and a rotational speed between 70 and 100 RPM. Die pressure was measured between 22 and 24 bars. An additional extrusion step was carried out using the Haake mini extruder previously used for the masterbatch, to compensate losses during the processing stage. **Table 6.1** shows the different conditions produced. The maximal MCC content by weight has been fixed at 15 % according to previous laboratory results, while the maximal NCC content by weight has been fixed at 5 % to avoid excessive aggregates.

Table 6.1 : PLA biocomposites and bionanocomposites conditions

	PLA (g)	MCC (g)	Masterbatch (g) (W _{NCC} = 20 %)	W _{MCC} (%)	W _{NCC} (%)
PLA	1000	0	0	0	0
MCC-5	950	50	0	5	0
MCC-10	900	100	0	10	0
MCC-15	850	150	0	15	0
NCC-1	950	0	50	0	1
NCC-3	850	0	150	0	3
NCC-5	750	0	250	0	5

6.2.4.d. *3D printing and hot-pressing processing*

To print the pelletized extrudates, an intermediate filament-making step was carried out on a 3DEVO filament maker (3DEVO, Utrecht, NLD). A temperature profile of 170-185-185-180 °C was applied, with a screw speed of 3,5 RPM and a cooling power of 40 %. 3D printing was performed on a CR-10 Max (Creality, Shenzhen, CHN) (**Figure 6.1**). **Table 6.2** shows the used parameters for the 3D printing. These parameters have been selected via preliminary tests, giving the best printing quality for all the different produced conditions. Neat PLA posed no printing problems, but the bed had to be sprayed with lacquer to improve adhesion and prevent delamination during printing of the high-filled biocomposites. Furthermore, the filaments were dried at 60 °C just before use to remove any traces of moisture that might alter the print quality. Three different shapes were produced: 10 and 25 mm diameter disks for dielectric analysis, and 60*10 mm

rectangles for DMA analysis. **Figure 6.1** presents DMA and 25 mm disk samples made from biocomposites and bionanocomposites.



Figure 6.1 : Creaform CR-10 Max 3D printer and used 3D printing parameters

Table 6.2 : Parameters used for the 3D printing process

Nozzle temperature (°C)	200
Nozzle diameter (mm)	0,8
Nozzle speed (mm·s ⁻¹)	40
Bed temperature (°C)	60
Samples thickness (mm)	4
Layer thickness (mm)	0,4
Infill ratio (%)	100
Infill pattern	± 45°

It is worth noting that the NCC-based samples switched from an orange color for the NCC-1 condition, to a dark caramel color for the NCC-5 condition. In contrast, the biocomposites went from a greenish to a beige color between the MCC-5 and MCC-15 conditions. To study the influence of the 3D printing, the hot-press process was chosen as the conventional process and realized with a LabEcon series (Fontjine Presses, Rotterdam, NDL). After drying the material at 60 °C, the material was hot-pressed at 180 °C for 3 minutes at 100 kN to form homogeneous sheets. The sheets were cut with an ML-W1290 150 W laser cutter (MLlaser, Pont-à-Mousson, FRA) to obtain the desired shapes.

6.2.4.e. *Methods used*

- *Scanning electron microscopy (SEM) analysis*

SEM analyses were performed with a Jeol JSM IT200 (Jeol, Akishima, JAP) to characterize the microstructure of the prepared composites. Tests were carried out on specimens obtained by hot-press. Samples were cryofractured with liquid nitrogen to obtain a clean cross-section, and the selected specimens were all carbon-coated. Tests were made at 5 kV with a x200 magnification.

- *Thermal analysis*

Differential scanning calorimeter (DSC) analyses were proposed to observe the thermal properties and the crystallinity of the materials. The measurements were performed on a DSC Q20 (TA Instruments, New Castle, USA) with 15 mg of material, inserted in Al pans. The used protocol consisted of one heating and one cooling ramp between 20 and 200 °C with a heating rate of 10 °C·min⁻¹ and a nitrogen flow of 20 ml·min⁻¹. The crystallinity degree (X_{cr}) determination was performed using the **Équation 9**. A dH_0 of 93 J·g⁻¹ has been fixed for PLA in agreement with the literature (Kang et al., 2018). Regarding the thermal stability, thermal gravimetry analyses (TGA) were performed using a Tg 209 F1 (Netzsch, Selb, DEU). A scanning rate of 10 °C·min⁻¹ under nitrogen in the temperature range starting from 20 to 600 °C was applied. For each sample, 20 mg of materials was characterized.

- *Rheological analysis*

To characterize the viscoelastic behavior of composites in the melt state, rheological analysis tests were conducted on an MCR 302 plane rheometer (Anton Paar, Graz, AUT). Disk samples with a diameter of 25 mm and a thickness of 2 mm were subjected to a temperature of 180 °C under nitrogen. All tests were performed in the Linear Viscoelastic Range (LVE), with a shear rate range between 0,1-631 rad·s⁻¹. The amplitude sweeps are presented in **Figure A 4c** (**Annexe 3**).

- *Broadband dielectric spectroscopy (BDS) analysis*

BDS analyses were carried out using two different BDSs to scan a wide range of electromagnetic frequencies. A low-frequency dielectric spectrometer Keysight E4980A Precision LCR Meter (Agilent Technologies, Santa Clara, USA) and a high-frequency dielectric spectrometer Keysight E4991A (Agilent Technologies, Santa Clara, USA) were employed. The frequency range of the low-frequency BDS and high-frequency BDS were respectively 20 Hz-2 MHz and 1 MHz-1 GHz. Analyses for both conditions are performed at 20 °C and the results were triplicated. To determine the porosity of 3D-printed samples, a method derived from the measured permittivity was applied (**Equation 28**):

$$Porosity (\%) = 100 - \left(\frac{\varepsilon_{3D-printed} - \varepsilon_{air}}{\varepsilon_{hot-pressed} - \varepsilon_{air}} \right) * 100 \quad \text{Equation 28}$$

Where $\varepsilon_{3D-printed}$ corresponds to the dielectric constant of hot-pressed sample ; $\varepsilon_{hot-pressed}$ corresponds to the dielectric constant of 3D-printed sample ; and ε_{air} corresponds to the dielectric constant of air and fixed at 1.

- *Dynamic mechanical analysis*

To characterize the viscoelastic behavior of composites in the solid state, measurements were realized in dual cantilever mode on a DMA 242 E Artemis (Netschz, Selb, DEU). The dual cantilever mode was chosen for the characterization to avoid collapsing phenomena due to the rubbery state of PLA. The samples were 60*10 rectangular shapes. Tests were carried out in a ramp from 30 °C to 140 °C at a heating rate of 5 °C·min⁻¹ and a controlled force of 1 N. All measurements were performed at a frequency of 1 Hz, the most common frequency used for PLA measurements in the literature.

6.2.5. Results and discussion

6.2.5.a. *Microstructural properties*

Figure 6.2 shows SEM pictures of biocomposites and bionanocomposites. The neat PLA (not presented here) showed a brittle and single-component morphology as expected. The addition of MCC fillers was clearly visible in the MCC-based biocomposites, forming a scattered morphology in the matrix. Pictures of the NCC-based bionanocomposites showed that NCC-1 was free of aggregates. NCC-3 presented few scattered aggregates, demonstrating a relatively good dispersion. For NCC-5, however, several aggregates were noted, indicating that the NCC content may be too high to ensure a proper dispersion.

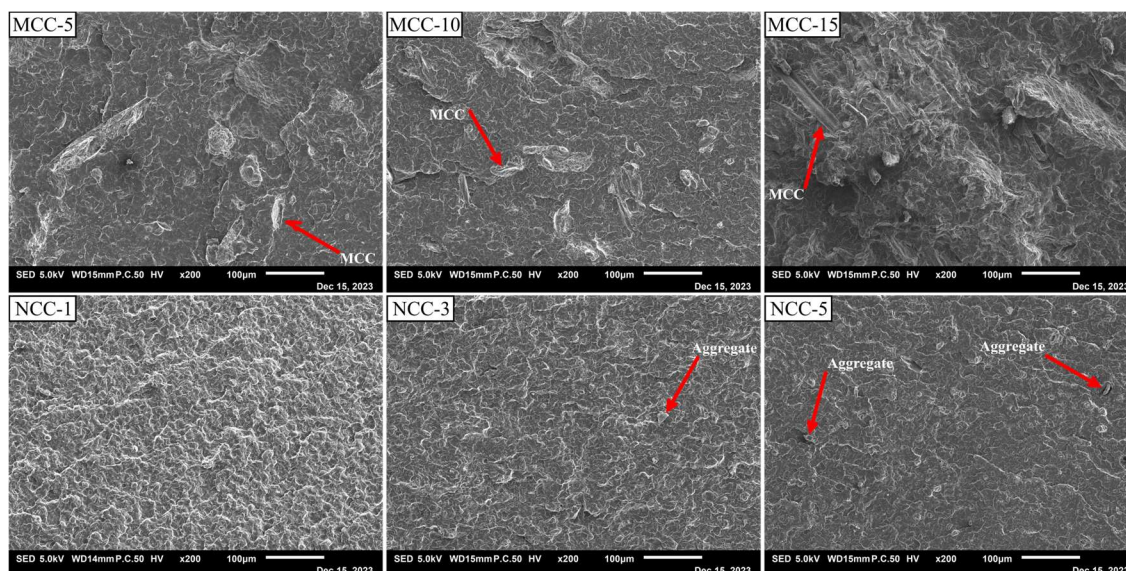


Figure 6.2 : SEM pictures of biocomposites and bionanocomposites

All the cellulose-based composites showed a very rough matrix, demonstrating that the matrix had undergone rearrangement into a new structure with the addition of fillers, possibly indicating an increased crystallinity degree.

Figure 6.3 and **Figure 6.4** show the complex viscosity η^* and storage modulus G' of neat PLA, biocomposites and bionanocomposites.

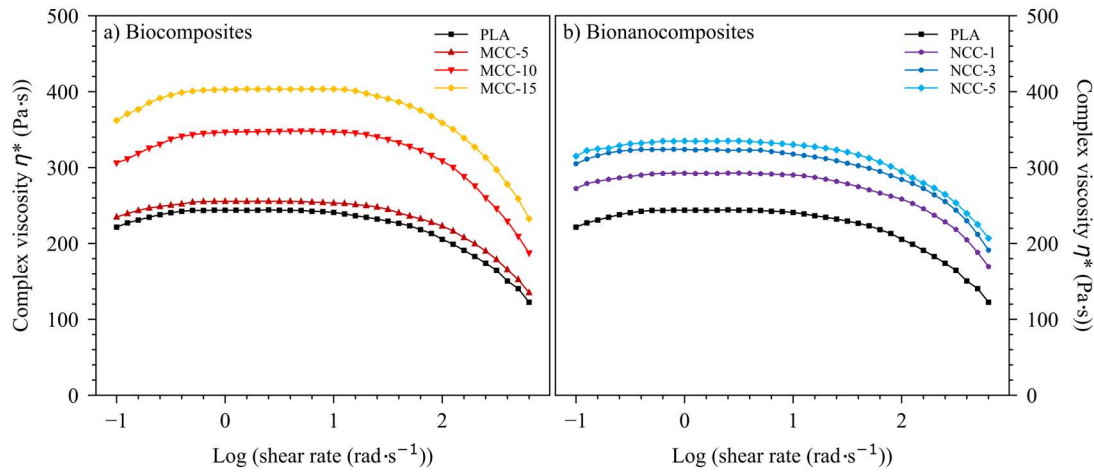


Figure 6.3 : Complex viscosity η^* versus shear rate of biocomposites and bionanocomposites

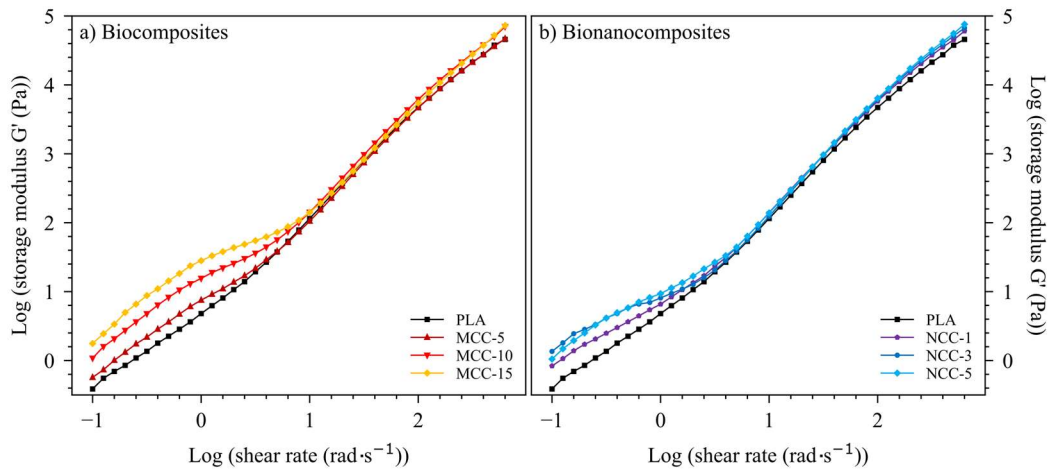


Figure 6.4 : Storage modulus G' versus shear rate of biocomposites and bionanocomposites

All conditions presented a shear-thinning behavior, with an increase in storage modulus G' as the shear rate frequencies increased. Regarding the complex viscosity, at high shear rate ($f > 10 \text{ rad}\cdot\text{s}^{-1}$), PLA presented a shear-thinning behavior, with a decrease in complex viscosity with an increasing frequency. At medium frequencies ($1 > f > 10 \text{ rad}\cdot\text{s}^{-1}$) PLA exhibited a Newtonian plateau, where the viscosity is independent of the shear rate, named zero shear viscosity (η_0) (Bakrani Balani et al., 2023). By applying the Cross equation, the $\eta_{0 \text{ PLA}}$ was found at 246 Pa·s (Table 6.3). At frequencies below $1 \text{ rad}\cdot\text{s}^{-1}$, η^*_{PLA} decreased due to a too-long application of temperature, degrading the PLA (Al-Itry et al., 2012). The addition of cellulosic fillers enhanced the viscoelastic behavior of PLA,

with an increase in the storage modulus at low frequencies as well as complex viscosity at all frequencies. The $\eta_{0 \text{ MCC-15}}$ showed the greatest increase, rising by 65 % compared to the neat PLA.

Table 6.3 : Zero-shear viscosity η_0 of PLA, biocomposites and bionanocomposites determined by the Cross equation

Condition	η_0 (Pa·s)
PLA	245,7
MCC-5	256,9
MCC-10	349,3
MCC-15	406,0
NCC-1	293,7
NCC-3	324,0
NCC-5	337,1

A slight increase of the PLA viscosity with the addition of MCC filler was also observed in the literature (Joseph et al., 2015). The addition of cellulosic fillers acted as a reinforcement, limiting the mobility of PLA's macromolecular chains and thus increasing its viscosity. Moreover, the viscosity increase may also be due to a good compatibility between the silanized filler and the matrix, resulting in filler:matrix interfacial adhesion hindering the PLA mobility. Although aggregation phenomena were noted for NCC-5 by SEM results, the latter possessed a more viscous behavior than MCC-5, demonstrating that the filler size plays an important role in composite viscosity. The reduction in filler size results in an increase in specific surface area and therefore in interfacial adhesion effects, which limits the fluidity of the composites. Even if the addition of cellulose fillers increased the viscosity of cellulose-based composites, this increase remained very limited. This proves that it is possible to increase cellulose content or use fillers with higher L:D factors, such as Kraft fiber or TMP, or even nanofibrillated cellulose, without compromising the printability of cellulose-based biocomposites.

6.2.5.b. *Thermal properties*

Figure 6.5 and **Table 6.4** present the DSC measurement in the tested materials. DSC results showed that the PLA possessed has a behavior typical of a low-crystalline PLA. Hot-pressed PLA had a glass transition temperature ($T_{g \text{ heat}}$) of 64 °C, a cold crystallization

temperature (T_{cc}) of 113,6 °C and a melting temperature (T_m) of 180 °C, which is in line with the literature (Kang et al., 2018; Yang et al., 2008).

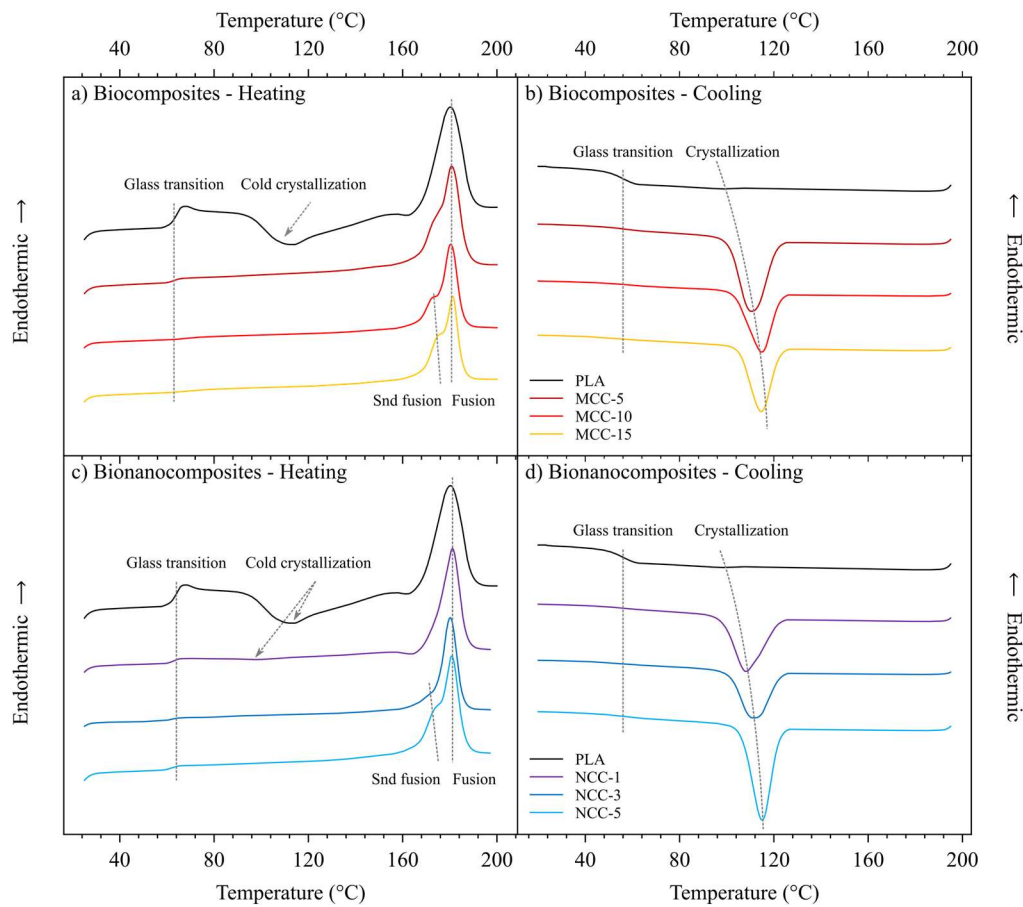


Figure 6.5 : DSC curves for hot-pressed biocomposites and bionanocomposites

For the hot-pressed PLA, the X_{cr} was measured at 11,8 %. It is worth noting that during the cooling ramp, the PLA did not significantly crystallize, but had still showed a weak crystallization relaxation, demonstrating that PLA can easily crystallize if sufficiently boosted. The addition of cellulose fillers had a critical impact on PLA crystallization, independently of the type of filler used. For example, the crystallinity of PLA rose from 11,8 % to 50,4 % when 5 % of MCC was added. Even at a $W_{NCC} = 1$ %, the crystallinity of PLA was sharply enhanced. Except for the latter condition, no T_{cc} was observed in the heating ramp. This positive effect on crystallinity was directly attributable to the nucleation role of the fillers, increasing the X_{cr} (Q. Wang et al., 2020). Filler content had a positive influence on the PLA crystallization kinetics for both fillers used, accelerating the kinetics. But filler content seemed to have only a limited effect on the X_{cr} value itself, implying that most of the available crystallizable PLA was crystallized. Furthermore, the

cellulose filler did not appear to play a significant role in either the T_g or T_m values. It demonstrated that the nature of the filler appeared to have only a very limited influence on the behavior of the DSC curves. The 3D printing process was significant on the DSC curves. Although neat PLA did not show any noticeable difference in crystallization, all 3D-printed MCC-based biocomposites and NCC-based bionanocomposites showed a crystallization rate lower than the hot-pressed ones. The 3D printing had a faster cooling rate, reducing the X_{cr} . According to Cuiffo et al. (2017), 3D printing can lead to changes in the nature and distribution of the crystalline phases formed, which can also decrease the crystallinity potential.

Table 6.4 : DSC results for biocomposites and bionanocomposites

Conditions	Cooling				Heating						
	T_g (°C)	T_c (°C)	dH_c (J·g ⁻¹)	X_{cr} (%)	T_g (°C)	T_{cc} (°C)	dH_{cc} (J·g ⁻¹)	dH_m (J·g ⁻¹)	T_m (°C)	X_{cr} (%)	
PLA	56,0	97,4	1,0	1,1	64,1	113,6	34,1	45,1	180,2	11,8	
Hot pressed	MCC-5	57,0	110,2	36,4	41,1	63,0	-	-	44,6	180,8	50,4
	MCC-10	57,4	114,7	37,9	45,3	64,7	-	-	45,6	180,4	54,5
	MCC-15	57,4	114,5	33,7	42,6	63,9	-	-	40,4	181,2	51,1
	NCC-1	58,1	108,1	36,2	39,3	62,6	98,8	1,1	43,8	181,1	46,3
	NCC-3	58,0	110,8	38,0	42,1	61,7	-	-	44,7	180,1	49,6
	NCC-5	58,4	115,5	39,3	44,4	62,0	-	-	44,8	180,8	50,7
3D printed	PLA	58,6	-	0,0	0,0	67,3	112,9	14,8	24,3	177,6	10,1
	MCC-5	62,6	108,0	33,5	37,9	63,4	101,4	16,0	31,6	184,6	17,6
	MCC-10	61,9	114,1	33,7	40,3	61,5	101,0	20,2	38,0	180,4	21,3
	MCC-15	61,1	107,2	31,1	39,4	63,6	104,4	20,0	36,0	180,5	20,2
	NCC-1	62,7	109,0	36,0	39,1	64,4	104,0	21,2	39,9	179,1	20,4
	NCC-3	61,2	117,5	39,1	43,3	63,3	101,0	22,1	42,0	179,3	22,1
NCC-5	59,6	109,8	32,6	36,8	63,9	100,9	19,1	37,2	178,6	20,5	

Figure 6.6 shows the TGA and derived TGA curves of the materials. Firstly, the neat PLA showed a typical behavior of a monocomponent material with a single degradation phenomenon at 348,6 °C determined by the T_{onset} . Biocomposites and bionanocomposites also exhibited a single degradation phenomenon. Cellulose and PLA had similar temperature degradation, resulting in an overlap of component degradation (**Annexe 5**).

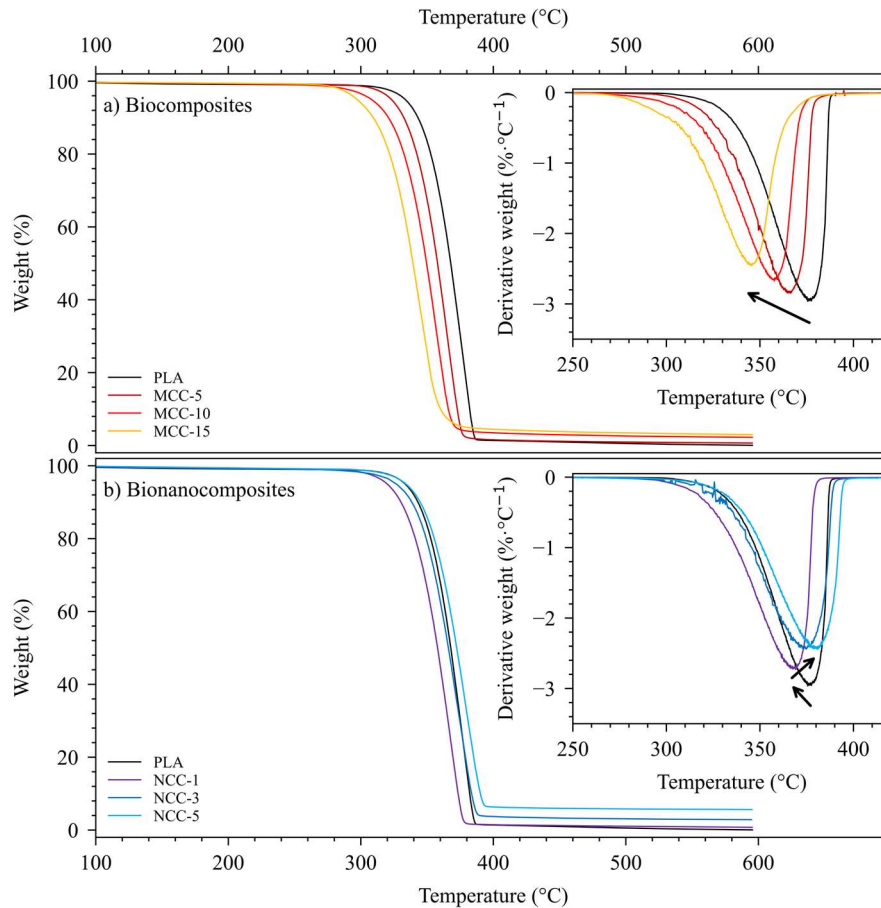


Figure 6.6 : TGA curves of biocomposites and bionanocomposites.

The addition of MCC steadily decreased the thermal stability of biocomposites. When 15 % of MCC was added, the $T_{\text{onset}}_{\text{PLA}}$ was reduced by 31 °C, from 348,6 to 316,2 °C. According to Qian et al. (2018), the thermal stability decreasing with the addition of fillers could come from a good interface between the filler and the matrix, increasing the possible heat transfer between the components. The bionanocomposites, on the other hand, exhibited a different behavior. Adding 1 % of NCC into PLA first decreased the bionanocomposites thermal stability, with T_{onset} decreased from 348,6 to 337,3 °C (**Table 6.5**), in agreement with the notion of a good filler:matrix interface.

Table 6.5 : Thermal stability of biocomposites and bionanocomposites

	PLA	MCC-5	MCC-10	MCC-15	NCC-1	NCC-3	NCC-5
$T_{95} \text{ } (^{\circ}\text{C})$	333,5	323,1	308,1	297,2	319,9	326,9	334,1
$T_{90} \text{ } (^{\circ}\text{C})$	343,1	332,5	320,9	309,5	330,3	338,6	344,8
$T_{\text{onset}} \text{ } (^{\circ}\text{C})$	348,6	340,3	330,1	316,2	337,3	345,4	348,6
Char yield (%)	0,1	0,7	2,2	3,0	0,8	2,8	5,6
Normalized char yield per filler content ($\%_{\text{ash}} \cdot W_f^{-1}$)	-	0,1	0,2	0,2	0,7	0,9	1,1

However, at higher NCC levels, the thermal stability was improved. NCC-5 presented a thermal stability similar to neat PLA. This increased thermal stability can be attributable to a decrease in filler:matrix quality, which may be due to the presence of aggregates. Concerning the char yield at 600 °C, neat PLA showed a char yield about 0,1 %. The addition of fillers increased the char yield. The NCC-5 bionanocomposite showed a maximum yield of 5,6 %. This increase may be due to the silanization of the fillers, releasing silica-based residues (Jin et al., 2020), or possibly residues from the reaction itself. It is also worth noting that NCC had the highest normalized char yield per filler content. The greater surface area of NCC fillers could lead to a higher silane content on their surface, and therefore to an increase of the char yield.

6.2.5.c. *Dielectric properties*

Figure 6.7 presents the dielectric constant of the tested materials, made by low-frequency BDS and high-frequency BDS. The two analyses used were complementary, giving comparable results. At 1 MHz, hot-pressed PLA, MCC-15 and NCC-5 exhibited dielectric constants of 2,66, 3,11 and 2,97 respectively. Firstly, all the materials tested showed a decrease in dielectric constant with increasing frequency measured at 20 °C. Hot-pressed PLA dropped its dielectric constant from 2,74 to 2,17 when the electrical frequency was increased from 100 Hz to 1 GHz. According to Khouaja et al. (2021), this decrease was due to the reduced ability of the material's polar functions to interact with the electric field, lowering its polar potential. The addition of cellulosic fillers increased the dielectric constant, independently of the used W_f and nature. Hot-pressed MCC-5 and NCC-5 showed a 17 and 18 % higher dielectric constant than the hot-pressed neat PLA. This increase can be directly attributed to the addition of more polar materials than PLA and therefore increase the material's permittivity by enhancing respectively the dipolar polarization and interfacial polarization phenomena. Furthermore, the fillers increased the crystallization rate, as seen in the DSC results. These cumulative effects enhanced the interfacial polarization, polarization occurring between two material phases with sufficiently different conductivities and permittivities, increasing the total permittivity of the material (Psarras, 2018; Yakubu et al., 2020). Although MCC-based composites showed the highest dielectric constants, at $W_f = 5\%$ and 1 MHz, the hot-pressed NCC-based bionanocomposite showed a 12 % higher ϵ' value than the hot-pressed MCC-based

biocomposite. This observation could be attributed to the specific surface area of the fillers used. Yakubu et al. (2020) have demonstrated that smaller charge sizes result in increased dielectric properties, by increasing the interfacial polarization phenomenon at the fiber-matrix interface. As NCC presented a smaller size, it possessed a higher specific surface area, and therefore proportionally more silane and hydroxyl functions present on its surface to interact with the applied electric field than MCC, which also increases the dipolar polarization phenomenon. The 3D printing process reduced the permittivity of all the tested composites. 3D-printed PLA, MCC-15 and NCC-5 showed respectively a dielectric constant 3,0, 5,7 and 3,8 % lower than their hot-pressed counterparts. This observation can probably be attributed to the 3D-printing process itself, adding defects in the produced samples.

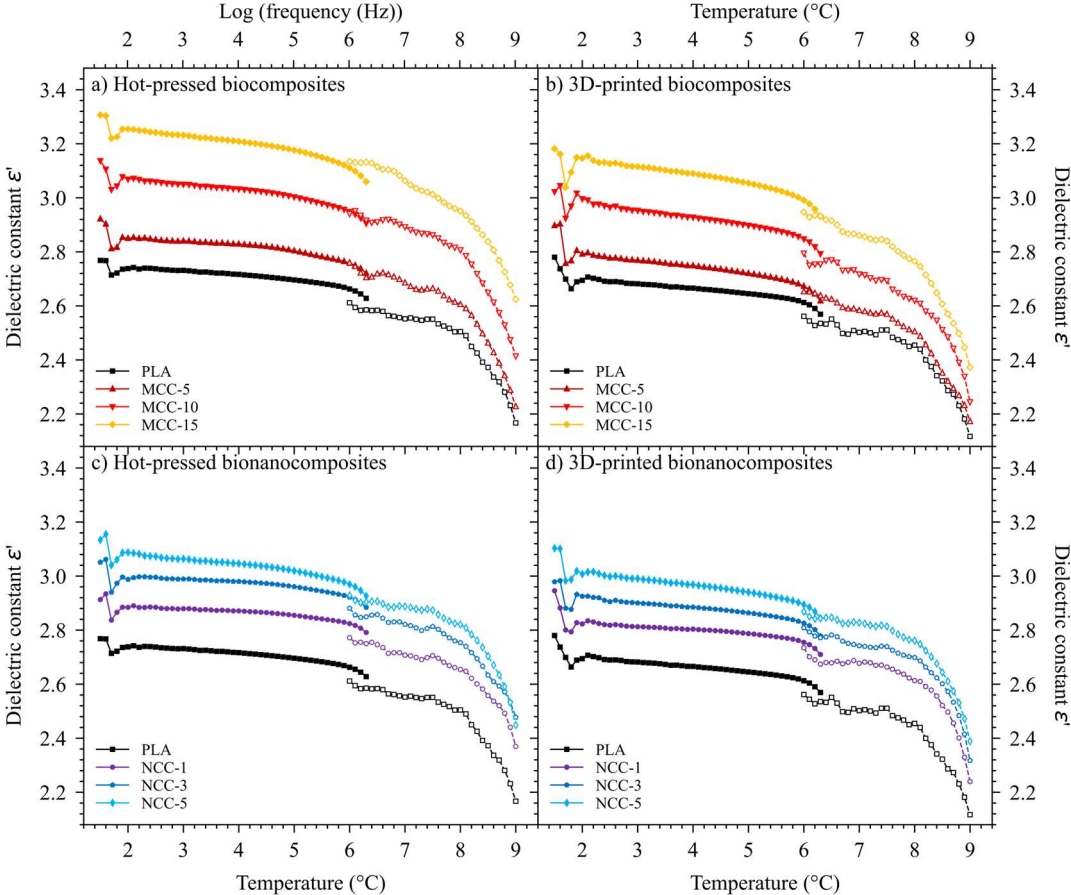


Figure 6.7 : Dielectric constant ϵ' of the tested materials. The plain lines correspond to the low frequency BDS analysis, and the dashed lines correspond to the high-frequency BDS analysis

To better understand this phenomenon and understand the impact of the 3D printing process on the produced structures, **Table 6.6** represent the porosity of the samples measured by the permittivity-derived method. The lowest porosity was measured for neat PLA at 2,51 %, while the highest was measured for MCC-15 at 4,79 %. The use of MCC and NCC increased the porosity of the associated composites. The observed porosity can directly be linked to the rheological results. As opposed to conventional processing like injection or hot-press, 3D printing can introduce printing defects such as voids or cracks (Lay et al., 2019). The use of cellulose fillers increased the complex viscosity of PLA, and a more viscous material may find difficulties to fill the imposed volume by the 3D printer and lead to triangular-shaped voids. As the dielectric constant of air is approximately 1, the inclusion of the latter decreased the potential of polarizable matter and therefore reduced the final dielectric constant (Zhang et al., 2016). It is worth noting that the calculation method is an empirical one, yielding relatively large standard deviations. Additional quantitative analysis using X-ray microtomography would be pertinent to fully clarify this point.

Table 6.6: Porosity of the 3D-printed samples measured by permittivity-derived method

Sample	Porosity (%)
PLA	2.5 ± 0.7
M5	3.1 ± 0.7
M10	3.5 ± 1.7
M15	4.8 ± 1.2
N1	3.3 ± 1.5
N3	3.1 ± 1.0
N5	3.8 ± 1.2

Figure 6.8 presents the dielectric loss (ϵ'') and electrical conductivity (σ_{AC}) of hot-pressed and 3D-printed biocomposites and bionanocomposites measured at 20 °C. The dielectric loss refers to the part of the applied electromagnetic energy that is absorbed by the material and converted into heat (Khouaja et al., 2021). It is therefore an important parameter to be kept as low as possible to avoid accelerated degradation of biobased materials. With the exception of MCC-15, the ϵ'' and σ_{AC} given by the two BDS analyses used were complementary. At 1 MHz, the lowest dielectric loss was measured for the 3D-printed PLA at $1,65 \cdot 10^{-2}$ and the highest was measured for the hot-pressed MCC-15 at $4,79 \cdot 10^{-2}$. A slight increase of the dielectric loss over the frequency was noticed, which can be linked to the presence of the β -relaxation of PLA according to Badia et al. (2014)

at 20 °C. Hot-pressed MCC-15 also showed the highest ϵ'' , with a value 59 % higher than for hot-pressed neat PLA. The literature also noted an increase in dielectric loss with the addition of fillers, associated with increased interfacial polarization (Jeszka et al., 2010; Yakubu et al., 2020). Moreover, they noted that this effect was more pronounced for smaller fillers, in agreement with the presented results. The 3D printing process also reduced the dielectric loss, with a 12 % decrease in ϵ'' for PLA measured at 1 MHz. This reduction can also be attributed to the presence of voids caused by the 3d printing process.

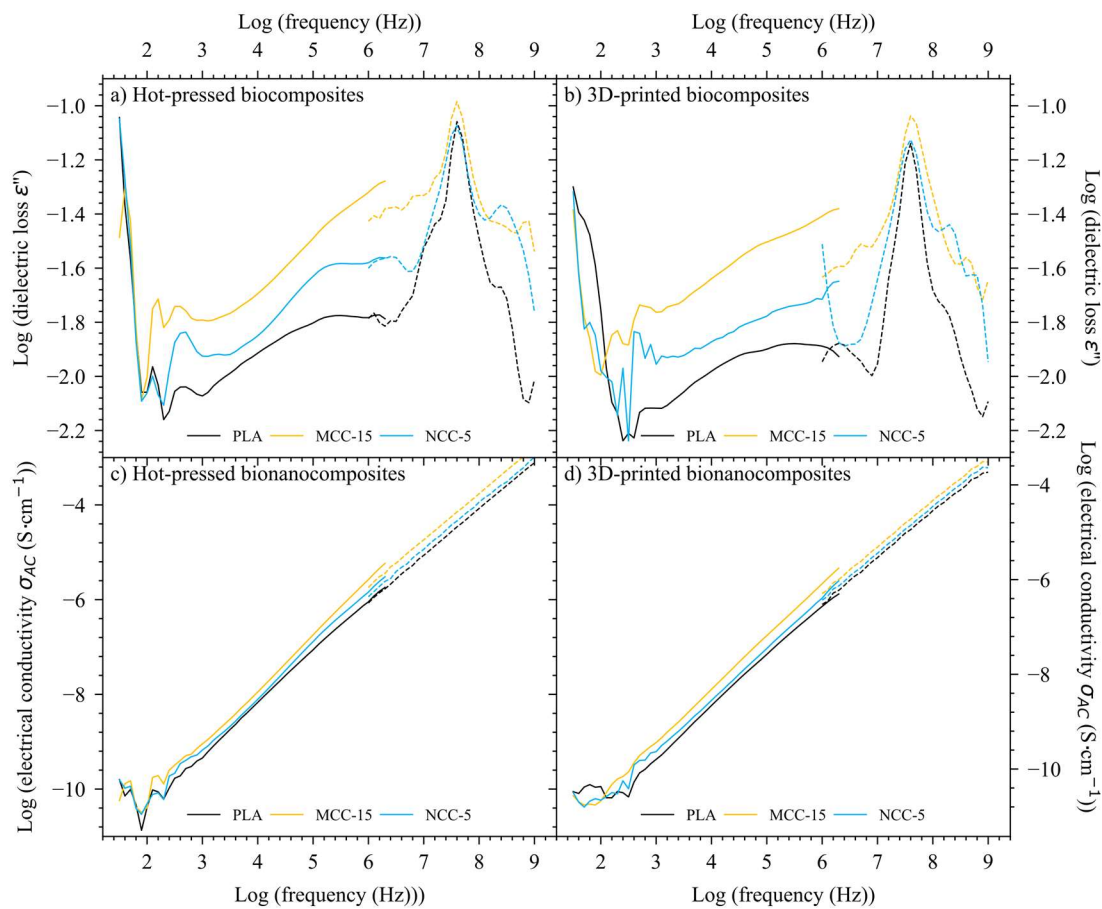


Figure 6.8 : Log (dielectric loss ϵ'') and log (electrical conductivity σ_{AC}) of materials.

The plain lines correspond to the low frequency BDS analysis, and the dashed lines correspond to the high-frequency BDS analysis

Regarding the electrical conductivity, the lowest σ_{AC} was measured for 3D-printed PLA at $7,20 \cdot 10^{-7} \text{ S} \cdot \text{cm}^{-1}$, and the highest for hot-pressed MCC-15 at $2,64 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$. The values observed for neat PLA are in agreement with the literature (Fal et al., 2021). For all the conditions tested, a clear increase in σ_{AC} as a function of applied electrical frequency was noted. Hot-pressed neat PLA showed an increase in σ_{AC} of $2 \cdot 10^7$ between

100 Hz and 1 GHz. Higher electrical frequencies favor the hopping carrier phenomenon, carrying the electrical current into the insulating materials. The strong frequency-dependent behavior is typical of the behavior of an insulating material (Wu et al., 2019). The addition of cellulosic fillers slightly increased the electrical conductivity. As the previous discussed results, this behavior could be associated with the more polar nature of the used fillers. No abrupt increase in electrical conductivity with the addition of fillers was observed, showing that even if a percolation threshold may be present, it does not alter the electrical insulating nature of these materials. The conductivity values were within the electrical insulation range noted by Solazzo et al. (2019), which also suggests that the proposed materials are suitable for the field of electrical insulation.

6.2.5.d. *Mechanical properties*

Figure 6.9 and **Figure 6.10** respectively represent the storage modulus E' and the damping factor $\tan \delta$ of hot-pressed and 3D-printed blends. $\tan \delta$ corresponds to the damping factor of the mechanical energy received by the material. At 30 °C the highest E' was measured for the hot-pressed MCC-15 at 2,28 GPa and the lowest E' was measured for the 3D-printed PLA at 1,27 GPa. Two different behaviors as a function of temperature were noted. Below 60 °C, The hot-pressed PLA showed a high E' and a very low $\tan \delta$, a PLA typical behavior in the glassy state. The temperature range between 60 and 70 °C is characterized by a sharp drop in E' and an intense increase in $\tan \delta$, a behavior related to the α -relaxation of PLA, shifting from a glassy state to a rubbery state (Bajwa et al., 2021; Ding et al., 2023). A rubbery state was present between 70 and 90 °C, with a relatively low E' and a decrease of the $\tan \delta$. After 90 °C, an increase in E' and a stable $\tan \delta$ value around 0,2 were noted. This behavior could be associated with the PLA cold crystallization phenomenon (Sang et al., 2017), also observed by DSC analysis. The heat was sufficiently high to cause a PLA rearrangement into crystal lattices, which logically increased the material's rigidity. However, hot-pressed biocomposites and bionanocomposites showed a different behavior, with a stiffness in rubbery state significantly higher for hot-pressed PLA, and a lower peak $\tan \delta$, without crystallization relaxation. This behavior can be explained by the DSC results. The addition of cellulose fillers promoted the PLA crystallization, and the combined effect of enhanced crystallization and filler presence compensated for the critical softening of

PLA, and provided a good stiffness (Gregorova et al., 2009; Sang et al., 2017). For all the tested conditions, the addition of fillers also improved the composite stiffness, validating the use of MCC and NCC for mechanical reinforcement. This improvement can be also linked to a good filler:matrix interface, efficiently transmitting mechanical loads into the material. The NCC-5 also produced results similar to those of the NCC-3, confirming that there an optimum NCC content must be used to fully exploit the advantages of this reinforcement.

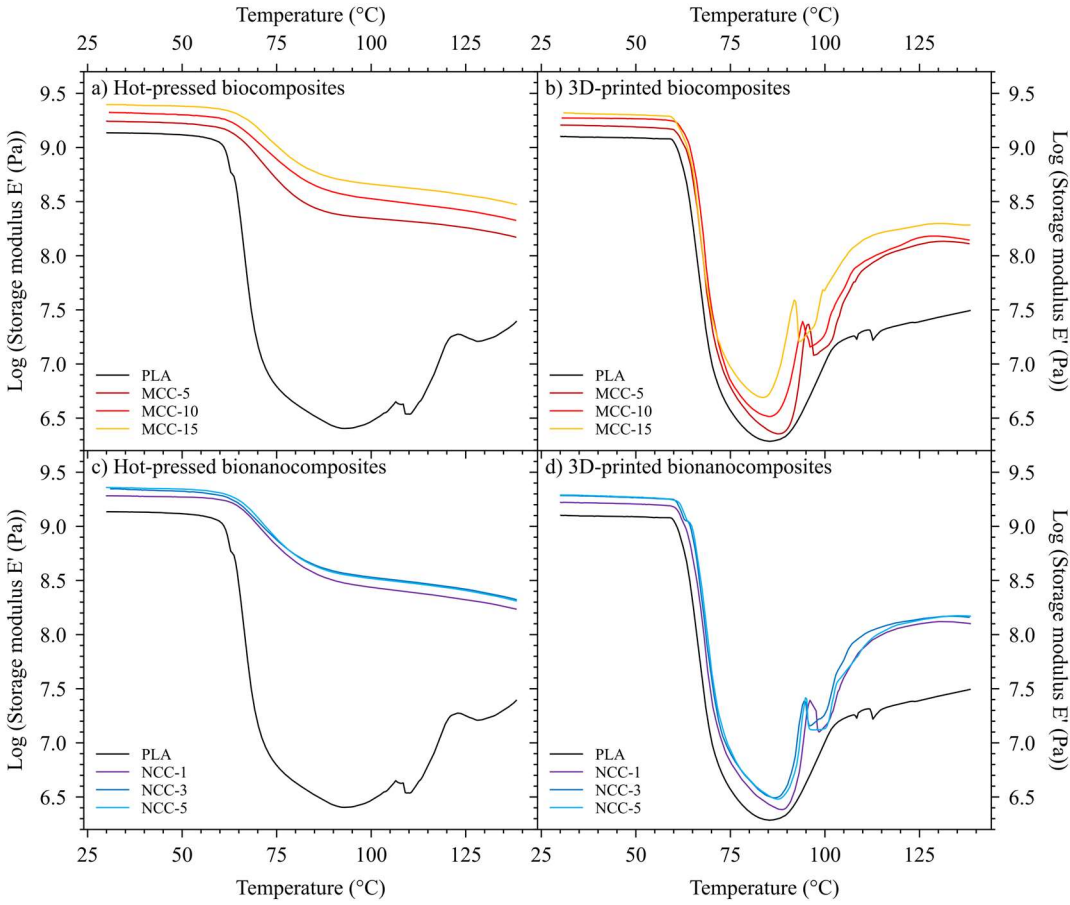


Figure 6.9 : Storage modulus E' versus temperature. NCC-3 and NCC-5 curves are overlapping

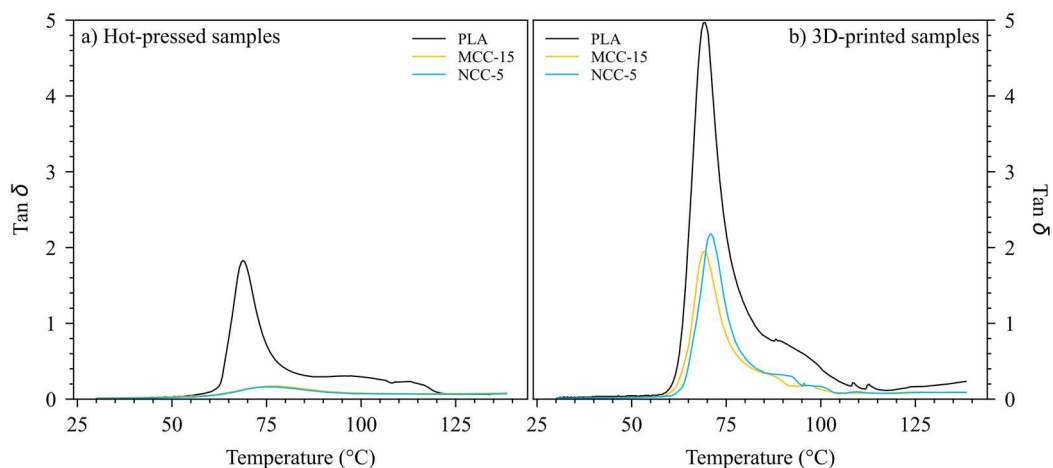


Figure 6.10 : Loss tangent $\tan \delta$ versus temperature

However, the 3D printing process gave weaker storage modulus than for hot-pressed. At 30 °C, 3D-printed MCC-15 presented a decrease of E' by 10 %, from 2,28 to 2,09 GPa compared to the hot-pressed MCC-15. The observed property reduction can also be attributed to the addition of defects due to the 3D printing processing, as shown in **Table 6.6**. The graphs showed that while crystallinity was around 20 % for 3D-printed biocomposites and bionanocomposites, the crystallinity was insufficient to compensate the mechanical properties lost in the rubbery state. Despite the reduction in mechanical performance due to the 3D printing process, the 3D-printed MCC-15 and NCC-3 exhibited better properties than hot-pressed neat PLA. These results showed that although the use of silanized fillers has increased the mechanical performance of 3D-printed PLA, the process used was still imperfect and will probably require post-curing treatment to fully exploit the material's increased rigidity and to replace PP in electrical insulation applications.

6.2.6. Conclusion

The proposed study investigated the dielectric and viscoelastic performances of cellulose-based materials produced by 3D printing process. Biocomposites based on microcrystalline cellulose and bionanocomposites based on nanocrystalline cellulose with different W_{MCC} and W_{NCC} were produced and tested with broadband dielectric spectroscopy (BDS), dynamic mechanical analysis (DMA), and dynamic rheology. Samples using a conventional processing method were also included to study the effect

of 3D printing itself. A nucleation effect was noted with the incorporation of cellulose fillers. This increasing crystallinity enhanced mechanical properties in the rubbery state of the hot-pressed reference specimens. Moreover, the addition of fillers both increased the viscoelastic and dielectric properties of the PLA. The increased dielectric properties can be associated with the polarity of the used fillers, and the increased mechanical properties with the presence of the stiff filler and the good filler:matrix interface. Although the tested properties were superior for MCC-15, the enhancement potential was greater for NCC fillers, due to the latter's higher specific surface area available. The 3D printing process showed lower dielectric properties than the reference process, conferring a better suitability for electrical insulation applications. This increased insulating power was associated with the presence of internal voids induced by the processing. Although the internal voids reduced the mechanical properties of the materials, 3D-printed MCC-15 and NCC-3 showed improved mechanical properties compared with hot-pressed PLA, with dielectric properties suitable for electrical insulation. The rheological results also highlighted the limited impact of filler content on MCC-based biocomposites and NCC-based bionanocomposites viscosity, suggesting that it would be possible to increase the filler content, or switching to a cellulose filler with a higher L:D ratio to further improve mechanical properties. These observations demonstrated the potential of the presented materials in this paper as a viable alternative to electrical insulating synthetic materials such as PP. Furthermore, to improve the mechanical strength of PLA in its rubbery state, a post-crystallization process might be considered.

6.3. Optimizing the dielectric and mechanical performance of 3D-printed cellulose-based biocomposites and bionanocomposites through factorial design

Morgan Lecoublet^{1,2}, Mohamed Ragoubi¹, Nathalie Leblanc¹ and Ahmed Koubaa²

¹ UniLaSalle, Unité de Recherche Transformations et Agro-Ressources (ULR 7519 UniLaSalle -Université d'Artois), Mont-Saint-Aignan, France

² UQAT, Campus de Rouyn-Noranda, 445, boul. de l'Université, Rouyn-Noranda, QC J9X 5E4, Canada

6.3.1. Abstract

Materials for low-k applications need to be re-engineered to achieve sustainable development. To address this challenge, the proposed study focused on the dielectric and mechanical optimization of 3D-printed cellulose-based composites for low-k applications. Two different fillers, crystalline microcellulose and crystalline nanocellulose, were used to create biocomposites and bionanocomposites respectively, blended into a polylactic acid (PLA) matrix. The effects of infill ratio, printing temperature and filler content on dielectric constant, alternative current electrical conductivity, and tensile and flexural static mechanics were measured using an incomplete L9 (3³) factorial design. The findings showed that the infill ratio was the most significant factor influencing the properties tested, directly attributable to the increase in material available for polarization and mechanical performance. The second most influential factor was W_f , increasing the polarity of the tested composites and decreasing the toughness of biocomposites and bionanocomposites by adding stress concentration area. Printing temperature had no significant effect. Results for biocomposites at 50 % infill ratio, 200 °C printing temperature and a $W_{MCC} = 15$ % gave a 60 % higher tensile-mode stiffness than neat PLA printed under the same conditions, while exhibiting lower dielectric properties than neat PLA printed with a 100 % infill ratio. These results pave the way for new lightweight materials for electrical insulation.

6.3.2. Résumé en français

Il devient nécessaire de repenser les matériaux pour les applications à faible constante diélectrique afin de les inscrire dans une perspective de développement durable. Pour

répondre à cette demande, l'étude proposée s'est concentrée sur l'optimisation diélectrique et mécanique des composites à base de cellulose imprimée en 3D pour des applications à faible constante diélectrique. Deux charges différentes, la microcellulose cristalline et la nanocellulose cristalline, ont été utilisées pour respectivement créer des biocomposites et des bionanocomposites, mélangés à une matrice d'acide polylactique (PLA). Les effets du taux de remplissage, de la température d'impression et de la teneur en charge sur la constante diélectrique, la conductivité électrique en courant alternatif et la mécanique statique en traction/flexion ont été mesurés à l'aide d'un plan factoriel incomplet L9 (3³). Les résultats ont montré que le taux de remplissage était le facteur le plus significatif influençant les propriétés testées, directement attribuable à l'augmentation de la quantité de matière disponible pour la polarisation et le comportement mécanique. Le deuxième facteur le plus significatif fut le W_f , augmentant la polarité des composites et diminuant la ténacité des biocomposites et des bionanocomposites en ajoutant une zone de concentration des contraintes. La température n'a pas eu d'effet significatif. Les résultats pour les biocomposites avec un taux de remplissage de 50 %, une température d'impression de 200 °C et une teneur en charge de MCC de 15 % ont donné une rigidité en traction supérieure de 60 % à celle du PLA pur imprimé dans les mêmes conditions, tout en présentant des propriétés diélectriques inférieures à celles du PLA pur imprimé avec un taux de remplissage de 100 %. Ces résultats ouvrent la voie à de nouveaux matériaux légers pour l'isolation électrique.

6.3.3. Introduction

The development of new materials for low-k dielectric applications is a key area research nowadays. The worldwide electronic materials market in 2022 has been estimated at USD 65,7 billion, and increasing by 6 % over the next 5 years (TechSci Research, 2023). The issues of recycling, limiting fossil resources and sustainable development require the replacement of conventional polymers such as polyethylene and propylene. Biobased polymers are one of the most promising options, however, a number of limitations need to be considered to ensure their industrial applications. These new materials have lower dielectric performance than their synthetic counterparts. Nakatsuka (2011) reported that the PLA had a 60 % higher permittivity compared to polyethylene. Moreover, Hegde et al. (2015) also noted that the PLA had a higher electrical conductivity than PP. To help promoting these materials, it is important to either find methods to improve their electrical

insulating properties or to confer them new properties, such as enhanced mechanical performance.

3D printing is a new processing technology that is potentially very well suited to rethinking the design of products. Unlike conventional processing technologies such as injection molding, it allows the control of the internal design of products. This technology involves the extrusion of molten plastics through a moving nozzle to produce solid parts according to a computer-assisted design (CAD) drawing. This technology has shown promising results in the field of electrical insulating applications. Barbosa et al. (2018) manufactured an electrical insulator for the development of a new generation of smart grid electrical insulator. They obtained 3D-printed electrical insulators capable of withstanding an electrical tension of 35 kV, validating their use for 13,8 kV voltage applications. Li et al. (2018) characterized the dielectric performances 3D-printed PLA parts. At 50 Hz and room temperature, PLA showed a dielectric constant of 3,25 and an electrical conductivity (σ_{DC}) of $2 \cdot 10^{-16} \text{ S} \cdot \text{cm}^{-1}$. As it exhibited a dielectric strength (E_{BR}) of $30 \text{ kV} \cdot \text{mm}^{-1}$, 3D-printed PLA was acceptable for a low voltage level system, according to the authors. This technology can control the quantity of material inside the piece (infill ratio) as well as the printing temperature through which the material is melted (printing temperature). According to Yang et al. (2019), electrical conductivity was proportionally linked to the printing temperature. An increase in printing temperature will promote interfacial adhesion of the layers, which will increase the layer bonding quality and thus promote the electron flow. Regarding the dielectric constant, Kuzmanić et al. (2023) demonstrated that a direct correlation between dielectric constant and infill ratio for PLA specimens existed. By varying the infill ratio from 100 to 33 %, they reduced the dielectric constant of PLA from 3,0 to 2,2 using a square-shaped infill pattern. Moreover, Zhang et al. (2016) have shown that it is possible to adjust the dielectric constant of 3D-printed PLA parts by fine-tuning the infill ratio to produce Fresnel lenses. But reducing the infill ratio leads to reduced mechanical properties, as the literature has broadly shown (Akhoundi and Behraves, 2019; Alafaghani et al., 2017; Öteyaka et al., 2021; Samykano, 2021). To counterbalance this effect, it is possible to insert fillers that improve mechanical properties, such as cellulose fillers, to create biocomposites. Adding 15 % of microcrystalline cellulose by weight into a PLA matrix can improve its Young's modulus from 3,6 to 4,4 GPa (Mathew et al., 2005). However, cellulose filler has been reported in

the literature to increase both the dielectric constant and conductivity of biobased polymers by adding more polar components than the matrix (Badia et al., 2017; Khouaja et al., 2021; Larguech et al., 2021).

The proposed study aims to understand how the design of biocomposites can influence both their dielectric and mechanical properties. The cellulose-based fillers chosen for the study are microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) to maintain the logic of 100 % compostable materials. PLA was chosen as the matrix due to its good availability and printability. To study the combined effect of filler content, printing temperature and infill ratio, an incomplete L9 (3^3) factorial experimental design was chosen. This study will investigate the potential of using 100% plant-based materials for 3D printing and electrical insulation, which to our knowledge has not yet been performed yet.

6.3.4. Materials and methods

6.3.4.a. Raw materials

The used PLA was a PLI-005, supplied by Natureplast (Mondeville, FRA), with a given MFI at 25-35 g·10 min⁻¹ (ISO 1133 @ 190 °C). Microcrystalline and nanocrystalline cellulose (MCC and NCC respectively) were used to reinforce the PLA. MCC was supplied by J. Rettenmaier (Fosston, MN, USA), obtained from bleached kraft pulp and NCC (DextraCel Nano HP) was supplied by Anomera (Montreal, QC, CAN).

6.3.4.b. Filler silanization and masterbatch processing

An MCC and NCC silanization step was performed according to the protocol used by Dammak (2022). The fillers were then washed to remove the remnants of the reaction and dried at 60 °C during 24 h to remove the moisture. Infrared results confirmed the presence of Si-O-C binding on the fillers surfaces, and therefore the presence of compatibilizer. TGA results of compatibilized fillers presented a thermal stability increase compared to the non-compatibilized fillers. The compatibilized MCC had a median and mean length of 34,1 and 51,9 μm respectively, and a median and mean width of 16,6 and 22,9 μm respectively.

A melt-based masterbatch intermediate step was carried out for the NCC-based composites and achieved on a Haake Minilab II (Thermo Scientific, Massachusetts, USA). This microcompounder operated by batch extrusion of 5 g of PLA:NCC blend. The PLA and NCC were conditioned at 60 °C until the moisture content of the components fell below 1 %. The masterbatch was prepared with a $W_{NCC} = 20 \%$, then melted with a screw speed of 70 RPM at 180 °C for 1 minute. Once obtained, the extrudates were finally granulated.

6.3.4.c. *Extrusion processing*

The extrusion step was made by The Coalia company (Thetford Mines, QC, CAN) with a twin-screw extruder, a temperature of 190 °C and a screw speed between 70 and 100 RPM. Die pressure was measured between 22 and 24 bars. **Table 6.7** shows the obtained composites. The maximal MCC and NCC content has been fixed at 15 % and 5 % respectively, according to previous laboratory results. Once extruded, the extrudates were pelletized and oven-dried at 60 °C to remove the remaining moisture.

Table 6.7 : Produced composites by extrusion

	PLA (g)	MCC (g)	Masterbatch (g) ($W_{NCC} = 20 \%$)	W_{MCC} (%)	W_{NCC} (%)
PLA	1200	0	0	0	0
MCC-5	950	50	0	5	0
MCC-10	900	100	0	10	0
MCC-15	850	150	0	15	0
NCC-1	950	0	50	0	1
NCC-3	850	0	150	0	3
NCC-5	750	0	250	0	5

6.3.4.d. *3D-printing processing*

To obtain the 3D printing filaments, a 3DEVO filament maker (3DEVO, Utrecht, NLD) was used with a temperature profile of 170-185-185-180 °C, a screw speed of 3,5 RPM and a cooling power of 40 %. A CR-10 Max (Crealitty, Shenzhen, CHN) 3D-printer was employed. The filaments were oven-dried at 60 °C just before the printing use to remove any traces of moisture. **Table 6.8** presents the used parameters for the 3D printing. These parameters were chosen as they provided the best compromise for all the different

conditions. Neat PLA posed no printing problems, but the bed had to be sprayed with lacquer to improve adhesion and prevent delamination during printing of the high-filled biocomposites.

Table 6.8 : 3D printing parameters

Nozzle temperature (°C)	190-210
Nozzle diameter (mm)	0,8
Nozzle speed (mm·s ⁻¹)	40
Bed temperature (°C)	60
Sample thickness (mm)	3,2-4
Layer thickness (mm)	0,4
Infill ratio (%)	50-100
Infill pattern	± 45°

6.3.4.e. *Application of factorial design*

The factorial design presented in **Table 6.9** was employed for the conception of cellulose-based composites.

Table 6.9 : Configuration of the used factorial design

Condition	Composite	Factor a W _f (%)	Factor b Infill ratio (%)	Factor c T _{printing} (°C)
M1	MCC-5	5	50	190
M2	MCC-5	5	75	210
M3	MCC-5	5	100	200
M4	MCC-10	10	50	210
M5	MCC-10	10	75	200
M6	MCC-10	10	100	190
M7	MCC-15	15	50	200
M8	MCC-15	15	75	190
M9	MCC-15	15	100	210
N1	NCC-1	1	50	190
N2	NCC-1	1	75	210
N3	NCC-1	1	100	200
N4	NCC-3	3	50	210
N5	NCC-3	3	75	200
N6	NCC-3	3	100	190
N7	NCC-5	5	50	200
N8	NCC-5	5	75	190
N9	NCC-5	5	100	210

The filler content (W_f) and infill ratio were chosen as the first and second factors. The minimum infill ratio was set at 50 % to avoid the collapsing phenomenon due to the rather

important MFI of the used PLA. The third factor chosen was the printing temperature T_{printing} . The lowest and highest temperatures were set according to the printability range for which all composites and neat PLA could be correctly printed. These temperatures were found at 190 °C and 210 °C respectively. The **Figure 6.11** presents the different conditions produced for flexural tests. Neat PLA specimens were added to these conditions to study the effect of infill ratio and T_{printing} on the neat matrix scale and resumed in **Table 6.10**. All samples were stored in a desiccator before being characterized.

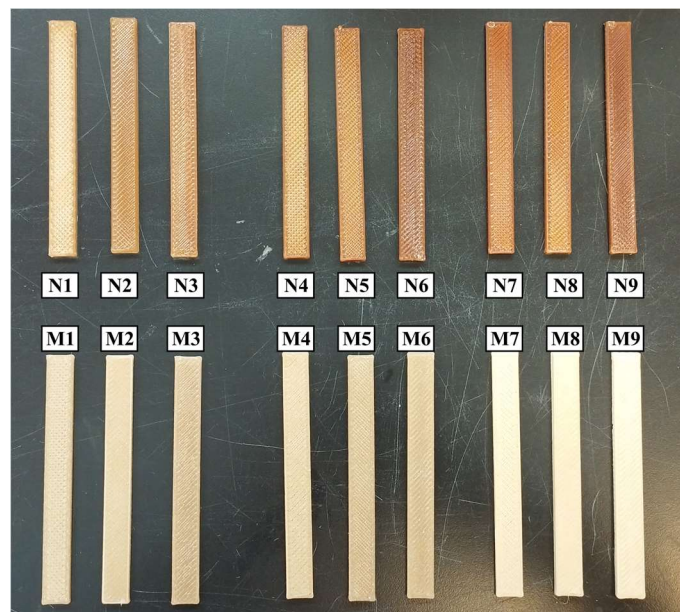


Figure 6.11 : Produced conditions for the flexural tests

Table 6.10 : Configuration of the PLA specimens

Condition	Infill ratio (%)	T_{printing} (°C)
PLA-0	50	200
PLA-1	75	200
PLA-2	100	190
PLA-3	100	200
PLA-4	100	210

6.3.4.f. *Methods used*

- *Broadband Dielectric Spectroscopy (BDS) analysis*

BDS analyses were carried out with a high-frequency dielectric spectrometer Keysight E4991A (Agilent Technologies, Santa Clara, USA). The frequency range of the used high-frequency BDS was 1 MHz-1 GHz. Analyses for both conditions were performed on 10*4 mm disks, at 20 °C. 5 samples per conditions were tested.

- *Mechanical analysis*

Tensile analyses were performed on a universal test machine Zwick Z020 (Zwick Roell Group, Ulm, DEU) according to the ASTM D638 Type 1 standard, equipped with a 20 kN load cell and with a crosshead speed of 2 mm·min⁻¹. The elongation of the sample was monitored with a Zwick Roell extensometer. 3 different specimens per condition was tested at room temperature.

3-point bending flexural analyses were also performed on a Zwick Z020 universal test machine (Zwick Roell Group, Ulm, DEU) according to the ASTM D790 standard, equipped with a 20 kN load cell and a crosshead speed of 2 mm·min⁻¹. To comply with ASTM D790 standard, the gap between the two supports was set at 64 mm. A total of 3 specimens per condition was tested at room temperature. The thickness of the tensile and flexural specimens was set at 4 mm based on the equipment available in the laboratory.

- *Impact analysis*

Impact tests were performed on a Zwick IZOD (Zwick Roell Group, Ulm, DEU) with the ASTM D256 standard. For the owned test equipment, the impact arm had an initial energy of 2,75 J. The impact resistance of the specimen is then expressed according to **Équation 23**. A total of 10 specimens for each condition was tested at room temperature. The width of the specimens was set at 10 mm, based on the equipment available in the laboratory.

6.3.5. Results and discussions

6.3.5.a. Influence of infill ratio and printing temperature on 3D-printed PLA.

A preliminary study was carried out on 3D-printed PLA to examine the influence of printing temperature and infill ratio used for the factorial design. **Figure 6.12** shows the influence of T_{printing} and the infill ratio on dielectric properties.

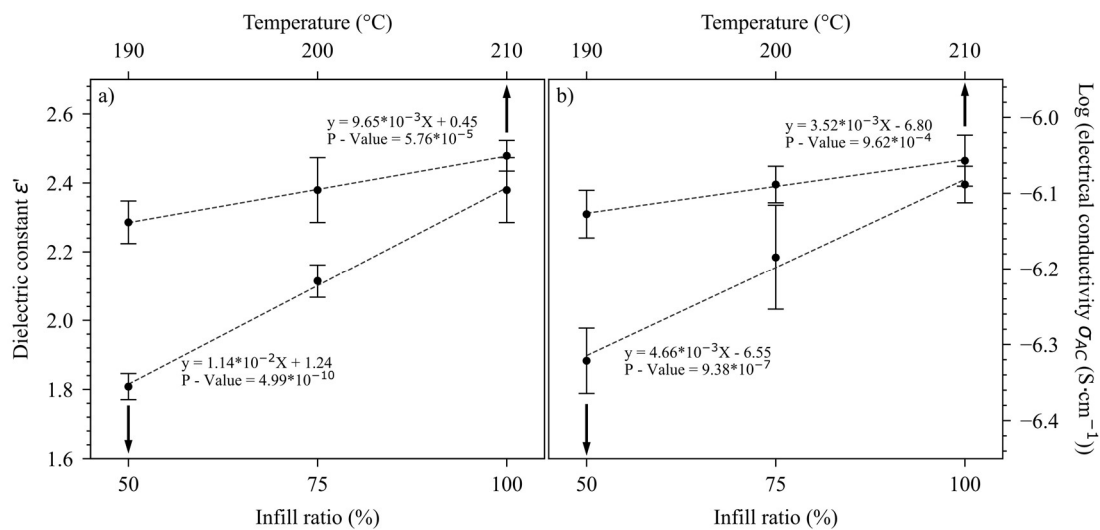


Figure 6.12 : Influence of infill ratio and printing temperature on a) dielectric constant ϵ' , b) log (electrical conductivity σ_{AC})

For all conditions, the influence of T_{printing} and infill ratio were significant on the dielectric constant and electrical conductivity. The measured behaviors were linear, with an excellent correlation factor. The positive effect of the infill ratio on the dielectric constant has already been noted in the literature (Kuzmanić et al., 2023; Zhang et al., 2016). Zhang et al. (2016) also demonstrated a linear variation of the dielectric constant with the infill ratio. The addition of voids through porosity decreased the polarizability potential of the material, as air has a permittivity ~ 1 compared to the permittivity of PLA (~ 3) (Badia et al., 2017; Kuzmanić et al., 2023). In addition, the effect of printing temperature could be linked to a better print quality, reducing defects and porosity. Concerning the influence on electrical conductivity, T_{printing} and infill ratio also had a positive influence. It has already been noted that increasing the printing temperature reduced the gap between the printed filaments and consequently the porosity, and

increased the interface quality (Patibandla and Mian, 2021). This improved quality favored the passage of electrons by reducing the probability of boundary area defects (Yang et al., 2019). The increase in electrical conductivity with infill ratio was also observed by Pentek et al. (2020). It is also worth noting that for PLA, dielectric properties were more sensitive to the infill ratio than to temperature, even if the effect on the latter is not negligible.

Figure 6.13 shows the influence of printing temperature and infill ratio on mechanical properties of 3D-printed PLA.

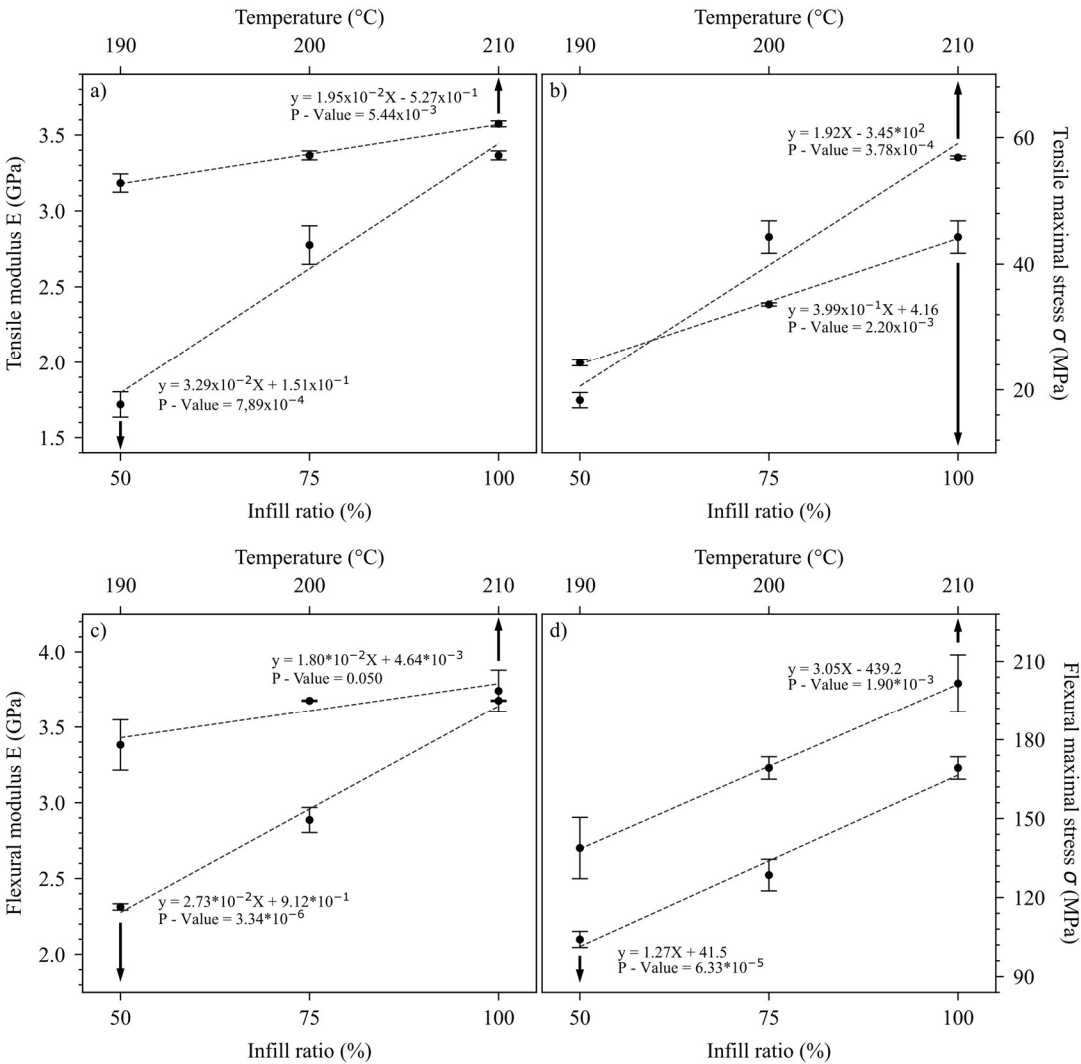


Figure 6.13 : Influence of infill ratio and printing temperature on a) tensile elastic modulus, b) tensile maximal stress, c) flexural elastic modulus, d) flexural maximal stress

For all conditions, the influence of T_{printing} and infill ratio were also significant. The measured behaviors were also linear, with a good correlation factor. The modulus decrease in tensile and flexural modes with a decreasing infill ratio has been reviewed in the literature (Fernandez-Vicente et al., 2016; Öteyaka et al., 2021). For maximal stress, Gunasekaran et al. (2021) also found an increase of the maximal stress in the traction and flexural mode with an increasing infill ratio. According to Samykano (2021), a lower infill ratio decreased the material's availability to withstand the internal mechanical forces, resulting in a decrease of the maximum stress. Concerning the printing temperature influence, as explained above, T_{printing} played a positive role in the quality of the interface, and therefore on its ability to withstand stress.

Figure 6.14 shows the influence of printing temperature and infill ratio regarding impact strength results. As impact strength represents the ability of a material to absorb energy through mechanical shocks, the noted behavior was expected given the previous results that the infill ratio and T_{printing} had positive impacts on its ability to withstand mechanical stress. Dharmalingam et al. (2022) also observed a near halving of the impact strength of 3D-printed PLA when the infill ratio was reduced from 100 % to 50 %, similar to our findings.

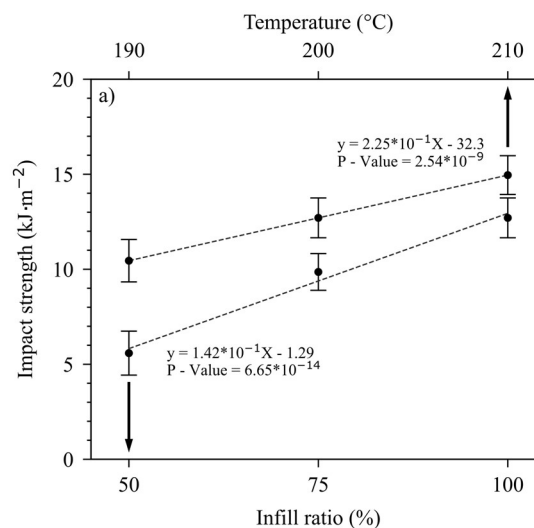


Figure 6.14 : Influence of infill ratio and printing temperature on impact strength

6.3.5.b. Dielectric properties

Figure 6.15 shows the dielectric properties obtained via BDS at room temperature from the biocomposites and bionanocomposites, using different factors (W_f , infill ratio, and T_{printing}).

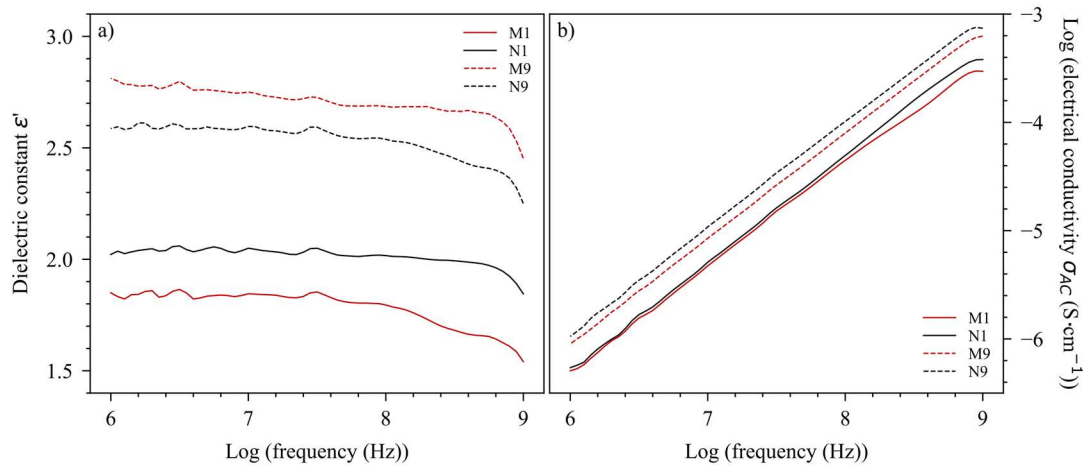


Figure 6.15 : Dielectric properties versus frequency of biocomposites and bionanocomposites, a) dielectric constant ϵ' , b) log (electrical conductivity σ_{AC})

Measured at 1 MHz, the lowest dielectric constant was obtained for M1 at 1,85, corresponding to a $W_{MCC} = 5\%$, an infill ratio = 50 %, and a $T_{\text{printing}} = 190\text{ }^{\circ}\text{C}$. The highest dielectric constant was obtained for M9 at 2,81, corresponding to a $W_{MCC} = 15\%$, an infill ratio = 100 %, and a $T_{\text{printing}} = 210\text{ }^{\circ}\text{C}$. The decrease in ϵ' with the frequency was widely reported in the literature (Badia et al., 2017; Khouaja et al., 2021; Larguech et al., 2021). A reduction in the molecular mobility of polar groups was observed when a high-frequency electric field was applied, reducing the polarization potential of the material. Under equivalent conditions and at a low filler content, the NCC-based bionanocomposites showed a dielectric constant on average 15 % higher than the MCC-based biocomposites. The higher dielectric constant of the NCC-based bionanocomposites resulted from a significantly higher filler specific surface area than MCC, providing more silane and hydroxyl functions on the filler surface, and therefore increasing the polarity potential of the composite (Yakubu et al., 2020). However, at high filler content, the biocomposite exhibited the highest dielectric constant. Preliminary results showed the presence of aggregates at 5 % NCC by mass (**Figure 6.16**).

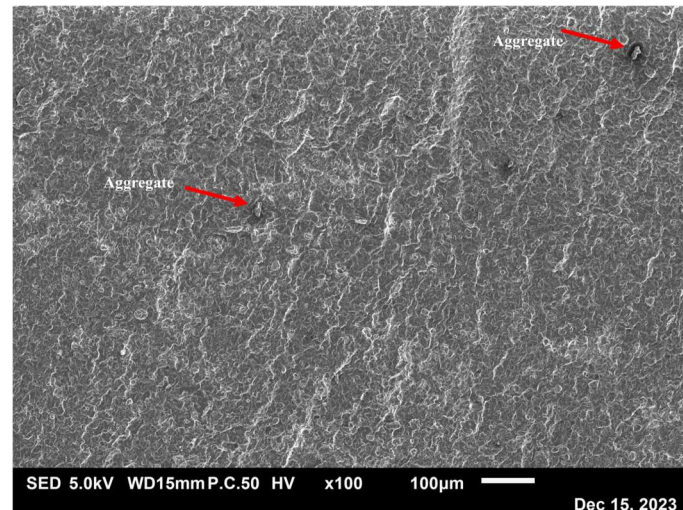


Figure 6.16 : SEM picture of aggregates evidence in PLA at a $W_{NCC} = 5\%$

These aggregates reduced the available specific surface area of the fillers, limiting its permittivity potential. **Figure 6.15b)** indicates that measured at 1 MHz, the lowest electrical conductivity was obtained for M1 at $5,1 \cdot 10^{-7} \text{ S} \cdot \text{cm}^{-1}$. The highest electrical conductivity was obtained for N9 at $1,1 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$, corresponding to a $W_{NCC} = 5\%$, an infill ratio = 100 %, and a $T_{\text{printing}} = 210 \text{ }^\circ\text{C}$. All the conditions tested showed a linear increase in electrical conductivity with frequency, which would be the evidence of an electrical insulating behavior (Wu et al., 2019). Despite the presence of mentioned aggregates, the bionanocomposites showed greater electrical conductivity, probably due to better diffusion of charges, which could favor the conductivity inside the material (Salaeh et al., 2020).

Table 6.11 shows the ANOVA results of the factorial design applied to dielectric properties.

Table 6.11 : ANOVA results with F values for dielectric results. * significant at 0,05;

** significant at 0,01; *** significant at 0,001; n.s. not significant

	MCC-based biocomposites		NCC-based bionanocomposites	
	Dielectric constant ϵ'	Electrical conductivity σ_{AC}	Dielectric constant ϵ'	Electrical conductivity σ_{AC}
W_f	5,2 **	2,9 n.s.	3,8 *	5,8 **
Infill ratio	46,5 ***	33,1 ***	39,9 ***	34,2 ***
T_{printing}	1,8 n.s.	3,2 *	1,5 n.s.	1,6 n.s.

The infill ratio appeared to be the most influential factor on the dielectric properties. For all conditions, the P-Value was below 0,001 for both dielectric constant and electrical conductivity. These results were in agreement with preliminary findings from PLA samples. The W_f factor also had an overall positive impact on ϵ' . Badia et al. (2017) pointed out that cellulosic fillers were more polar than the PLA matrix, increasing the permittivity of the resulting composites. Considering the filler type, NCC was found to exert less influence on the dielectric constant than MCC, contrary to the expected result. For equivalent mass, NCC had a much greater specific surface area than MCC. A greater specific surface area logically provides more hydroxyl and silane groups. This reduced value could be due to aggregation phenomena at high filler content, reducing the polarization potential. The W_f factor was significant for NCC but not significant for MCC regarding σ_{AC} . This could be due to the charge size. It has been shown that the electrical conductivity of an insulating material can be improved if polar charges are well distributed in the matrix (Salaeh et al., 2020). It can facilitate the flow of electrons induced by the phenomenon of carrier hopping, without however forming conductive bridges that can alter the material's electrical insulation properties. Finally, the printing temperature had little influence on dielectric properties. The positive effect observed for PLA specimens may be overshadowed by the overwhelming effect of the infill ratio.

6.3.5.c. *Mechanical properties*

Figure 6.17 shows the tensile and flexural mechanical properties of biocomposites and bionanocomposites using different factors. The same overall trends were observed for both tensile and flexural results. All conditions showed an increase in mechanical stress with the imposed elongation applied to the specimen. Tensile tests showed a brittle fracture with very little plasticization, in contrast to flexural tests, which showed a plateau of maximal stress followed by a decrease in flexural stress, a typical behavior of 3-point bending tests (Akhoundi and Behraves, 2019; Öteyaka et al., 2021). In addition, the maximum stress and elongation in flexural tests were greater than in tensile tests. The difference in tensile and flexural strength values could be attributed to the stress orientation in both tests: stretching in the tensile test and bending in the flexure test. At low printing temperatures, W_f and infill ratio, the influence of the filler nature does not seem to be significant, with a slight stiffening effect with the use of MCC.

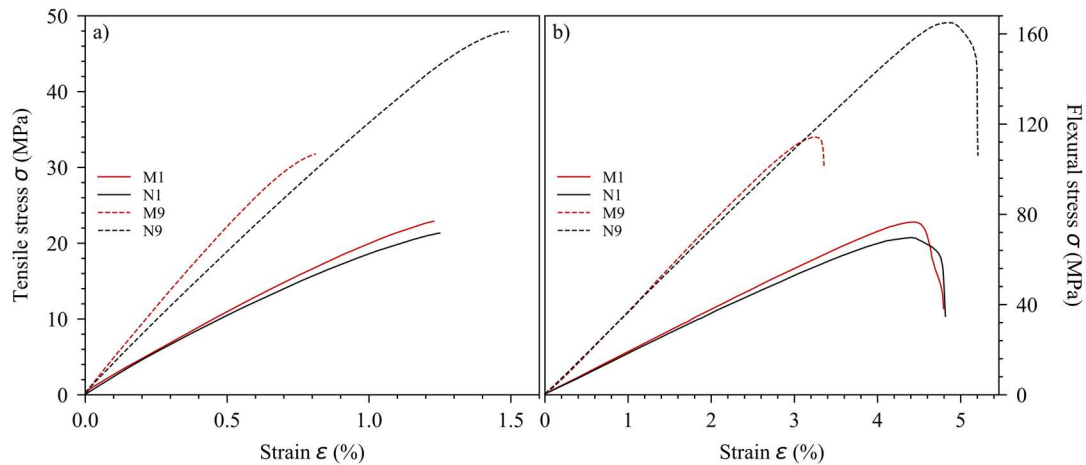


Figure 6.17 : Stress-strain curves of biocomposites and bionanocomposites in a) tensile mode, b) 3-point bending flexural mode

Although the addition of cellulosic fillers reduced the maximum stress of the composites compared with neat PLA, the N9s showed much higher maximum stress than the M9s in both test modes. The presence of MCC into PLA created microscopic stress concentration areas, resulting in lower mechanical resistance capacity (Dammak, 2022). Moreover, filler size also played a role in a material's ability to transfer mechanical stress. Yakubu et al. (2020) noted that smaller fillers were better dispersed in the matrix, improving the homogeneity of composites and thus increasing the maximal tensile and flexural stress.

Table 6.12 shows the ANOVA results of the factorial design applied to mechanical properties.

Table 6.12 : ANOVA results with F values for mechanical results. * significant at 0,05; ** significant at 0,01; *** significant at 0,001; n.s. not significant

		MCC			NCC		
		Elastic modulus	Maximal stress	Elongation at max stress	Elastic modulus	Maximal stress	Elongation at max stress
Tensile results	W_f	0,3 n.s	7,4 **	79 ***	0,5 n.s	0,6 n.s	0,7 n.s
	Infill ratio	110 ***	9,3 ***	0,1 n.s	87 ***	140 ***	3,2 n.s
	T_{printing}	0,7 n.s	1,7 n.s	0,9 n.s	0,4 n.s	0,1 n.s	0,3 n.s
Flexural results	W_f	1,4 n.s	0,9 n.s	39,3 ***	2,5 n.s.	2,2 n.s.	2,4 n.s.
	Infill ratio	31,8 ***	24,2 ***	0,2 n.s	18,2 ***	22,1 ***	4,4 *
	T_{printing}	2,4 n.s	2,8 n.s	0,2 n.s	3,1 n.s.	2,3 n.s.	3,8 *

The infill ratio had also the greatest impact of all the factors tested, with a strong effect on mechanical moduli and maximum stress. This positive influence is well documented in the literature. For Alafaghani et al. (2017), a higher infill ratio improved the mechanical properties by providing more materials that can undergo the applied mechanical loads. Moreover, Samykano (2021) also found that a specimen with a higher infill ratio was mechanically stronger, resulting in a higher maximum stress capacity. However, our infill ratio influence on elongation at maximal stress was not significant. The W_f also has a significant influence on the MCC-based biocomposites ability to withstand mechanical stress, reducing the maximal stress and elongation at maximal stress by adding defects and stress concentration areas. Printing temperature presented no significant impact. The behavior was slightly different for NCC-based bionanocomposites. Although the effect of the infill ratio was just as noticeable as for MCC, the W_f had no negative effect on maximal stress and elongation. T_{printing} had a slight positive on the elongation maximal stress. The results show that the reinforcing effect of cellulose fillers was minimal, probably overshadowed by the infill ratio factor.

Finally, **Table 6.13** presents the ANOVA results of the factorial design applied to impact strength. These results were very similar to the maximal stress results as expected. According to the previous results, the effect of infill ratio was very predominant. In addition, a highly significant effect of W_f was noted for MCC-based biocomposites.

Table 6.13 : ANOVA results with F values for impact strength. * significant at 0,05; ** significant at 0,01; *** significant at 0,001; n.s. not significant

	MCC	NCC
	Impact strength	Impact strength
W_f	8,1 ***	1,1 n.s.
Infill ratio	7,7 ***	261 ***
T_{printing}	2,4 n.s.	2,2 n.s.

6.3.5.d. *Discussions*

To compare the results of biocomposites with the neat PLA, **Table 6.14** shows a comparison between neat PLA, M7 and N7. The two latter were chosen because they provided a relevant comparison with PLA-0 and PLA-3, as they are printed at the same temperature. The M7 and N7 results were globally intermediate between the 50 % infill

ratio PLA (PLA-0) and the 100 % infill ratio PLA (PLA-3), although with a decrease in the tenacity of the composites. The lower values for NCC-based bionanocomposites could be linked to the aggregation phenomena mentioned above, limiting the reinforcing potential of NCC. Currently, M7s could be relevant for lightweight materials, with improved stiffness compared to 50 % infill PLA, while presenting a stronger electrical insulating property than neat PLA. These observations demonstrate not only the relevance of such materials, but also the need for further research to improve the mechanical properties of 3D-printed biocomposites for high-performance electrical insulation applications.

Table 6.14 : Comparative study of M7 and N7 composites with 3D-printed neat PLA

		PLA-0	PLA-3	M7	N7
Used parameters	W_f	-	-	15 % MCC	5 % NCC
	Infill ratio	50	100	50	50
	T_{printing}	200	200	200	200
BDS @ 1MHz	ϵ'	$1,81 \pm 0,04$	$2,38 \pm 0,09$	$2,19 \pm 0,05$	$2,20 \pm 0,03$
	$\text{Log}(\sigma_{AC} \cdot \text{cm}^{-1})$	$-6,32 \pm 0,04$	$-6,09 \pm 0,02$	$-6,19 \pm 0,04$	$-6,14 \pm 0,02$
Tensile	Modulus (GPa)	$1,72 \pm 0,08$	$3,37 \pm 0,03$	$2,73 \pm 0,06$	$1,88 \pm 0,09$
	Max stress (MPa)	$24,3 \pm 0,5$	$44,3 \pm 2,6$	$19 \pm 1,4$	$20,4 \pm 0,7$
	Elongation (%)	$1,97 \pm 0,08$	$1,45 \pm 0,08$	$0,76 \pm 0,01$	$1,29 \pm 0,1$
Flexural	Modulus (GPa)	$2,31 \pm 0,02$	$3,68 \pm 0,01$	$2,76 \pm 0,16$	$1,94 \pm 0,06$
	Max stress (MPa)	107 ± 3	171 ± 4	$75,7 \pm 3,2$	$72,7 \pm 2,8$
	Elongation (%)	$5,34 \pm 0,46$	$6,55 \pm 0,04$	$3,06 \pm 0,02$	$4,40 \pm 0,33$
Impact strength ($\text{kJ} \cdot \text{m}^{-2}$)		$5,59 \pm 1,16$	$12,7 \pm 1,1$	$3,83 \pm 1,06$	$6,63 \pm 0,99$

6.3.6. Conclusion

This study investigated the influence of infill ratio, filler content (W_f) and printing temperature (T_{printing}) on the dielectric and static mechanical properties of cellulose-based biocomposites and bionanocomposites obtained by 3D printing. The incomplete factorial design L9 (3^3) was chosen for the sample creation. A preliminary analysis of the influence of T_{printing} and infill ratio on neat 3D-printed PLA showed that such factors increased dielectric constant, electrical conductivity, impact strength, as well as the modulus, maximal stress and elongation at max stress in both tensile and flexural modes. Increasing the infill ratio increased the available material and therefore the associated physical quantities. The application of the factorial design showed that the infill ratio was the most influential factor of the three tested on both mechanical and dielectric properties,

reducing the tested quantities as expected. The W_f factor had a moderate effect, generally increasing the polarity of the samples by adding polar compounds and decreasing the toughness of biocomposites and bionanocomposites by adding stress concentration areas. The effect of temperature was negligible, indicating that this factor was marginal and masked by the other factors. The produced materials were finally compared with the neat PLA. The NCC results were mediocre at a filler content of 5 %, probably linked to the aggregation phenomena of nanofillers. To efficiently use NCC as a mechanical reinforcement, it may be necessary to opt for lower filler content, such as 3 % to fully exploit the potential of this reinforcement. However, the M7 biocomposite exhibited dielectric and mechanical results between PLA with a 50 % and 100 % infill ratio, paving the way for biobased materials combining good electrical insulation and mechanical properties, as well as being lightweight. To go further, it would be possible to improve the mechanical results of biocomposites by using other cellulose-based fillers such as kraft to increase the fillers' form factor. In addition, it would also be possible to increase the filler content, as conditions with high filler content did not show any nozzle clogging nor fluidity issues. These two perspectives would improve the material stiffness without altering too much the electrical insulating properties

6.4. Discussions et bilan du Chapitre 6

Les trois objectifs de ce chapitre ont pu être atteints avec succès. Un total de trois biocomposites à base de microcristaux de cellulose (MCC) ainsi que trois bionanocomposites à base de nanocristaux de cellulose (NCC) ont été produits par impression 3D, puis caractérisés. Premièrement, toutes les conditions ont été imprimées avec succès sans présenter de difficultés majeures. L'utilisation d'un PLA avec un haut MFI a été bénéfique, car les biocomposites avec 15 % de MCC en masse ont pu être imprimés correctement. Les seuls échecs d'impression ont été causés par la présence de rugosités sur les filaments à base de MCC. Ces rugosités n'arrivaient pas à passer le détecteur de filaments, démontrant l'importance de la qualité du filament et de l'étape de filamentage. Les bionanocomposites pour toutes les conditions ont parfaitement été imprimés, avec aucune présence de rugosité sur le filament. Les résultats rhéologiques ont confirmé que même si les ajouts de MCC et de NCC ont augmenté la viscosité complexe des composites, cette augmentation n'était que modérée et n'entravait pas l'imprimabilité des conditions.

L'effet des charges cellulosiques a été tout aussi positif sur la constante diélectrique et la conductivité électrique des échantillons produits. Ces charges étant plus polaires, cela a augmenté la capacité des matériaux à interagir avec le champ électrique appliqué. De plus, une légère augmentation du module de stockage avec la concentration des charges a été notée. La MCC et NCC ont joué le rôle de site de nucléation, augmentant drastiquement la rigidité des composites à l'état caoutchoutique par l'effet combiné du réseau cristallin et des renforts. Concernant le choix des charges, les biocomposites ont présenté les meilleurs modules de stockage, mais aussi les plus grandes constantes diélectriques et conductivité électrique. Comme attendu, à un trop grand taux de charge, la NCC s'est réorganisée en agrégats, limitant l'effet bénéfique de cette dernière. Comme observé dans le précédent chapitre, l'impression 3D a ajouté des vides internes, diminuant les propriétés mécaniques et augmentant le pouvoir isolant des échantillons 3D. Le MCC-15 et le NCC-3 imprimés en 3D ont montré des propriétés mécaniques améliorées par rapport au PLA thermocompressé, avec des propriétés diélectriques adaptées à l'isolation électrique.

L'utilisation du plan factoriel incomplet pour l'optimisation des propriétés diélectriques et mécaniques a été cependant donnée des résultats mitigés. Des trois paramètres testés (taux de remplissage, taux de charge et température d'impression), seul le taux de remplissage a montré un effet significatif sur à la fois les propriétés mécaniques et diélectriques. L'effet positif des charges sur les propriétés mécaniques statiques n'a pas pu être noté. De plus, la température d'impression n'a, contrairement aux résultats du PLA pur, pas présenté l'effet positif attendu. Le plan factoriel incomplet choisi a nécessité un compromis entre précision des résultats et rapidité d'exécution, ce qui peut expliquer cette observation. L'effet du taux de remplissage étant bien plus important que les autres, a pu noyer les autres facteurs les rendant imperceptibles. Néanmoins, le biocomposite M7 (soit la condition imprimée à 200 °C, avec un taux de remplissage de 50 % et un taux de MCC de 15 %) a présenté une rigidité 50 % plus importante que le PLA imprimé dans les mêmes conditions, tout en exhibant des propriétés d'isolation électrique améliorée comparé au PLA imprimé avec un taux de remplissage de 100 %. Les résultats diélectriques du M7 et du N7 sont comparables aux valeurs du PP données par la littérature, tout en présentant une rigidité mécanique supérieure (**Table 6.15**). Ces résultats démontrent la pertinence de tels matériaux pour remplacer le PP pour des applications en isolation électrique.

Table 6.15 : Étude comparative du biocomposite M7 ($W_{MCC} = 15\%$, taux de remplissage = 50 % and $T_{impression} = 200\text{ °C}$) et bionanocomposite N7 ($W_{MCC} = 5\%$, taux de remplissage = 50 % and $T_{impression} = 200\text{ °C}$) comparé aux valeurs de la littérature du PP

	M7	N7	PP	
ϵ' (@ 1 MHz)	$2,19 \pm 0,05$	$2,20 \pm 0,03$	2,0	(Uyor et al., 2022)
			1,79	(Erdönmez and Güven Özdemir, 2020)
			2,31	(Izci and Bowler, 2019)
$\text{Log}(\sigma_{AC} \text{ (S}\cdot\text{cm}^{-1} \text{ @ 1 MHz)})$	$-6,19 \pm 0,04$	$-6,14 \pm 0,02$	-6,3	(Erdönmez and Güven Özdemir, 2020)
			-7,1	(Islam et al., 2021)
E traction (GPa)	$2,73 \pm 0,06$	$1,88 \pm 0,09$	1,23	(Uyor et al., 2022)
			1,25	(Yeole et al., 2021)
			1,04	(Nurul and Mariatti, 2013)
E flexion (GPa)	$2,76 \pm 0,16$	$1,94 \pm 0,06$	0,81	(Yeole et al., 2021)
			1,07	(Liang et al., 2018)
			1,30	(Wang et al., 2021)

Ce chapitre a démontré que les charges cellulosiques permettaient d'améliorer légèrement les propriétés mécaniques du PLA imprimé en 3D, tout en gardant des propriétés

diélectriques similaires au PLA mis en œuvre de manière conventionnelle. Cela démontre aussi l'intérêt de tels matériaux pour des applications nécessitant des propriétés mécaniques plus élevées que pour les mélanges PLA:CA présentés précédemment. Il serait possible d'améliorer davantage les propriétés mécaniques en choisissant de nouvelles charges cellulosiques comme la fibre de pâte chimique Kraft, voire d'augmenter davantage le taux de charge grâce au choix initial de la matrice. En ce qui concerne l'utilisation de nanocharges, des travaux supplémentaires seraient nécessaires pour trouver le taux de charge optimal, mais les résultats présentés ici montrent que 3 % serait un bon compromis.

Conclusion Générale

Cette thèse s'intègre dans une logique de promotion de matériaux biosourcés dans le domaine diélectrique. Elle présente une étude avancée des propriétés multiphysiques, notamment diélectriques, des polymères biosourcés pour identifier les applications en domaine diélectrique envisageables pour de tels matériaux.

Une synthèse bibliographique a permis de comprendre ce qu'est la diélectricité, ainsi que les propriétés diélectriques des polymères biosourcés les plus communs en littérature. Les objectifs de cette partie furent aussi d'identifier les polymères biosourcés les plus pertinents pour une application en domaine diélectrique. Il s'est avéré que l'acide polylactique (PLA), le polyhydroxybutyrate-co-valérate (PHBV) et l'acétate de cellulose (CA) présentent des propriétés diélectriques similaires à certains polymères conventionnels comme le polyéthylène, le polypropylène et la résine époxy, des polymères déjà bien présents dans le domaine de l'isolation électrique. Il fut donc décidé d'orienter plus précisément le projet sur l'utilisation du PLA, PHBV et CA en isolation électrique pour proposer une alternative aux polymères conventionnels susmentionnés. De plus, la synthèse a aussi permis d'identifier trois différentes stratégies pour favoriser l'intégration des polymères biosourcés dans le domaine de l'isolation électrique. Ces trois stratégies sont la création de mélanges polymériques, l'utilisation de charges cellulosiques et l'utilisation de la technique de l'impression 3D comme procédé de fabrication. Ces stratégies sont donc retenues pour la suite du projet. Pour finir, différentes applications récentes proposées par différentes équipes de recherche ont été listées.

Le premier travail expérimental, proposé en **Chapitre 4**, fut de concevoir et caractériser les mélanges polymériques à base de PLA, PHBV et de CA. Les objectifs de ce chapitre furent de :

- Caractériser les propriétés diélectriques, mécaniques et viscoélastiques du PLA, PHBV et CA, ainsi que leurs mélanges binaires obtenus par thermocompression.
- Identifier les mélanges avec un potentiel fort pour une application future en impression 3D.

Les propriétés diélectriques du PLA, PHBV et CA sont en accord avec les valeurs de la littérature évoquées en **Chapitre 2**. Le PLA et PHBV possèdent une constante diélectrique et conductivité électrique plus faible que celle du CA, même si les valeurs de ce dernier sont toujours comparables avec les valeurs de la résine époxy, matériau courant en isolation électrique. Les groupes hydroxyles du CA ont cependant créé des liaisons hydrogène entre le PLA:CA et le PHBV:CA, phénomène bien mis en évidence avec les analyses FTIR et rhéologiques. De plus, le plastifiant contenu dans le CA a diminué linéairement toutes les températures des relaxations du PLA et du PHBV lorsqu'ils sont associés ensemble. Même si le PHBV présentait une bonne stabilité thermomécanique, il n'a pas été retenu pour l'étape d'impression 3D à cause de sa trop faible tenue à la température, comme démontré en analyse rhéologique, au profit du mélange PLA:CA. Ce mélange fut retenu pour l'étape d'impression 3D.

Le **Chapitre 5** prend la suite directe du **Chapitre 4** en proposant une étude sur les mélanges polymériques PLA:CA pour impression 3D. Les objectifs furent de :

- Étudier l'imprimabilité des mélanges PLA:CA et évaluer le potentiel du CA dans le domaine diélectrique par impression 3D.
- Étudier comment le CA influencera les propriétés diélectriques, mécaniques et viscoélastiques des mélanges PLA:CA.
- Optimiser les propriétés mécaniques et diélectriques de tels matériaux pour une application en isolation électrique par l'utilisation d'un plan d'expérience.

L'impression 3D a eu un effet positif sur les propriétés d'isolation électrique, mais aussi un effet négatif sur les propriétés mécaniques par ajout de porosité et d'interface entre les plans d'impression. Le CA a eu un effet positif sur la rigidité mécanique du PLA lorsque ce dernier est en état caoutchoutique, ce qui est non négligeable pour améliorer l'applicabilité du PLA pour le domaine de l'isolation électrique, où ces températures peuvent facilement être rencontrées. Grâce à l'application d'un plan de Taguchi, il a été possible d'obtenir des éprouvettes imprimées en 3D contenant 40 % de CA, tout en présentant des propriétés diélectriques et mécaniques équivalentes au PEBD. Cela

démontre à la fois la pertinence de l'impression 3D pour le domaine de l'isolation électrique, et cela rend de tels matériaux intéressants pour remplacer le PEBD pour des applications d'isolation électrique.

Pour finir, le second travail expérimental détaillé en **Chapitre 6** fut réservé à la conception et la caractérisation de biocomposites et bionanocomposites à base de cellulose pour impression 3D. Les objectifs furent de :

- Caractériser les propriétés diélectriques, mécaniques et viscoélastiques de biocomposites à base de MCC et bionanocomposites à base de NCC obtenues par impression 3D.
- Optimiser les propriétés mécaniques et diélectriques de tels matériaux pour une application en isolation électrique par l'utilisation d'un plan d'expérience.

L'ajout de charges cellulosiques, qu'elles soient de taille microscopique ou nanoscopique, a légèrement amélioré les propriétés mécaniques du PLA imprimé, mais a aussi diminué les propriétés d'isolation électrique de ce dernier par ajout de matériaux polaires. Cette diminution n'entrave cependant pas l'applicabilité du PLA en isolation électrique. De plus, un fort effet de nucléation a été observé avec l'ajout des charges, ce qui améliore davantage la stabilité des résultats diélectriques et mécaniques en fonction de la température en supprimant le phénomène de cristallisation froide. Grâce à l'application d'un plan factoriel, il a été possible de produire des biocomposites et bionanocomposites imprimés en 3D avec un taux de remplissage de 50 %, et présentant une rigidité supérieure au PP, tout en offrant des constantes diélectriques similaires à ces derniers. Cela démontre aussi la pertinence de l'impression 3D pour le domaine de l'isolation électrique, et de l'intérêt des charges cellulosiques pour améliorer la rigidité d'éprouvettes imprimées en 3D. Cela rend ces biocomposites et bionanocomposites pertinents pour remplacer le PP pour des applications d'isolation électrique.

Ce projet de thèse a donc ainsi permis d'étudier le potentiel des polymères biosourcés pour une utilisation en isolation électrique. Grâce à l'utilisation de différentes stratégies, des alternatives prometteuses au PP et au PEBD ont été proposées. Cela pourrait

permettre de remplacer ces matériaux pour des applications concrètes comme en blindage de transformateurs haute tension, emballage fonctionnalisé, isolateur électrique, composants électroniques, voire en PCB à basse température. Pour compléter les recherches menées, différentes pistes pourraient être envisageable :

- Des tests de rigidité diélectriques devront être réalisés afin de tester l'applicabilité des matériaux proposés soumis à hautes tensions électriques. De plus, des tests de vieillissement accélérés devront être menés pour attester de la tenue dans le temps des matériaux proposés.
- Pour les mélanges PLA:CA, un renforcement mécanique avec des charges cellulosiques permettrait d'atteindre des rigidités mécaniques similaires au PEHD, voire au PP, mais il convient de veiller tout particulièrement à ce que la viscosité de ces mélanges soit adéquate. Il serait aussi envisageable d'utiliser un CA avec un taux réduit de plastifiant, voire non plastifié pour pleinement bénéficier de l'effet isolant du PLA et de l'effet renforçant du CA, avec les mêmes problématiques de viscosité à surveiller.
- Pour l'utilisation de charges cellulosiques, nous avons trouvé que le taux de charge optimal de NCC devrait se trouver entre 1 et 3 %, il est donc nécessaire de continuer ces travaux pour trouver ce taux optimal. De plus, il serait possible d'améliorer davantage les propriétés mécaniques en utilisant des fibres à meilleur rendement mécanique comme la fibre de pâte chimique Kraft au lieu de la MCC, voire d'augmenter davantage le taux de charge utilisé.

Annexes

Annexe 1 : Chapitre 3 - Analyses FTIR et ATG de la MCC et la NCC greffée

Afin de confirmer un bon greffage de l'APTES sur la MCC et la NCC, des analyses FTIR ont été proposées. Les analyses infrarouges ont été menées sur une IRTracer-100 (Shimadzu, Kyoto, JAP) sur une plage de nombre d'onde entre 4000 et 500 cm^{-1} pour observer de potentielles modifications chimiques dues au greffage. La **Figure A 1** présente les spectres infrarouges de la MCC et NCC, avant et après greffage.

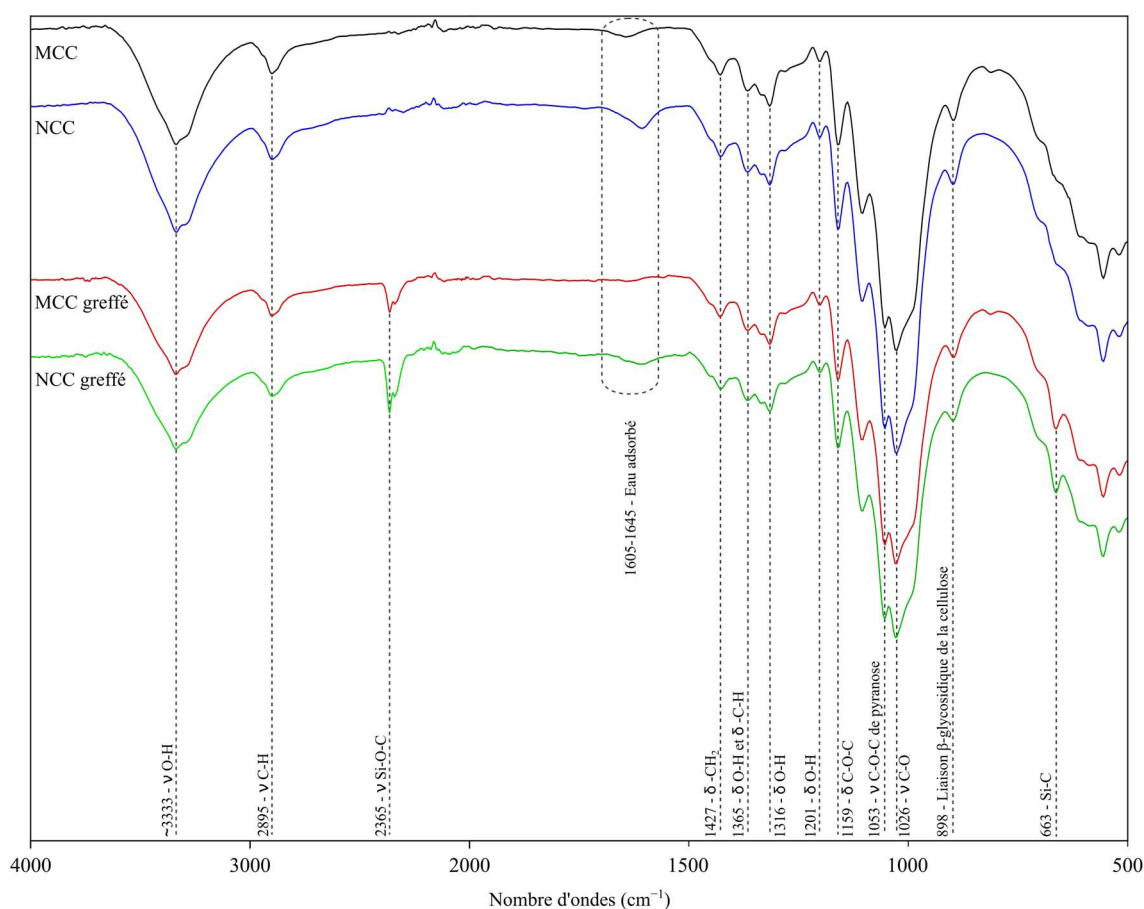


Figure A 1 : Spectres infrarouge des charges cellulosiques, avant et après greffage

Pour toutes les conditions, les pics attendus sont bien présents (Buzón-Durán et al., 2021; Hossain et al., 2020; Li et al., 2015; Rathnayake et al., 2020; Supeno et al., 2014). Le large pic à 3333 cm^{-1} environ correspondait à l'étirement de la liaison O–H de la cellulose. De plus, la série de pics à 1365, 1316 et 1201 cm^{-1} environ est causée par le groupe –OH. Hossain et al. (2020) a aussi évoqué que le pic vers 1365 cm^{-1} peut être causé par la déformation de la liaison C–H. Les pics présents à 2895 et 1427 cm^{-1}

correspondaient respectivement à l'étirement de la liaison C-H, et aux déformations symétriques du groupe chimique CH₂ de la phase cristalline de la cellulose. La série de pics entre 1160 et 1025 cm⁻¹ correspondait aux groupes présents sur le cycle de la cellulose. Pour finir, le pic à 898 cm⁻¹ correspondait aux liaisons β-glycosidiques de la cellulose. On peut noter que les charges greffées ont présenté deux nouveaux pics à 2361 et 663 cm⁻¹, respectivement attribuables à la présence de liaisons Si-O-C et Si-C. De plus, le faible pic à 1641 cm⁻¹ visible sur la MCC non greffée n'était pas présent. Ce pic étant associable à la vibration de la molécule d'eau adsorbée par les fibres, il peut en être déduit que la MCC greffée est plus hydrophobe que la MCC non greffée, et donc que l'APTES a été correctement greffée sur la MCC. Concernant la NCC greffée, le pic Si-O-C de l'APTES était aussi présent, et plus intense que pour la MCC greffée. Le pic associé à l'adsorption d'eau était encore présent, mais étant moins intense que pour la NCC non greffée. Il peut en être déduit que l'APTES a été au moins partiellement greffé sur la NCC.

Les analyses ATG permettent d'observer une modification de la cinétique de dégradation due au greffage. Le protocole appliqué fut une rampe de chauffe allant jusqu'à 600 °C avec une vitesse de 10 °C·min⁻¹, un flux d'azote de 20 ml·min⁻¹ et réalisé sur les mêmes fibres que pour les analyses FTIR. Les résultats sont présentés en **Figure A 2**. Une très faible amélioration de la stabilité thermique de la MCC est observée avec le greffage, avec un décalage positif de 2 °C du pic de dégradation entre la MCC non greffée et la MCC greffée. Cependant, le greffage sur les NCC était beaucoup plus visible, car elle a supprimé la première phase de dégradation de la NCC pure vers 252 °C et retarde de 20 °C la seconde phase de dégradation de la NCC. L'amélioration de la stabilité thermique pourrait être associable à une diminution de l'oxydation de la NCC par une diminution des sites hydroxyles disponibles grâce à un greffage efficace.

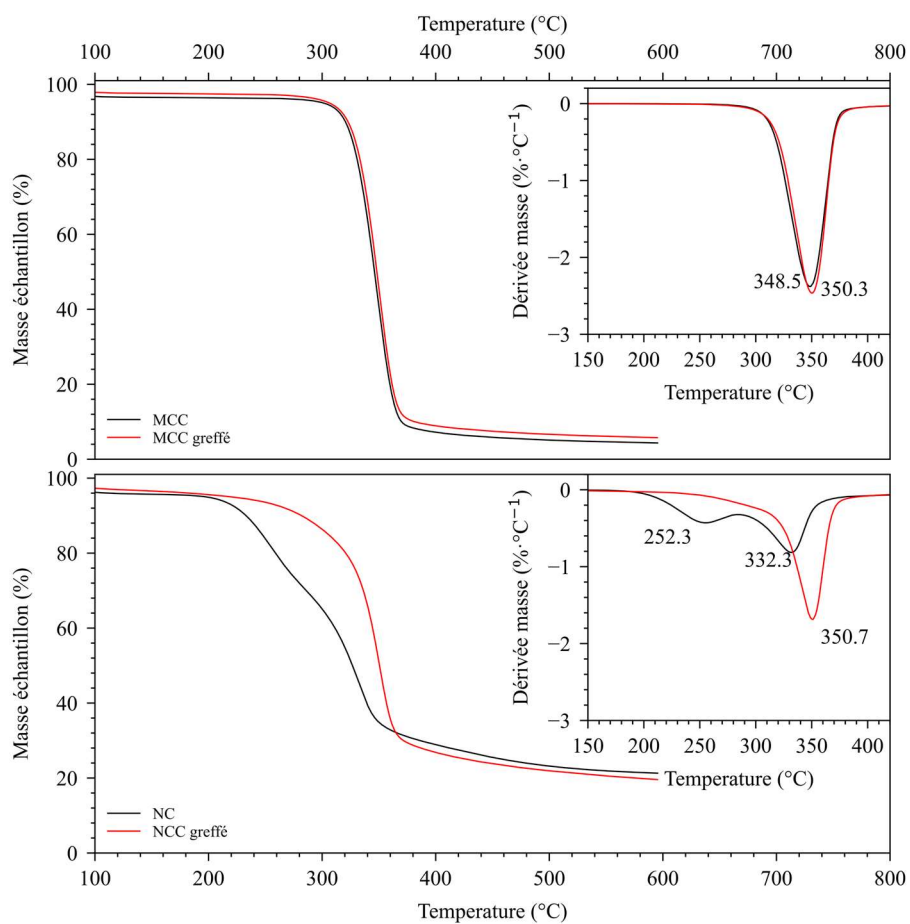


Figure A 2 : Courbes ATG de la MCC et NCC, avant et après greffage

Annexe 2 : Chapitre 3 - Granulométrie de la MCC greffée

Les analyses granulométriques ont été réalisées sur un échantillon de 2088 particules de MCC greffées, avec un microscope confocal VK-X100 Series (Keyence, Osaka, JAP). Le traitement d'image a été effectué avec le logiciel ImageJ. Lors de l'analyse des particules, la morphologie du MCC greffé a été associée à des ellipses, la longueur et la largeur de l'ellipse équivalente correspondant respectivement à la longueur et à la largeur de la particule de MCC. Les longueurs médiane et moyenne, et les largeurs médiane et moyenne calculées étaient respectivement de 34,14, 51,90, 16,60 et 22,86 μm , avec un rapport L/D moyen de 2,23. Les courbes granulométriques sont présentées en **Figure A 3**.

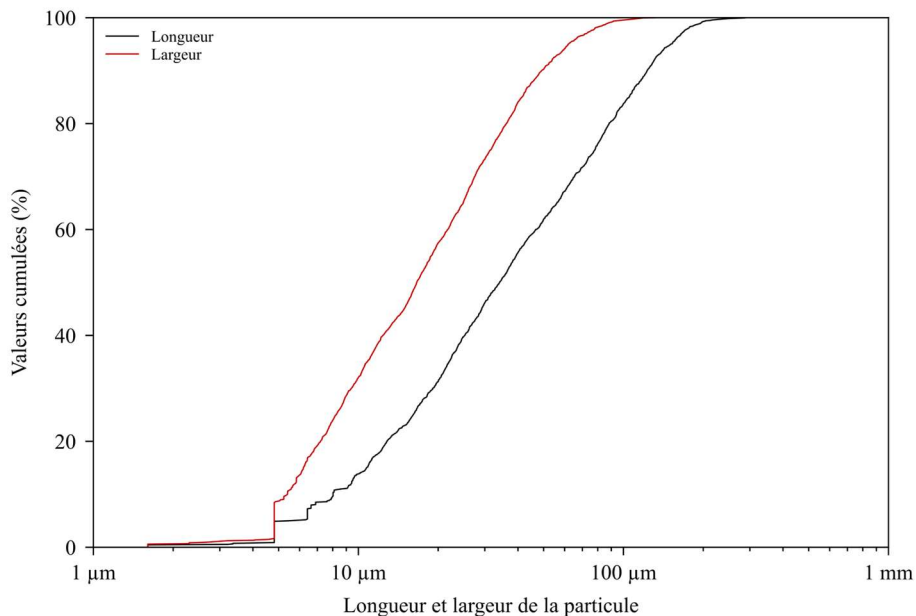


Figure A 3 : Courbes granulométriques de la MCC greffée

Annexe 3 : Chapitre 3 - Balayage en amplitude des tests rhéologiques réalisés durant le projet

La **Figure A 4** présente les courbes de balayage en amplitude des mélanges réalisées à $10 \text{ rad}\cdot\text{s}^{-1}$. Cette étape permet de déterminer la limite linéaire de viscoélasticité.

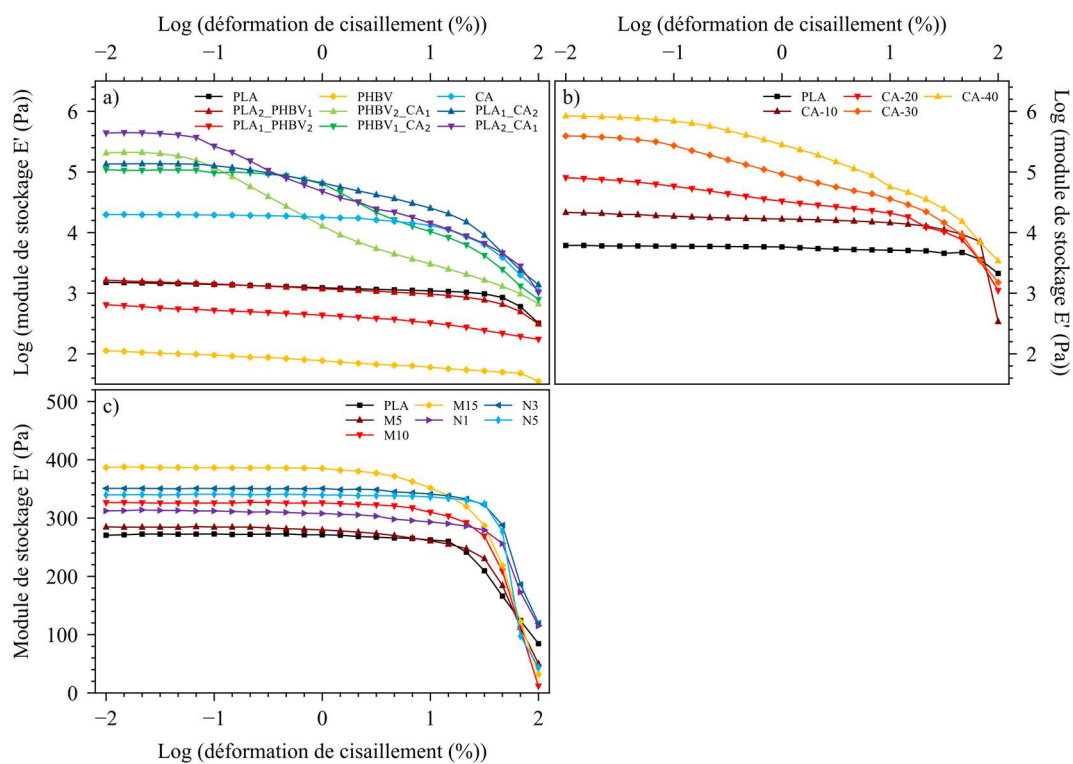


Figure A 4 : Balayage en amplitude des tests rhéologiques des a) **Chapitre 4**,
b) **Chapitre 5**, c) **Chapitre 6**

Annexe 4 : Chapitre 4 - Compléments des analyses diélectriques

La **Table A 1** présente une synthèse de la conductivité électrique en courant alternatif mesurée à 20 °C (σ_{AC}), non évoquée durant le **Chapitre 4**. De plus, les **Figure A 5**, **Figure A 6** et **Figure A 7** présentent les graphiques 3D de respectivement la constante diélectrique (ϵ'), la σ_{AC} et la perte diélectrique (ϵ'') en fonction de la fréquence et de la température. La précision du maillage est de 10 points par décade pour la fréquence et de 1 point tous les 5 °C pour la température.

Table A 1 : Log (conductivité électrique σ_{AC}) des mélanges

Mélanges	log (σ_{AC} (S·cm ⁻¹))				
	@ 100 Hz	@ 1 kHz	@ 10 kHz	@ 100 kHz	@ 1 MHz
PLA	-12,27	-11,34	-10,20	-9,10	-8,06
PLA ₂ _PHBV ₁	-11,85	-10,74	-9,84	-8,97	-8,05
PLA ₁ _PHBV ₂	-11,60	-10,60	-9,77	-8,92	-7,92
PHBV	-11,50	-10,46	-9,63	-8,81	-7,88
PHBV ₂ _CA ₁	-11,69	-10,60	-9,45	-8,37	-7,34
PHBV ₁ _CA ₂	-11,61	-10,79	-9,75	-8,64	-7,52
CA	-11,84	-10,54	-9,34	-8,22	-7,10
PLA ₁ _CA ₂	-11,36	-10,31	-9,29	-8,29	-7,27
PLA ₂ _CA ₁	-12,01	-10,91	-9,79	-8,74	-7,71

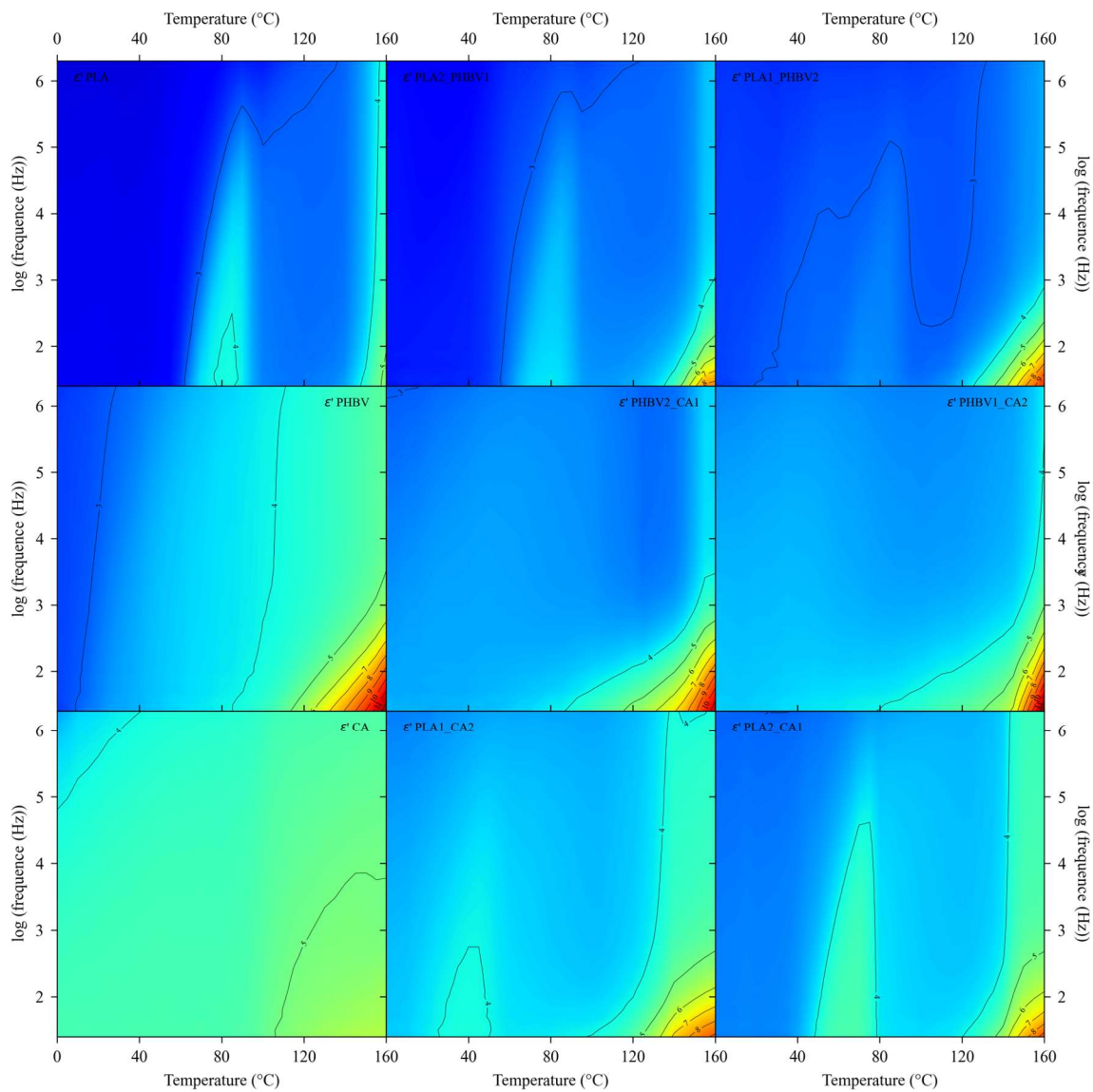


Figure A 5 : Constante diélectrique ϵ' des mélanges en fonction de la température et de la fréquence

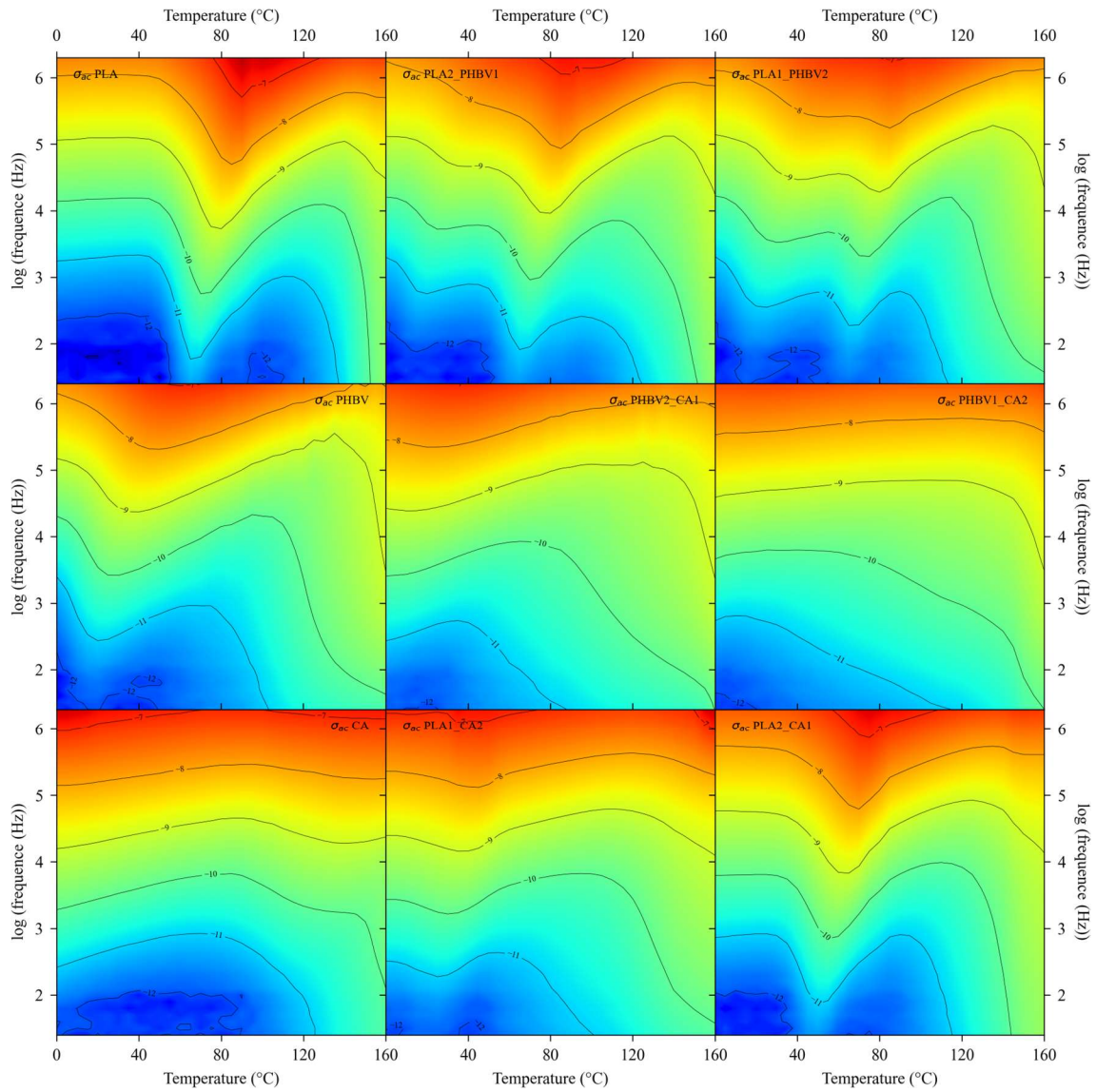


Figure A 6 : Log (conductivité électrique σ_{AC}) des mélanges en fonction de la température et de la fréquence

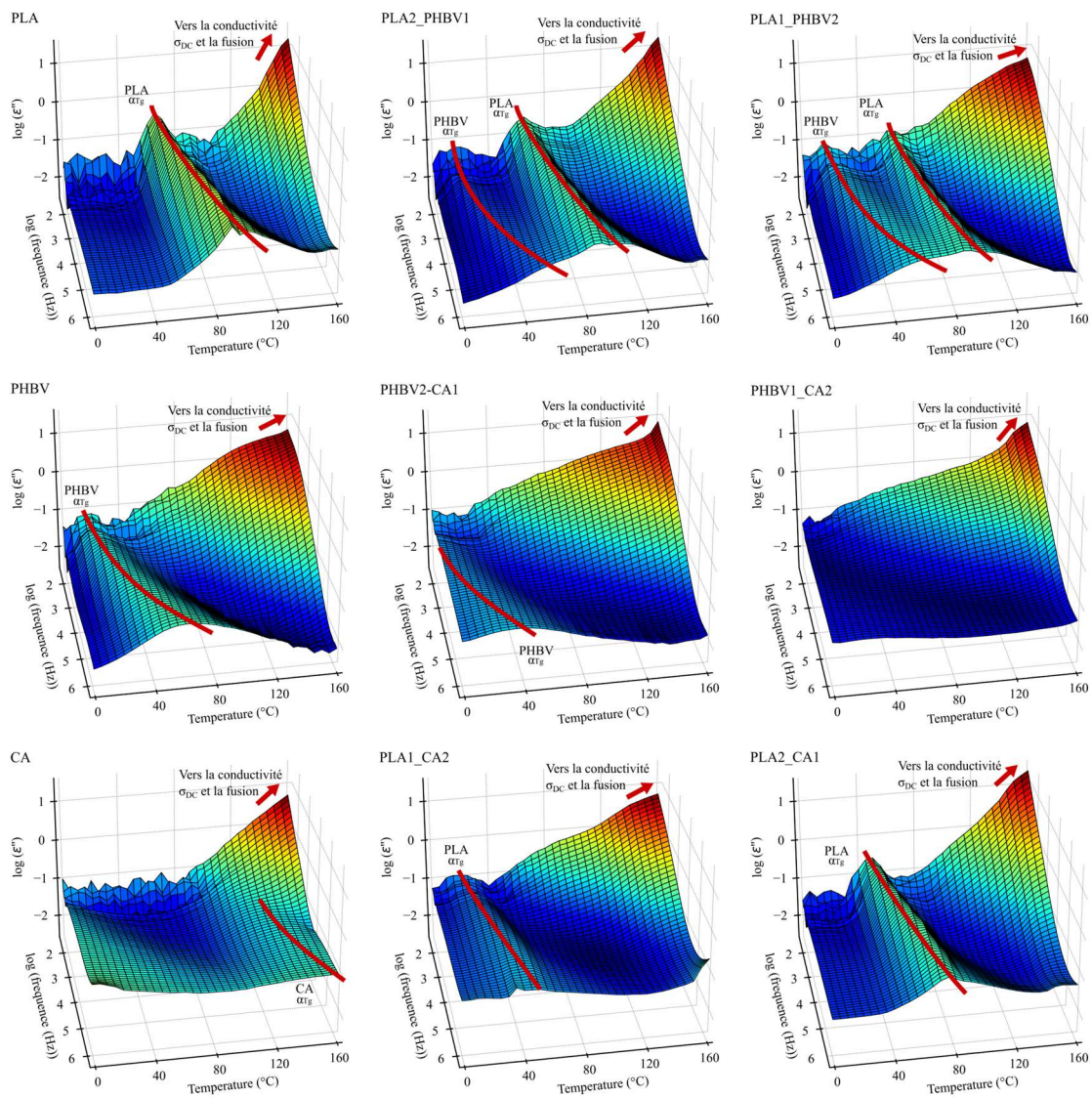


Figure A 7 : Log (perte diélectrique ϵ'') des mélanges en fonction de la température et de la fréquence. Les relaxations spécifiques sont mise en évidence

En plus des mesures diélectriques réalisées à Unilasalle, des analyses diélectriques complémentaires ont été conduites à l'UQAT sur une Keysight E4991A (Agilent Technologies, Santa Clara, USA). Les mesures sont faites sur des disques de 0,5 mm d'épaisseur et de 10 mm de diamètre, à température ambiante dans une plage de fréquence de 1 MHz à 1 GHz. La **Table A 2** présente l' ϵ' des mélanges mesurés à 1 MHz et le **Figure A 8** présente l' ϵ' des mélanges en fonction de la fréquence, tous les deux mesurés à 20 °C. Le comportement de tous les mélanges testés est en adéquation avec ceux obtenus avec le BDS basse fréquence présenté dans le **Chapitre 4**.

Table A 2 : Constante diélectrique ϵ' des mélanges mesuré à 1 MHz et à 20 °C

	ϵ' @ 1 MHz
PLA	$1,82 \pm 0,08$
PLA ₂ _PHBV ₁	$1,93 \pm 0,01$
PLA ₁ _PHBV ₂	$2,02 \pm 0,02$
PHBV	$2,09 \pm 0,01$
PHBV ₂ _CA ₁	$2,27 \pm 0,05$
PHBV ₁ _CA ₂	$2,53 \pm 0,05$
CA	$2,75 \pm 0,03$
PLA ₁ _CA ₂	$2,46 \pm 0,07$
PLA ₂ _CA ₁	$2,12 \pm 0,02$
PLA_PHBV_CA	$2,28 \pm 0,10$

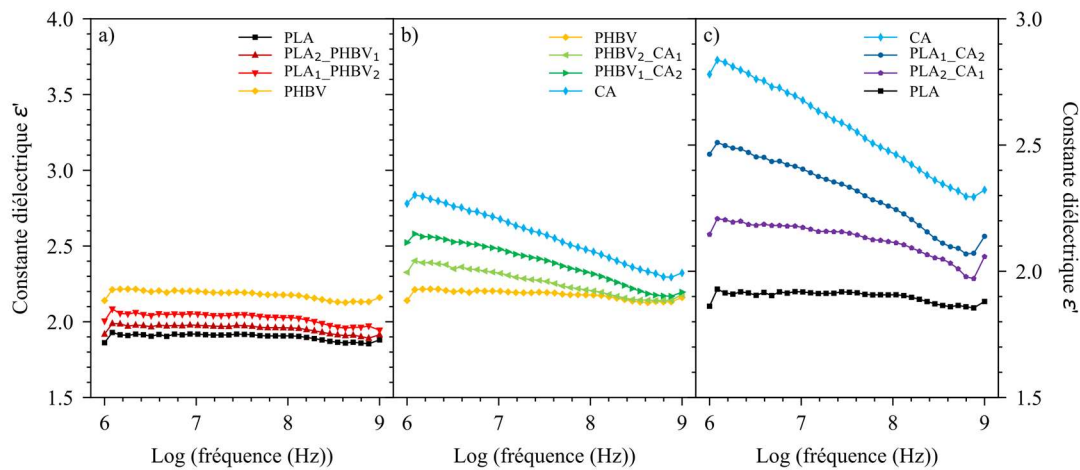


Figure A 8 : Constante diélectrique ϵ' des mélanges PLA, PHBV et CA en fonction de la fréquence, mesuré à 20 °C et à haute fréquence

Annexe 5 : Chapitre 4 - Analyses thermiques

La **Figure A 9** présente les courbes DSC des mélanges durant la rampe de refroidissement et la seconde rampe de chauffe. En outre, la **Table A 3** présente les températures caractéristiques observées, ainsi que le taux de cristallinité (X_{cr}) des mélanges. La température de transition vitreuse (T_g) du PLA a été mesurée à $55,6 \pm 0,2$ °C durant la rampe de refroidissement et à $63,3 \pm 0,15$ °C durant la rampe de chauffe. Ces valeurs sont en accord avec la littérature (Kang et al., 2018; Maiza et al., 2015; Yang et al., 2008). Bien que le PLA pur n'ait pas cristallisé durant la phase de refroidissement, il a présenté une petite cinétique de cristallisation froide et un faible pic de fusion à $155,5 \pm 0,3$ °C (Kang et al., 2018; Maiza et al., 2015; Yang et al., 2008).

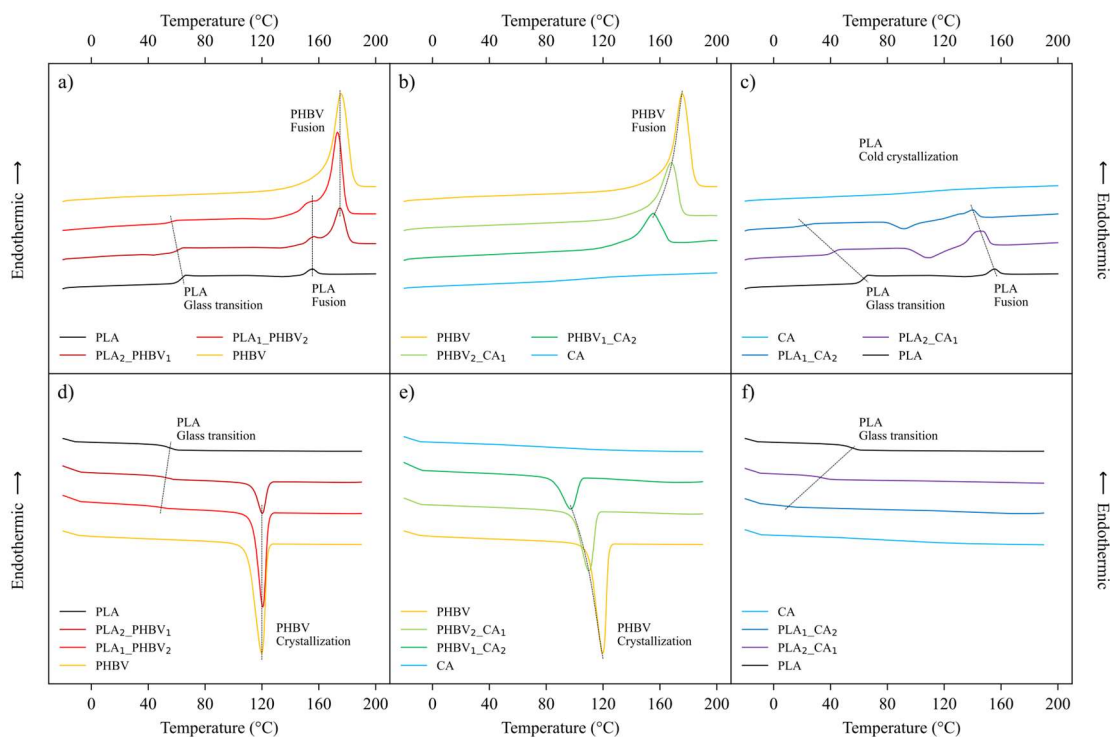


Figure A 9 : Courbes DSC des mélanges. Les courbes a), b) et c) sont réalisées avec la seconde chauffe tandis que les courbes d), e) et f)) sont réalisées avec le premier refroidissement

Table A 3 : Températures remarquable des mélanges mesurées par DSC

	T _g PLA (°C)		T _c PHBV (°C)	T _{cc} PLA (°C)		T _f PLA (°C)	T _f PHBV (°C)	X _{cr} (%)
	Refroidis.	Chauffé	Refroidis.	Chauffé	Chauffé	Chauffé		
PLA	55,6 ± 0,2	63,3 ± 0,5	-	133,7 ± 0,9	155,5 ± 0,3	-	0	
PLA ₂ _PHBV ₁	54,1 ± 0,2	61,7 ± 0,2	120,1 ± 0,6	127,8 ± 4,1	156,1 ± 0,5	175,2 ± 0,5	20,7 ± 1,0	
PLA ₁ _PHBV ₂	52,0 ± 1,9	57,9 ± 2,5	121,0 ± 0,6	122,4 ± 2,0	153,1 ± 2,1	177,2 ± 2,8	41,7 ± 1,2	
PHBV	-	-	120,7 ± 1,4	-	-	175,5 ± 0,6	59,6 ± 4,2	
PHBV ₂ _CA ₁	-	-	111,7 ± 2,4	-	-	170,9 ± 1,2	36,5 ± 4,0	
PHBV ₁ _CA ₂	-	-	97,2 ± 0,2	-	-	156,0 ± 1,2	18,1 ± 0,6	
CA	-	-	-	-	-	-	0	
PLA ₁ _CA ₂	13,9 ± 0,5	21,0 ± 0,9	-	90,5 ± 2,6	126,0 ± 1,2	-	0	
PLA ₂ _CA ₁	34,9 ± 0,8	43,0 ± 0,3	-	108,5 ± 1,9	149,1 ± 1,3	-	0	
PLA_PHBV_CA	29,0 ± 1,4	37,5 ± 2,1	110,5 ± 2,8	117,2 ± 3,7	149,1 ± 2,1	171,6 ± 3,9	18,9 ± 0,4	

Le PHBV a montré un faible signal de transition autour de 8 °C dans la rampe de chauffage, associable à sa transition vitreuse. Une température de cristallisation T_c à 120,7 ± 1,4 °C et une température de fusion (T_f) à 175 ± 0,5 °C ont également été mesurées. Ces résultats sont également cohérents avec la littérature (Chea et al., 2016; Nuchanong et al., 2021; Tomano et al., 2022). Le degré de cristallinité mesuré du PHBV pur était important avec un X_{cr} de 59,6 ± 4,1 %, en accord ici aussi avec la littérature (Chea et al., 2016; Nuchanong et al., 2021; Tomano et al., 2022). Le X_{cr} élevé est à l'origine du très faible signal associé à la transition vitreuse, la phase amorphe étant très faible par rapport à la phase cristalline (Tomano et al., 2022). Le CA possède une légère T_g mesurée à 91 °C avec la rampe de refroidissement et à 105 °C avec la rampe de chauffage. Aucune température de fusion ou de cristallisation n'a été mesurée pour le CA. Concernant les mélanges PLA:PHBV, la T_g PLA diminue légèrement, mais significativement avec l'ajout de PHBV (P-Value = 2,27*10⁻² en refroidissement et P-Value = 4,67* 10⁻⁴ en seconde chauffe). Cette diminution de la T_g PLA avec l'ajout de PHBV est caractéristique d'un mélange PLA:PHBV partiellement miscible. Mofokeng and Luyt (2015) ont également observé une diminution de la T_g PLA avec l'ajout de PHBV. La température de cristallisation à froid (T_{cc}) du PLA a également diminué avec l'incorporation de PHBV (P-Value = 4,53*10⁻³). Cependant, aucune variation significative des T_c et T_f n'est visible pour les mélanges à base de PLA et de PHBV. Le CA s'est avéré être le polymère le plus impactant pour le comportement thermique des mélanges. Toutes les températures de relaxation du PLA et du PHBV ont fortement diminué avec l'ajout de CA. Par exemple, les PLA₂_CA₁ et PLA₁_CA₂ avaient une T_g

PLA inférieure de 21 °C et 42 °C respectivement à celle du PLA pur. Le plastifiant diminue l'énergie nécessaire à la relaxation du PLA et ce comportement linéaire de diminution de T_g a également été observé par Maiza et al. (2015). Selon ces derniers, les chaînes macromoléculaires du PLA ont gagné en mobilité avec l'ajout d'un plastifiant, ce dernier augmentant le volume libre et diminuant les interactions entre les chaînes polymériques. De plus, le plastifiant a augmenté l'enthalpie du pic de fusion du PLA. Le PLA pur, le PLA₂_CA₁ et le PLA₁_CA₂ avaient une enthalpie de fusion de 5,8, 16,2 et 5,7 J·g⁻¹ respectivement. L'augmentation de l'enthalpie est également directement liée à l'augmentation de la mobilité de la chaîne du PLA induite par le plastifiant. Le PLA des mélanges PLA:CA a également montré un pic de fusion secondaire à une température plus basse que le pic principal. Cela prouverait que le CA a favorisé un réseau cristallin secondaire, moins ordonné et avec un réseau plus fin que le réseau principal.

La **Figure A 10** présente les courbes ATG ainsi que les courbes dérivées d'ATG des mélanges.

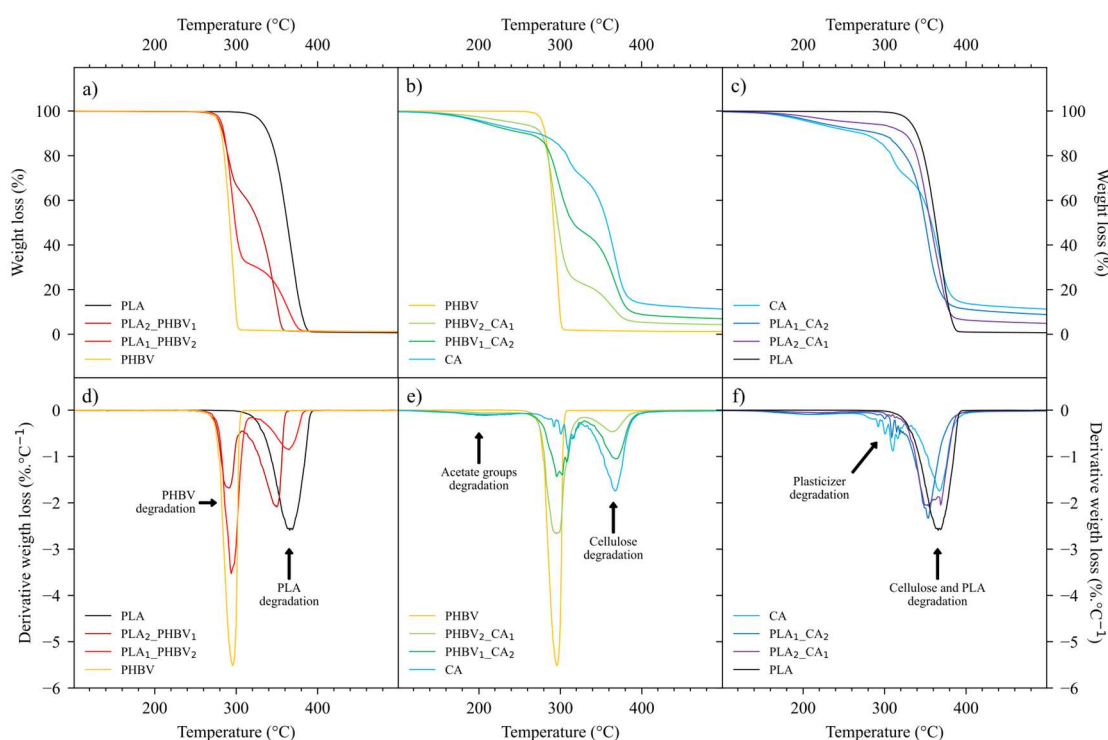


Figure A 10 : Courbes ATG et dérivées ATG des mélanges PLA:CA

Tout d’abord, le PLA et le PHBV ont montré un comportement typique d’un matériau monocomposant : une unique dégradation était présente pour le PLA et le PHBV vers respectivement 360 et 290 °C (Chea et al., 2016; Kang et al., 2018; Mofokeng and Luyt, 2015a; Nuchanong et al., 2021; Yang et al., 2008). Le CA a quant à lui montré trois dégradations. Une dégradation faible et étalée était visible autour de 200 °C, associée à la dégradation des groupes acétyles du CA, ce dernier se transformant chimiquement en cellulose (Shaikh et al., 2022). Vers 300 °C, une perte instable a été observée, associée à la dégradation du plastifiant. Enfin, vers 360 °C, la cellulose restante a commencé sa dégradation thermique. Comme la dégradation du PLA et de la cellulose se produisent à la même température, se traduisant par la présence d’un seul pic de dégradation.

La **Table A 4** présente les températures associées à une perte de matière de 5 et 10 % (T_{95} % et T_{90} % respectivement), ainsi que le taux de cendre à 600 °C. Le PLA pur présentait les T_{95} % et T_{90} % les plus élevés des mélanges testés, et le CA pur présentait la stabilité thermique la plus faible. L’ajout de CA semble avoir un impact plus important sur la stabilité thermique que le PHBV. Cela s’explique par la dégradation des groupes acétyles, comme évoqué précédemment. Concernant le taux de cendre à 600 °C, les rendements les plus faibles ont été observés pour le PLA, le PHBV ainsi que leurs mélanges binaires avec un taux d’environ 1 %. Les mélanges favorisant le CA avaient un rendement beaucoup plus élevé que le PLA et le PHBV. Ceci serait dû à un niveau plus élevé d’impuretés de CA ou de la présence de résidus de plastifiants.

Table A 4 : Stabilité thermique des mélanges

	T_{95} (°C)	T_{90} (°C)	Taux cendre @ 600 °C (%)
PLA	330,8 ± 2,0	338,8 ± 2,1	0,6 ± 0,1
PLA ₂ _PHBV ₁	279,6 ± 0,7	284,4 ± 0,3	1,3 ± 0,9
PLA ₁ _PHBV ₂	280,1 ± 0,1	270,8 ± 1,7	0,8 ± 0,2
PHBV	278,1 ± 0,2	284,4 ± 0,7	1,1 ± 0,1
PHBV ₂ _CA ₁	239,0 ± 1,9	281,7 ± 0,2	3,7 ± 0,2
PHBV ₁ _CA ₂	210,1 ± 1,3	276,9 ± 2,5	6,4 ± 0,5
CA	205,8 ± 3,5	264,1 ± 1,5	9,1 ± 0,7
PLA ₁ _CA ₂	212,8 ± 3,3	281,3 ± 2,2	7,7 ± 0,2
PLA ₂ _CA ₁	257,9 ± 2,2	284,1 ± 7,5	4,3 ± 0,3
PLA_PHBV_CA	265,0 ± 2,1	321,4 ± 2,5	4,3 ± 0,9

Annexe 6 : Chapitre 4 - Analyses DMA

La **Figure A 11** présente le module de stockage (E') et la tangente de perte ($\tan \delta$) des mélanges. Le PLA a montré un comportement typique observé dans la littérature (Sang et al., 2017). À basse température ($T < 50$ °C), ce dernier a présenté un E' de 2,8 GPa à 25 °C avec une tangente de perte très faible ($< 0,05$), caractéristique d'un matériau à l'état vitreux. Lorsque la température de transition vitreuse est atteinte, le PLA pur connaît une forte baisse de son module de stockage. De plus, le $\tan \delta$ a montré un pic mesuré à 63 °C avec une valeur de 3, indiquant que la partie visqueuse était le principal contributeur du module complexe. Un état caoutchoutique a été constaté entre 65 et 100 °C, caractérisé par une perte de E' moins prononcée que pendant la transition vitreuse, ainsi qu'une diminution de la tangente de perte. Cette dernière reste néanmoins plus élevée que durant l'état vitreux, avec des valeurs $\tan \delta$ supérieures à 0,17. Enfin, entre 100 et 140 °C, une augmentation de E' et du $\tan \delta$ a été observée, associable à la relaxation de la cristallisation froide du PLA (Sang et al., 2017), également observée par analyse DSC. À 20 °C, le PHBV possédait un E' de 3,3 GPa et un $\tan \delta$ de 0,07. Comme l'a montré les analyses DSC, le PHBV était en état caoutchoutique vers 20 °C. Mais malgré son état caoutchoutique, il présentait toujours un $\tan \delta$ relativement faible, probablement en raison de son réseau cristallin très développé favorisant la composante élastique du module complexe. Aucune relaxation n'était perceptible dans la plage de température mesurée, seulement une légère diminution et continue du E' . À 135 °C, le PHBV avait un module de stockage de 480 MPa et une tangente de perte de 0,11. Le CA, quant à lui, avait un E' de 1,9 GPa à 20 °C, avec un $\tan \delta$ de 0,07. Trois comportements différents ont été observés dans la plage de température utilisée. Jusqu'à 80 °C, le CA a montré un comportement vitreux, avec une tangente de perte relativement faible ($< 0,2$). Cette valeur reste néanmoins beaucoup plus élevée que celle du PLA à l'état vitreux, probablement en raison de la présence du plastifiant augmentant la partie visqueuse du CA. Son comportement entre 80 et 110 °C a pu être assimilé à sa transition vitreuse, avec un pic de $\tan \delta$ mesuré à 110 °C. Enfin, entre 110 et 140 °C, le CA a vu son E' diminuer et son $\tan \delta$ stagner vers 0,64. Il est à noter que, contrairement au PLA, le CA possédait toujours un comportement élastique prédominant en état caoutchoutique par rapport au PLA. Concernant les mélanges polymériques, les mélanges PLA:PHBV ont présenté un comportement mécanique analogue à une loi des mélanges. L'ajout de PHBV dans le

PLA a globalement augmenté le module de stockage des mélanges. En outre, une diminution de la tangente de perte du PLA a été observée avec l'incorporation de PHBV. L'ajout de 33 % de PHBV en poids dans le PLA a divisé le pic de $\tan \delta$ du PLA par 6, le passant de 3,15 à 0,5. L'augmentation de E' lors de la cristallisation à froid du PLA a également diminué avec l'ajout de PHBV.

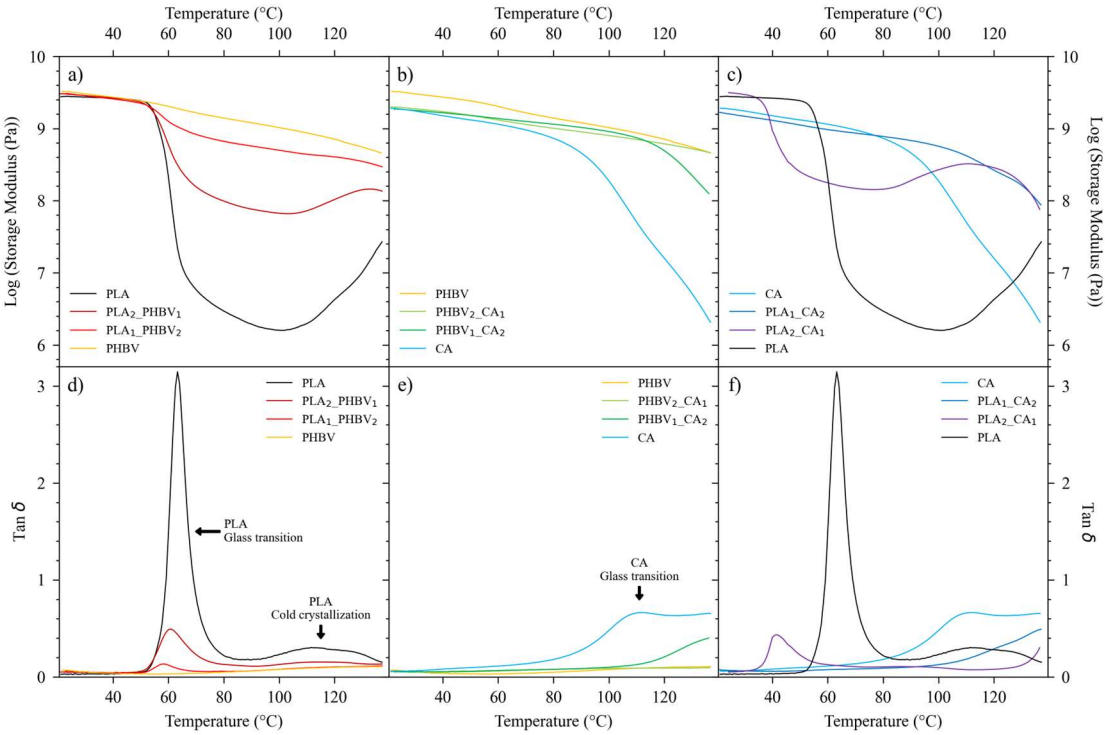


Figure A 11 : Propriétés mécaniques dynamiques des mélanges PLA:CA

Annexe 7 : Chapitre 5 - Compléments des analyses diélectriques

Les **Figure A 12**, **Figure A 13** et **Figure A 14** présentent les graphiques 3D de respectivement la constante diélectrique (ϵ'), la conductivité en courant alternatif (σ_{AC}) et la perte diélectrique (ϵ'') en fonction de la fréquence et de la température du PLA, CA et des mélanges associés. La précision du maillage est de 10 points par décade pour la fréquence et d'1 point tous les 4 °C pour la température.

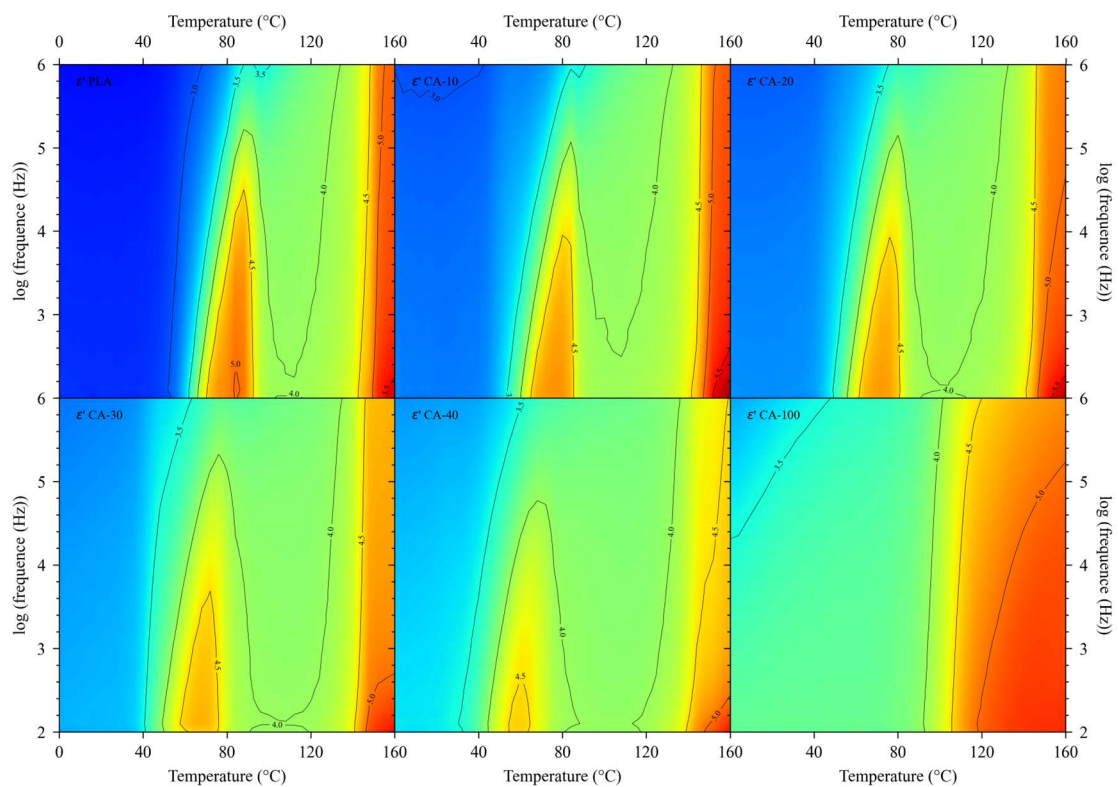


Figure A 12 : ϵ' des mélanges PLA:CA versus température et fréquence

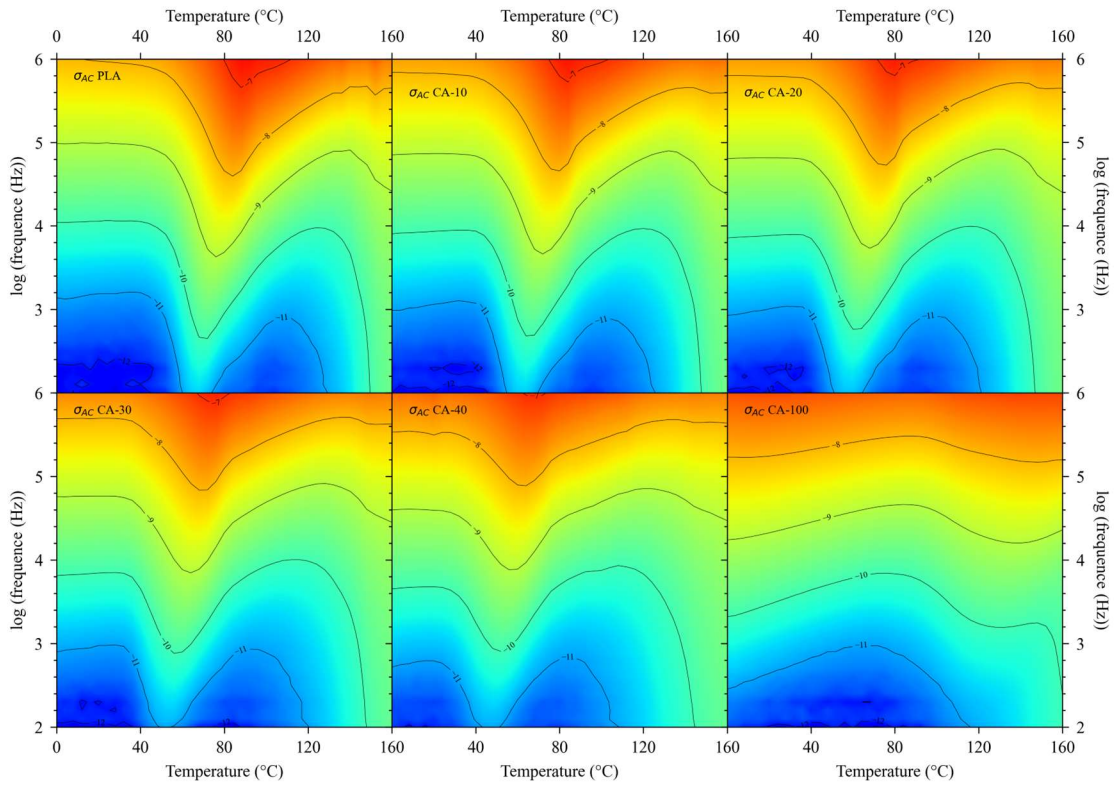


Figure A 13 : Log (σ_{AC}) des mélanges PLA:CA versus température et fréquence

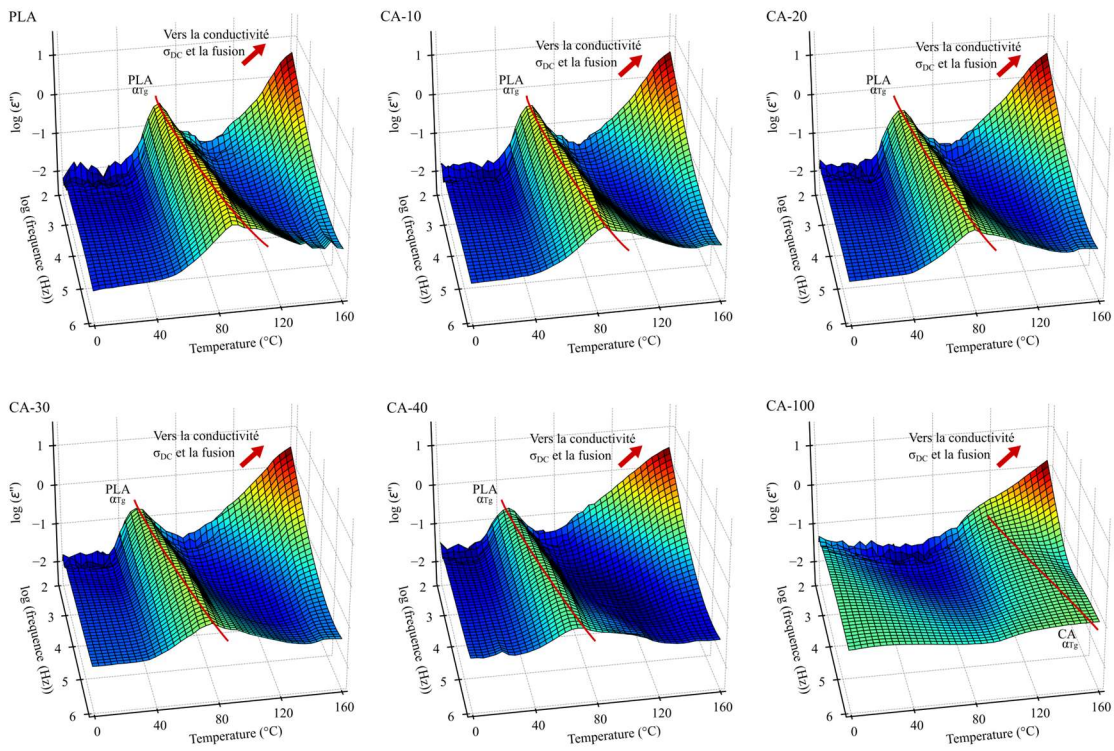


Figure A 14 : Log (ϵ'') des mélanges PLA:CA versus température et fréquence

Annexe 8 : Chapitre 5 - Compléments des analyses statistiques du plan de Taguchi

Table A 5 : Analyse de variance pour la constante diélectrique ϵ'

Source	DF	Seq SS	Adj SS	Adj MS	F – Value	P – Value
W_{CA} (%)	2	0,019957	0,019957	0,009978	30,53	0,032
Remplissage (%)	2	0,197962	0,197962	0,098981	302,8	0,003
Épaisseur (mm)	2	0,009617	0,009617	0,004809	14,71	0,064
Erreurs résiduelles	2	0,000654	0,000654	0,000327		
Total	8	0,228189				

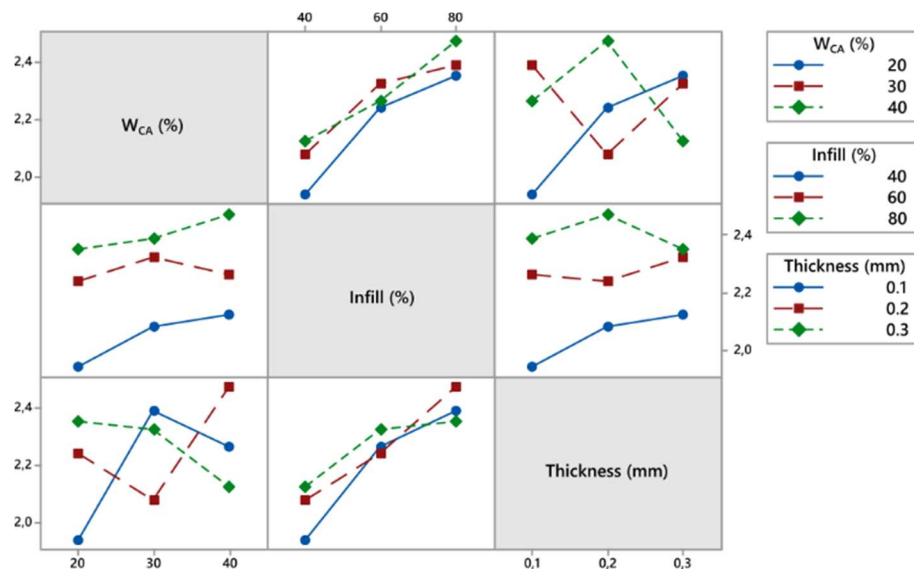


Figure A 15 : Diagramme d'interactions pour la constante diélectrique ϵ'

Table A 6 : Table de réponse pour la constante diélectrique ϵ'

Level	W_{CA} (%)	Infill (%)	Thickness (mm)
1	2,179	2,048	2,198
2	2,265	2,278	2,266
3	2,288	2,407	2,269
Delta	0,109	0,359	0,071
Rank	2	1	3

Table A 7 : Analyse de variance pour le log (conductivité électrique σ_{AC})

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
W_{CA} (%)	2	0,034228	0,034228	0,017114	29,91	0,032
Remplissage (%)	2	0,088931	0,088931	0,044466	77,72	0,013
Épaisseur (mm)	2	0,005803	0,005803	0,002902	5,07	0,165
Erreurs résiduelles	2	0,001144	0,001144	0,000572		
Total	8	0,130107				

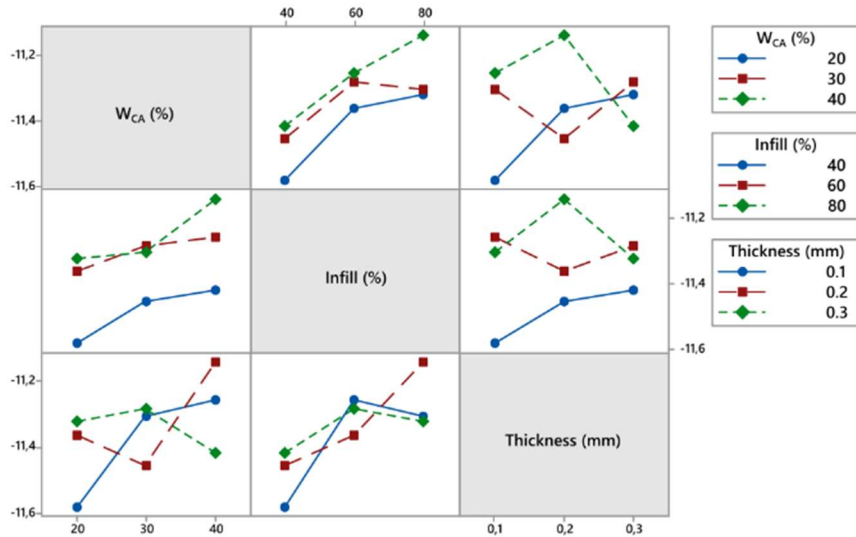


Figure A 16 : Diagramme d'interactions pour le log(conductivité électrique σ_{AC})

Table A 8 : Table de réponse pour le log(conductivité électrique σ_{AC})

Niveau	W_{CA} (%)	Remplissage (%)	Épaisseur (mm)
1	-11,1668	-11,2296	-11,1251
2	-11,0918	-11,0451	-11,0638
3	-11,0158	-10,9997	-11,0854
Delta	0,1511	0,2299	0,0613
Rang	2	1	3

Table A 9 : Analyse de variance du module de stockage E' à 30 °C

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
W_{CA} (%)	2	104368	104368	52184	8,69	0,103
Remplissage (%)	2	52391	52391	26195	4,36	0,186
Épaisseur (mm)	2	28730	28730	14365	2,39	0,295
Erreurs résiduelles	2	12010	12010	6005		
Total	8	197499				

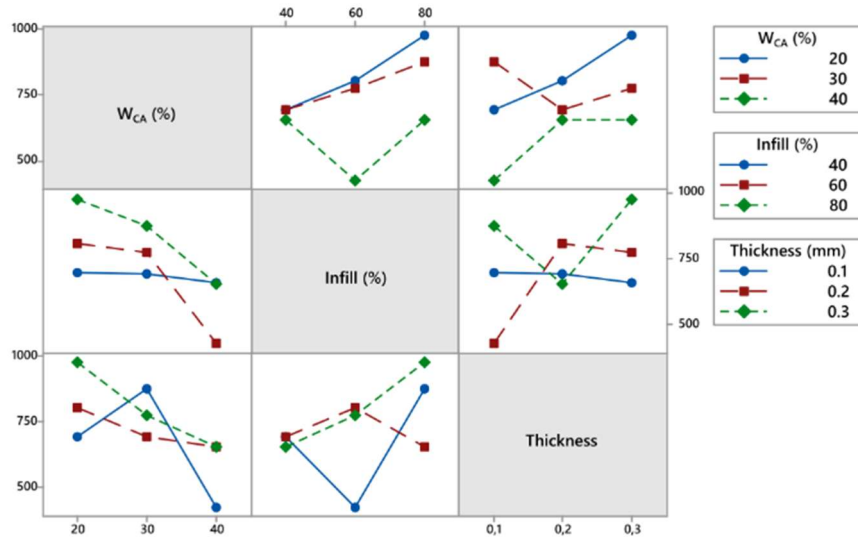


Figure A 17 : Diagramme d'interactions pour le module de stockage E'

Table A 10 : Table de réponse pour le module de stockage E'

Level	W _{CA} (%)	Infill (%)	Thickness (mm)
1	825,6	680,9	665,5
2	781,4	668,3	717,4
3	578,3	836,1	802,5
Delta	247,3	167,8	137,1
Rank	1	2	3

Table A 11 : Analyse de variance pour la température de transition vitreuse du PLA

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value
W _{CA} (%)	2	179,336	179,336	89,6678	180,14	0,006
Infill (%)	2	0,642	0,642	0,3211	0,65	0,608
Thickness (mm)	2	0,576	0,576	0,2878	0,58	0,634
Residual Error	2	0,996	0,996	0,4978		
Total	8	181,549				

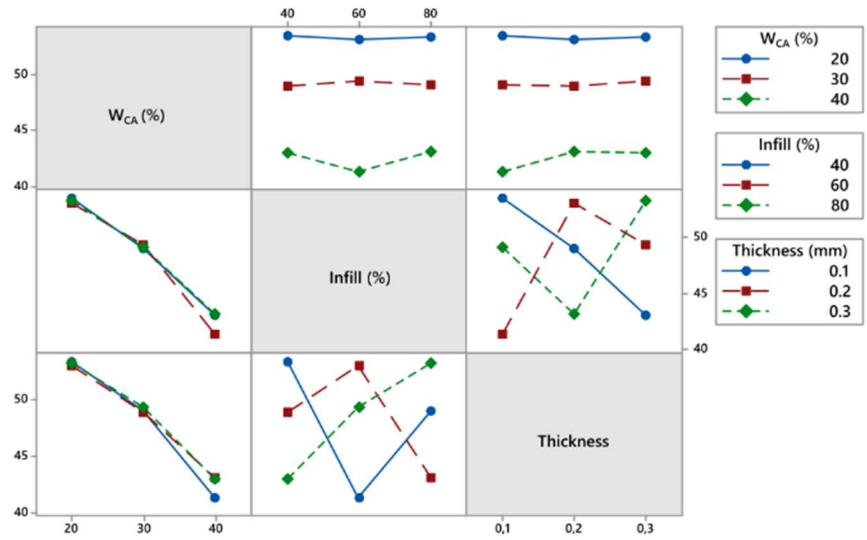


Figure A 18 : Diagramme d'interactions pour la température de transition vitreuse du PLA

Annexe 9 : Chapitre 5 - Analyses thermiques

La **Figure A 19** présente les résultats DSC réalisés sur les éprouvettes thermocompressées et imprimées. La figure montre que dans l'ensemble toutes les relaxations spécifiques du PLA diminuent linéairement avec l'ajout de CA, à cause de la présence du plastifiant du CA. De plus, tous les échantillons thermocompressés sont amorphes, avec des taux de cristallinité inférieurs à 1 % (**Table A 12**). Le taux de cristallinité des échantillons 3D ne dépassant pas 2 %, les éprouvettes sont, elles aussi, considérées amorphes.

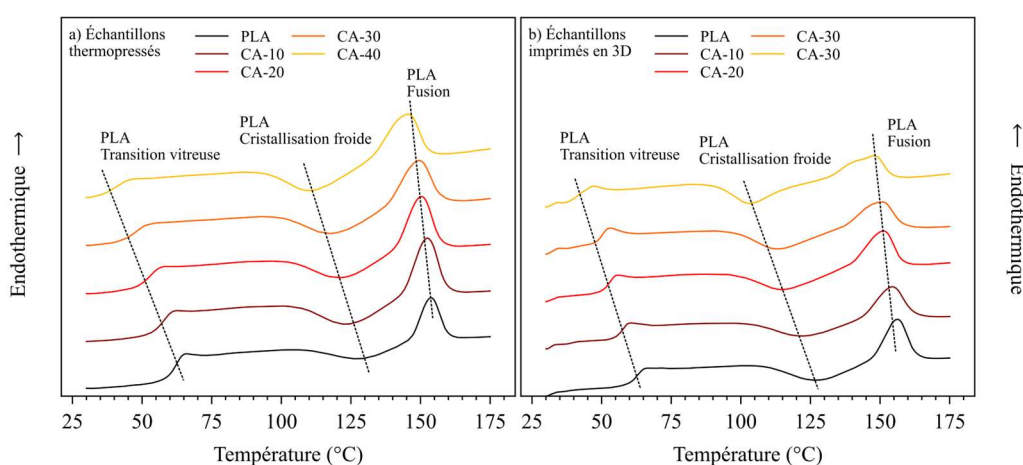


Figure A 19 : Courbe DSC de la seconde chauffe des mélanges PLA:CA thermocompressés et imprimés en 3D

Table A 12 : Températures remarquable des mélanges PLA:CA thermocompressés mesurées par DSC

	$T_{g\text{ PLA (refroidis.)}}$	$T_{g\text{ PLA (chauffe)}}$	$T_{cc\text{ PLA}}$	$T_{f\text{ PLA}}$	$X_{cr}\text{ (%)}$
PLA	$52,6 \pm 0,9$	$61,7 \pm 0,4$	$127,6 \pm 0,1$	$154,2 \pm 0,6$	0,7
CA-10	$46,4 \pm 0,2$	$56,4 \pm 0,7$	$122,9 \pm 1,1$	$152,4 \pm 0,5$	> 0,5
CA-20	$41,4 \pm 0,1$	$51,6 \pm 0,4$	$120,6 \pm 0,6$	$150,2 \pm 0,2$	> 0,5
CA-30	$35,1 \pm 0,9$	$47,1 \pm 1,2$	$117,3 \pm 1,2$	$148,9 \pm 1,0$	> 0,5
CA-40	$31,3 \pm 1,5$	$41,1 \pm 1,5$	$110,8 \pm 1,4$	$145,9 \pm 0,4$	> 0,5

La **Table A 13** présente la stabilité thermique des mélanges PLA:CA. Cette table montre bien que peu importe la méthode choisie, le CA influence négativement la stabilité thermique du mélange PLA:CA comme évoqué en **Chapitre 5.2.**

Table A 13 : Stabilité thermique des mélanges PLA:CA

	T ₉₉ (°C)	T ₉₇ (°C)	T ₉₅ (°C)	T ₉₀ (°C)	T _{onset} (°C)	Taux cendre (%)
PLA	296,1 ± 4,1	312,6 ± 2,6	319,2 ± 2,4	328,5 ± 1,9	333,2 ± 1,4	0,04
CA-10	213,8 ± 5,1	298,8 ± 2,9	312,9 ± 1,9	324,5 ± 0,8	330,1 ± 1,3	1,23
CA-20	178,6 ± 3,4	250,4 ± 7,8	298,2 ± 3,1	320,7 ± 0,8	327,5 ± 1,0	2,35
CA-30	165,0 ± 4,4	217,1 ± 5,1	268,4 ± 8,2	313,4 ± 1,8	325,1 ± 1,1	3,54
CA-40	155,3 ± 1,5	197,8 ± 2,9	230,8 ± 4,8	301,8 ± 2,4	321,0 ± 2,8	4,72

Références

- 2.10: Dynamic Mechanical Analysis [WWW Document], 2016. Chem. Libr. URL [https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Chemistry_and_Nano_Science_\(Barron\)/02%3A_Physical_and_Thermal_Analysis/2.10%3A_Dynamic_Mechanical_Analysis](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/02%3A_Physical_and_Thermal_Analysis/2.10%3A_Dynamic_Mechanical_Analysis) (accessed 8.12.23).
- 18 Lecture Supplement: Infrared Spectroscopy [WWW Document], n.d. URL <https://cdn-prod-pdfsimply-wpcontent.azureedge.net/pdfseofoms/pdf-20180219t134432z-001/pdf/ir-spectroscopy-chart-1.pdf> (accessed 8.11.23).
- Abdel Moteleb, M.M., Saad, G.R., Nessim, R.I., 1992. The effects of preheating on the dielectric relaxation and of temperature on the static dielectric constant of cellulose acetate fibers. *Polym. Degrad. Stab.* 36, 217–224. [https://doi.org/10.1016/0141-3910\(92\)90058-D](https://doi.org/10.1016/0141-3910(92)90058-D)
- Abdul Rahman, N., Gizdavic-Nikolaidis, M., Ray, S., Easteal, A.J., Travas-Sejdic, J., 2010. Functional electrospun nanofibres of poly(lactic acid) blends with polyaniline or poly(aniline-co-benzoic acid). *Synth. Met.* 160, 2015–2022. <https://doi.org/10.1016/j.synthmet.2010.07.031>
- Abeykoon, C., Sri-Amphorn, P., Fernando, A., 2020. Optimization of fused deposition modeling parameters for improved PLA and ABS 3D printed structures. *Int. J. Lightweight Mater. Manuf.* 3, 284–297. <https://doi.org/10.1016/j.ijlmm.2020.03.003>
- Abou-Aiad, T.H.M., Abd-El-Nour, K.N., Hakim, I.K., El-Sabee, M.S., 2007. Dielectric relaxation and spectroscopic investigation of polyhydroxybutyrate PHB blended with polyvinyl acetate PVAc and Poly(vinylacetate-co-vinyl alcohol) PACA. *Polym.-Plast. Technol. Eng.* 46, 1–6. <https://doi.org/10.1080/03602550600901441>
- Abou-Aiad, T.H.M., El-Sabee, M.Z., Abd-El-Nour, K.N., Saad, G.R., El-Sayed, E.-S.A., Gaafar, E.A., 2002. Miscibility and the specific interaction of polyhydroxybutyrate blended with polyvinylacetate and poly(vinyl acetate-co-vinyl alcohol) with some biological applications. *J. Appl. Polym. Sci.* 86, 2363–2374. <https://doi.org/10.1002/app.11137>
- Ahmed Dabbak, S., Illias, H., Ang, B., Abdul Latiff, N., Makmud, M., 2018. Electrical properties of polyethylene/polypropylene compounds for high-voltage insulation. *Energies* 11, 1448. <https://doi.org/10.3390/en11061448>
- Ajitha A.R., Thomas, S., 2020. Introduction: polymer blends, thermodynamics, miscibility, phase separation, and compatibilization, in: *Compatibilization of Polymer Blends*. Elsevier, pp. 1–29. <https://doi.org/10.1016/B978-0-12-816006-0.00001-3>
- Akhoundi, B., Behravesh, A.H., 2019. Effect of filling pattern on the tensile and flexural mechanical properties of FDM 3D printed products. *Exp. Mech.* 59, 883–897. <https://doi.org/10.1007/s11340-018-00467-y>
- Alafaghani, A., Qattawi, A., Alrawi, B., Guzman, A., 2017. Experimental optimization of fused deposition modelling processing parameters: a design-for-manufacturing

- approach. *Procedia Manuf.* 10, 791–803.
<https://doi.org/10.1016/j.promfg.2017.07.079>
- AlFannakh, H., Ibrahim, S.S., 2022. The AC conductivity and dielectric permittivity for PVA-treated MWCNT electrolyte composite. *J. Mater. Sci. Mater. Electron.* 33, 24137–24150. <https://doi.org/10.1007/s10854-022-09092-x>
- Ali, S.F.A., 2020. Cellulose acetate, cellulose acetate propionate and cellulose acetate butyrate membranes for water desalination applications. *Cellulose* 27, 9525–9543.
- Al-Itry, R., Lamnawar, K., Maazouz, A., 2012. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polym. Degrad. Stab.* 97, 1898–1914. <https://doi.org/10.1016/j.polymdegradstab.2012.06.028>
- Amorim, P.H.O., Oliveira, F.Q., dos Santos, H.C., Pereira, R.P., Dornellas, R.M., Semaan, F.S., 2022. Cellulose acetate/ABS blends as insulating phases for 3D printing of carbon-based composite sensors, in: Rocha, Á., Fajardo-Toro, C.H., Rodríguez, J.M.R. (Eds.), *Developments and Advances in Defense and Security*. Springer Singapore, Singapore, pp. 249–258.
- Ando, Y., Minato, M., Nishida, K., 1986. Primary piezoelectric relaxation in a copolymer of β -hydroxybutyrate and β -hydroxyvalerate, in: 1985 5th International Symposium on Electrets. pp. 871–876. <https://doi.org/10.1109/ISE.1985.7341587>
- Andritsch, T., Kochetov, R., Gebrekiros, Y.T., Morshuis, P.H.F., Smit, J.J., 2010. Short term DC breakdown strength in epoxy based BN nano- and microcomposites, in: 2010 10th IEEE International Conference on Solid Dielectrics. Presented at the 2010 10th IEEE International Conference on Solid Dielectrics (ICSD), IEEE, Potsdam, Germany, pp. 1–4. <https://doi.org/10.1109/ICSD.2010.5568098>
- Anh, T.T., Vanga-Bouanga, C., David, E., Frechette, M., 2016. Dielectric response and breakdown strength improvement of LDPE/TiO₂ nanocomposites by using POSS as compatibilizing agent, in: 2016 IEEE Electrical Insulation Conference (EIC). Presented at the 2016 IEEE Electrical Insulation Conference (EIC), IEEE, Montreal, QC, Canada, pp. 65–68. <https://doi.org/10.1109/EIC.2016.7548567>
- Ankit, Saha, L., Kumar, V., Tiwari, J., Sweta, Rawat, S., Singh, J., Baudhdh, K., 2021. Electronic waste and their leachates impact on human health and environment: global ecological threat and management. *Environ. Technol. Innov.* 24, 102049. <https://doi.org/10.1016/j.eti.2021.102049>
- Ashraf, S.S., Frounchi, M., Dadbin, S., 2020. Gamma irradiated electro-conductive polylactic acid/polyaniline nanofibers. *Synth. Met.* 259, 116204. <https://doi.org/10.1016/j.synthmet.2019.116204>
- Assis, R.Q., Rios, P.D., Rios, A.D.O., Olivera, F.C., 2020. Biodegradable packaging of cellulose acetate incorporated with norbixin, lycopene or zeaxanthin. *Ind. Crops Prod.*, * 147, 112212. <https://doi.org/10.1016/j.indcrop.2020.112212>
- Auras, R., Harte, B., Selke, S., 2004. An overview of polylactides as packaging materials. *Macromol. Biosci.* 4, 835–864. <https://doi.org/10.1002/mabi.200400043>
- Avella, A., Idström, A., Mincheva, R., Nakayama, K., Evenäs, L., Raquez, J.-M., Lo Re, G., 2022. Reactive melt crosslinking of cellulose nanocrystals/poly(ϵ -caprolactone) for heat-shrinkable network. *Compos. Part Appl. Sci. Manuf.* 163, 107166. <https://doi.org/10.1016/j.compositesa.2022.107166>
- Aziz, S.B., Brza, M.A., Nofal, M.M., Abdulwahid, R.T., Hussen, S.A., Hussein, A.M., Karim, W.O., 2020a. A Comprehensive Review on Optical Properties of Polymer Electrolytes and Composites. *Materials* 13, 3675. <https://doi.org/10.3390/ma13173675>

- Aziz, S.B., Hamsan, M.H., M. Nofal, M., Karim, W.O., Brevik, I., Brza, Mohamad.A., Abdulwahid, R.T., Al-Zangana, S., Kadir, M.F.Z., 2020b. Structural, impedance and electrochemical characteristics of electrical double layer capacitor devices based on chitosan: dextran biopolymer blend electrolytes. *Polymers* 12, 1411. <https://doi.org/10.3390/polym12061411>
- Aziz, T., Haq, F., Farid, A., Kiran, M., Faisal, S., Ullah, A., Ullah, N., Bokhari, A., Mubashir, M., Chuah, L.F., Show, P.L., 2023. Challenges associated with cellulose composite material: Facet engineering and prospective. *Env. Res* 223, 115429. <https://doi.org/10.1016/j.envres.2023.115429>
- Azmi, A.I., Lau, K.Y., Ahmad, N.A., Abdul-Malek, Z., Rahman, W., 2018. Thermal and breakdown properties of polypropylene homopolymer, copolymer, and blend, in: 2018 IEEE 7th International Conference on Power and Energy (PECon). Presented at the 2018 IEEE 7th International Conference on Power and Energy (PECon), IEEE, Kuala Lumpur, Malaysia, pp. 107–110. <https://doi.org/10.1109/PECON.2018.8684178>
- Badia, J.D., Monreal, L., Sáenz de Juano-Arbona, V., Ribes-Greus, A., 2014. Dielectric spectroscopy of recycled polylactide. *Polym. Degrad. Stab.* 107, 21–27. <https://doi.org/10.1016/j.polymdegradstab.2014.04.023>
- Badia, J.D., Reig-Rodrigo, P., Teruel-Juanes, R., Kittikorn, T., Strömberg, E., Ek, M., Karlsson, S., Ribes-Greus, A., 2017. Effect of sisal and hydrothermal ageing on the dielectric behaviour of polylactide/sisal biocomposites. *Compos. Sci. Technol.* 149, 1–10. <https://doi.org/10.1016/j.compscitech.2017.05.026>
- Bajwa, D., Eichers, M., Shojaeiarani, J., Kallmeyer, A., 2021. Influence of biobased plasticizers on 3D printed polylactic acid composites filled with sustainable biofiller. *Ind. Crops Prod.* 173, 114132. <https://doi.org/10.1016/j.indcrop.2021.114132>
- Bakrani Balani, S., Chabert, F., Nassiet, V., Cantarel, A., 2019. Influence of printing parameters on the stability of deposited beads in fused filament fabrication of poly(lactic) acid. *Addit. Manuf.* 25, 112–121. <https://doi.org/10.1016/j.addma.2018.10.012>
- Bakrani Balani, S., Mokhtarian, H., Coatanéa, E., Chabert, F., Nassiet, V., Cantarel, A., 2023. Integrated modeling of heat transfer, shear rate, and viscosity for simulation-based characterization of polymer coalescence during material extrusion. *J. Manuf. Process.* 90, 443–459. <https://doi.org/10.1016/j.jmapro.2023.02.021>
- Balasubramanyam, J., Lohith K S, M., Thomas, S., 2014. Lecture notes on engineering physics.
- Bandara, T.M.W.J., Dissanayake, M.A.K.L., Albinsson, I., Mellander, B.-E., 2011. Mobile charge carrier concentration and mobility of a polymer electrolyte containing PEO and Pr4N+I- using electrical and dielectric measurements. *Solid State Ion.* 189, 63–68. <https://doi.org/10.1016/j.ssi.2011.03.004>
- Barbosa, J., Correia, D.M., Fidalgo-Marijuan, A., Gonçalves, R., Fernandes, M., Bermudez, V., Silva, M., Lanceros-Méndez, S., Costa, C., 2021. Sustainable lithium-ion battery separators based on poly(3-hydroxybutyrate-co-hydroxyvalerate) pristine and composite electrospun membranes. *Energy Technol* 10, 2100761. <https://doi.org/10.1002/ente.202100761>
- Barbosa, K.M., Martinez, G.A., Pereira, F. da C., Higuti, R.T., Kitano, C., Galeti, J.H., 2018. High voltage optical sensor insulation using PLA (polylactic acid), in: 2018 13th IEEE International Conference on Industry Applications (INDUSCON). Presented at the 2018 13th IEEE International Conference on Industry

- Applications (INDUSCON), IEEE, São Paulo, Brazil, pp. 1362–1367. <https://doi.org/10.1109/INDUSCON.2018.8627188>
- Bartnikowski, M., Dargaville, T.R., Ivanovski, S., Hutmacher, D.W., 2019. Degradation mechanisms of polycaprolactone in the context of chemistry, geometry and environment. *Prog. Polym. Sci.* 96, 1–20. <https://doi.org/10.1016/j.progpolymsci.2019.05.004>
- Beg, M.D.H., Pickering, K.L., Gauss, C., 2023. The effects of alkaline digestion, bleaching and ultrasonication treatment of fibre on 3D printed harakeke fibre reinforced polylactic acid composites. *Compos. Part Appl. Sci. Manuf.* 166, 107384. <https://doi.org/10.1016/j.compositesa.2022.107384>
- Bello, A., Laredo, E., Grimau, M., 2007. Comparison of analysis of dielectric spectra of PCL in the ϵ^* and the M^* formalism. *J. Non-Cryst. Solids* 353, 4283–4287. <https://doi.org/10.1016/j.jnoncrysol.2007.08.041>
- Benabed, F., Seghier, T., 2015. Dielectric properties and relaxation behavior of high density polyethylene (HDPE). *Appl. Mech. Mater.* 799–800, 1319–1324. <https://doi.org/10.4028/www.scientific.net/AMM.799-800.1319>
- Bergmann, A., Owen, A., 2004. Dielectric relaxation spectroscopy of poly[(R)-3-hydroxybutyrate](PHB) during crystallization. *Polym. Int.* 53, 863–868. <https://doi.org/10.1002/pi.1445>
- Bi, H., Ren, Z., Guo, R., Xu, M., Song, Y., 2018. Fabrication of flexible wood flour/thermoplastic polyurethane elastomer composites using fused deposition molding. *Ind. Crops Prod.* 122, 76–84. <https://doi.org/10.1016/j.indcrop.2018.05.059>
- Bian, J., Zhao, Q., Hou, Z., Dong, J., Yang, Q., Zhang, G., 2019. Effect of alumina shapes on dielectric properties of UV-cured epoxy acrylic composite with alumina. *R. Soc. Open Sci.* 6, 181509. <https://doi.org/10.1098/rsos.181509>
- Billah, A., 2016. Investigation of multiferroic and photocatalytic properties of Li doped BiFeO₃ nanoparticles prepared by ultrasonication (PhD Thesis). Bangladesh university of engineering and technology, Department of physics bangladesh university of engineering and technology dhaka 1000, bangladesh. <https://doi.org/10.13140/RG.2.2.23988.76166>
- Blandón, L., Alvarado-Campo, K.L., Patiño, A.D., Jiménez-Vergara, E., Quintero, M., Montoya-Giraldo, M., Jutinico-Shubach, L.M., Santos-Acevedo, M., Gómez-León, J., 2020. Polyhydroxyalkanoate production from two species of marine bacteria: a comparative study. *J. Polym. Environ.* 28, 2324–2334. <https://doi.org/10.1007/s10924-020-01770-3>
- Bohmert-Tatarev, K., Balbo, I., Kopka, J., Mittendorf, V., Nawrath, C., Poirier, Y., Tischendorf, G., Trethewey, R.N., Willmitzer, L., 2000. Transgenic Arabidopsis plants can accumulate polyhydroxybutyrate to up to 4% of their fresh weight. *Planta* 211, 841–845. <https://doi.org/10.1007/s004250000350>
- Bohmert-Tatarev, K., McAvoy, S., Daughtry, S., Peoples, O.P., Snell, K.D., 2011. High levels of bioplastic are produced in fertile transplastomic tobacco plants engineered with a synthetic operon for the production of polyhydroxybutyrate. *Plant Physiol.* 155, 1690–1708. <https://doi.org/10.1104/pp.110.169581>
- Bonardd, S., Robles, E., Barandiaran, I., Saldías, C., Leiva, A., Kortaberria, G., 2018. Biocomposites with increased dielectric constant based on chitosan and nitrile-modified cellulose nanocrystals. *Carbohydr. Polym.* 199, 20–30. <https://doi.org/10.1016/j.carbpol.2018.06.088>
- Boss, A.F., Braghiroli, F.L., Amaral-Labat, G., Souza, A.A., Baldan, M.R., Bouafif, H., Koubaa, A., 2020. Dielectric characterization of white birch-activated biochar

- composites: A sustainable alternative to radar-absorbing materials. *J. Compos. Mater.* 54, 1233–1244. <https://doi.org/10.1177/0021998319877493>
- Brás, A.R., Malik, P., Dionísio, M., Mano, J.F., 2008. Influence of crystallinity in molecular motions of poly(L-lactic acid) investigated by dielectric relaxation spectroscopy. *Macromolecules* 41, 6419–6430. <https://doi.org/10.1021/ma800842a>
- Brunner, C.T., Baran, E.T., Pinho, E.D., Reis, R.L., Neves, N.M., 2011. Performance of biodegradable microcapsules of poly(butylene succinate), poly(butylene succinate-co-adipate) and poly(butylene terephthalate-co-adipate) as drug encapsulation systems. *Colloids Surf. B Biointerfaces* 84, 498–507. <https://doi.org/10.1016/j.colsurfb.2011.02.005>
- Buschow, K.H.J. (Ed.), 2001. *Encyclopedia of materials: science and technology*. Elsevier, Amsterdam ; New York.
- Butturi, M.A., Marinelli, S., Gamberini, R., Rimini, B., 2020. Ecotoxicity of plastics from informal waste electric and electronic treatment and recycling. *Toxics* 8, 99. <https://doi.org/10.3390/toxics8040099>
- Buzón-Durán, L., Martín-Gil, J., Martín-Ramos, P., 2021. Chapter 4. characterization of cellulose nanoparticles. pp. 86–112. <https://doi.org/10.1039/9781788019521-00086>
- Cao, Y., Zhu, D., Ngai, T., Qin, L., Wu, C., Shen, J., 2014. Dielectric investigations on how Mg salt is dispersed in and released from polylactic acid. *Chin. J. Polym. Sci.* 32, 497–508. <https://doi.org/10.1007/s10118-014-1421-1>
- Carli, L.N., Crespo, J.S., Mauler, R.S., 2011. PHBV nanocomposites based on organomodified montmorillonite and halloysite: The effect of clay type on the morphology and thermal and mechanical properties. *Compos. Part Appl. Sci. Manuf.* 42, 1601–1608. <https://doi.org/10.1016/j.compositesa.2011.07.007>
- Castilho, L.R., Mitchell, D.A., Freire, D.M.G., 2009. Production of polyhydroxyalkanoates (PHAs) from waste materials and by-products by submerged and solid-state fermentation. *Bioresour. Technol.* 100, 5996–6009. <https://doi.org/10.1016/j.biortech.2009.03.088>
- Chai, J., Wang, G., Zhang, A., Li, S., Zhao, J., Zhao, G., Park, C.B., 2022. Ultra-ductile and strong in-situ fibrillated PLA/PTFE nanocomposites with outstanding heat resistance derived by CO₂ treatment. *Compos. Part Appl. Sci. Manuf.* 155, 106849. <https://doi.org/10.1016/j.compositesa.2022.106849>
- Chambers, R., Daly, J.H., Hayward, D., Liggat, J.J., 2001. The effect of processing on the properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymers. *J. Mater. Sci.* 36, 3785–3792.
- Chea, V., Angellier-Coussy, H., Peyron, S., Kemmer, D., Gontard, N., 2016. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) films for food packaging: Physical-chemical and structural stability under food contact conditions. *J. Appl. Polym. Sci.* 133, 41850. <https://doi.org/10.1002/app.41850>
- Chen, C., Kine, A., Nelson, R.D., LaRue, J.C., 2015. Impedance spectroscopy study of conducting polymer blends of PEDOT:PSS and PVA. *Synth. Met.* 206, 106–114. <https://doi.org/10.1016/j.synthmet.2015.05.003>
- Chen, J.-Q., Wang, X., Sun, W.-F., Zhao, H., 2020. Improved water-tree resistances of SEBS/PP semi-crystalline composites under crystallization modifications. *Molecules* 25, 3669. <https://doi.org/10.3390/molecules25163669>
- Chen, K., Yang, F., Yao, C., Liu, T., Jiang, H., 2023. Single material FDM printed nacre-like composite structure with high fracture resistance: Utilizing interface as soft

- phase. *Compos. Commun.* 42, 101682. <https://doi.org/10.1016/j.coco.2023.101682>
- Chen, Yun, Zhang, D., Wu, X., Wang, H., Zhang, C., Yang, W., Chen, Yunfa, 2017. Epoxy/alpha-alumina nanocomposite with high electrical insulation performance. *Prog. Nat. Sci. Mater. Int.* 27, 574–581. <https://doi.org/10.1016/j.pnsc.2017.09.003>
- Chen, Z., Aziz, T., Sun, H., Ullah, A., Ali, A., Cheng, L., Ullah, R., Khan, F.U., 2023. Advances and applications of cellulose bio-composites in biodegradable materials. *J. Polym. Environ.* 31, 2273–2284. <https://doi.org/10.1007/s10924-022-02561-8>
- Chen, Z., Hu, J., Ju, J., Kuang, T., 2019. Fabrication of poly(butylene succinate)/carbon black nanocomposite foams with good electrical conductivity and high strength by a supercritical CO₂ foaming process. *Polymers* 11, 1852. <https://doi.org/10.3390/polym11111852>
- Chiteme, C., McLachlan, D.S., Sauti, G., 2007. AC and DC percolative conductivity of magnetite-cellulose acetate composites. *Phys. Rev. B* 75, 094202. <https://doi.org/10.1103/PhysRevB.75.094202>
- Cho, C.-J., Chen, S.-Y., Kuo, C.-C., Veeramuthu, L., Au-Duong, A.-N., Chiu, Y.-C., Chang, S.-H., 2018. Morphology and optoelectronic characteristics of organic field-effect transistors based on blends of polylactic acid and poly(3-hexylthiophene). *Polym. J.* 50, 975–987. <https://doi.org/10.1038/s41428-018-0087-x>
- Chohan, J.S., Singh, R., Boparai, K.S., Penna, R., Fraternali, F., 2017. Dimensional accuracy analysis of coupled fused deposition modeling and vapour smoothing operations for biomedical applications. *Compos. Part B Eng.* 117, 138–149. <https://doi.org/10.1016/j.compositesb.2017.02.045>
- Ciuprina, F., Andrei, L., Stoian, S., Gabor, R., Panaitescu, D., 2020. Dielectric response and dynamic mechanical analysis of PHBV-TiO₂ nanocomposites, in: 2020 IEEE 3rd International Conference on Dielectrics (ICD). Presented at the 2020 IEEE 3rd International Conference on Dielectrics (ICD), IEEE, Valencia, Spain, pp. 201–204. <https://doi.org/10.1109/ICD46958.2020.9341988>
- Ciuprina, F., Plesa, I., 2011. DC and AC conductivity of LDPE nanocomposites, in: 2011 7TH International Symposium on Advanced Topics in Electrical Engineering (ATEE). pp. 1–6.
- CNRS, 2021. Conférence sur la pollution plastique : du constat aux solutions, la recherche mobilisée. CNRS, En ligne.
- Colbrook, R., Roberts, G.G., 1989. Physical mechanisms of pyroelectricity in Langmuir-Blodgett films. *Thin Solid Films* 179, 335–341. [https://doi.org/10.1016/0040-6090\(89\)90204-6](https://doi.org/10.1016/0040-6090(89)90204-6)
- Colella, R., Chietera, F.P., Catarinucci, L., 2021. Analysis of FDM and DLP 3D-printing technologies to prototype electromagnetic devices for RFID applications. *Sensors* 21, 897. <https://doi.org/10.3390/s21030897>
- Coltelli, M.-B., Mallegni, N., Rizzo, S., Fiori, S., Signori, F., Lazzeri, A., 2021. Compatibilization of poly(Lactic Acid) (PLA)/plasticized cellulose acetate extruded blends through the addition of reactively extruded comb copolymers. *Molecules* 26, 2006. <https://doi.org/10.3390/molecules26072006>
- Compound Interest, 2015. Analytical-Chemistry-Infrared-Spectroscopy.png [WWW Document]. www.compoundchem.com. URL <https://i0.wp.com/www.compoundchem.com/wp->

- content/uploads/2015/02/Analytical-Chemistry-Infrared-Spectroscopy.png (accessed 8.12.23).
- Crétois, R., Delbreilh, L., Dargent, E., Follain, N., Lebrun, L., Saiter, J.M., 2013. Dielectric relaxations in polyhydroxyalkanoates/organoclay nanocomposites. *Eur. Polym. J.* 49, 3434–3444. <https://doi.org/10.1016/j.eurpolymj.2013.07.009>
- Cristea, M., Ionita, D., Iftime, M.M., 2020. Dynamic mechanical analysis investigations of PLA-based Renewable Materials: How Are They Useful? *Materials* 13, 5302. <https://doi.org/10.3390/ma13225302>
- Cristofaro, F., Gigli, M., Bloise, N., Chen, H., Bruni, G., Munari, A., Moroni, L., Lotti, N., Visai, L., 2018. Influence of the nanofiber chemistry and orientation of biodegradable poly(butylene succinate)-based scaffolds on osteoblast differentiation for bone tissue regeneration. *Nanoscale* 10, 8689–8703. <https://doi.org/10.1039/C8NR00677F>
- Cui, C.-H., Yan, D.-X., Pang, H., Jia, L.-C., Xu, X., Yang, S., Xu, J.-Z., Li, Z.-M., 2017. A high heat-resistance bioplastic foam with efficient electromagnetic interference shielding. *Chem. Eng. J.* 323, 29–36. <https://doi.org/10.1016/j.cej.2017.04.050>
- Cuiffo, M.A., Snyder, J., Elliott, A.M., Romero, N., Kannan, S., Halada, G.P., 2017. Impact of the fused deposition (FDM) printing process on polylactic acid (PLA) chemistry and structure. *Appl. Sci.* 7, 579. <https://doi.org/10.3390/app7060579>
- Dalai, S., Parida, C., 2022. Interpretation of Cole–Cole dielectric dispersion of green composites from medical LINAC modified luffa fiber/PLA. *J. Mater. Sci. Mater. Electron.* 33, 6911–6925. <https://doi.org/10.1007/s10854-022-07871-0>
- Dammak, Y., 2022. Propriétés mécaniques et stabilité dimensionnelle des biocomposites fabriqués par impression 3d par extrusion de filament. UQAT, Rouyn-Noranda.
- Dawy, M., Nada, A. -A. M.A., 2003. IR and dielectric analysis of cellulose and Its derivatives. *Polym.-Plast. Technol. Eng.* 42, 643–658. <https://doi.org/10.1081/PPT-120023100>
- de Freitas, R.R.M., Senna, A.M., Botaro, V.R., 2017. Influence of degree of substitution on thermal dynamic mechanical and physicochemical properties of cellulose acetate. *Ind. Crops Prod.* 109, 452–458. <https://doi.org/10.1016/j.indcrop.2017.08.062>
- Delpouve, N., Araujo, S., Domenek, S., Guinault, A., Delbreilh, L., Dargent, E., 2018. Relaxation dynamics in plasticized polylactide. *AIP Conf. Proc.* 1981, 20055. <https://doi.org/10.1063/1.5045917>
- Delpouve, N., Delbreilh, L., Stoclet, G., Saiter, A., Dargent, E., 2014. Structural dependence of the molecular mobility in the amorphous fractions of polylactide. *Macromolecules* 47, 5186–5197. <https://doi.org/10.1021/ma500839p>
- Deshmukh, K., Ahamed, M.B., Deshmukh, R.R., Pasha, S.K.K., Sadasivuni, K.K., Polu, A.R., Ponnamma, D., AlMaadeed, M.A.-A., Chidambaram, K., 2017. Newly developed biodegradable polymer nanocomposites of cellulose acetate and Al₂O₃ nanoparticles with enhanced dielectric performance for embedded passive applications. *J. Mater. Sci. Mater. Electron.* 28, 973–986. <https://doi.org/10.1007/s10854-016-5616-9>
- Desmars, L., Galy, J., Bachellerie, D., Cristiano-Tassi, A., Haller, S., Pruvost, S., 2018. High voltage electrical properties of epoxy/h-BN microcomposites, in: 2018 IEEE 2nd International Conference on Dielectrics (ICD). IEEE, pp. 1–5. <https://doi.org/10.1109/ICD.2018.8514777>
- Dhakal, H., Bourmaud, A., Berzin, F., Almansour, F., Zhang, Z., Shah, D.U., Beaugrand, J., 2018. Mechanical properties of leaf sheath date palm fibre waste biomass

- reinforced polycaprolactone (PCL) biocomposites. *Ind. Crops Prod.* 126, 394–402. <https://doi.org/10.1016/j.indcrop.2018.10.044>
- Dhal, J.P., Mishra, S.C., 2013. Processing and properties of natural fiber-reinforced polymer composite. *J. Mater.* 2013, 297213. <https://doi.org/10.1155/2013/297213>
- Dharmalingam, G., Arun Prasad, M., Salunkhe, S., 2022. Investigation of impact strength at different infill rates biodegradable PLA constituent through fused deposition modeling. *Mater. Today Proc.* 62, 551–558. <https://doi.org/10.1016/j.matpr.2022.03.591>
- Dichtl, C., Sippel, P., Krohns, S., 2017. Dielectric properties of 3D printed polylactic acid. *Adv. Mater. Sci. Eng.* 2017, 6913835. <https://doi.org/10.1155/2017/6913835>
- Dicker, M.P.M., Duckworth, P.F., Baker, A.B., Francois, G., Hazzard, M.K., Weaver, P.M., 2014. Green composites: a review of material attributes and complementary applications. *Compos. Part Appl. Sci. Manuf.* 56, 280–289. <https://doi.org/10.1016/j.compositesa.2013.10.014>
- Ding, R., Duan, Z., Sun, Y., Yuan, Q., Tien, T.T., Zúniga, M.G., Oh, E., Nam, J.-D., Suhr, J., 2023. Enhancement of 3D printability and mechanical properties of polylactic acid/lignin biocomposites via interface engineering. *Ind. Crops Prod.* 194, 116286. <https://doi.org/10.1016/j.indcrop.2023.116286>
- Drakopoulos, S.X., Karger-Kocsis, J., Kmetty, Á., Lendvai, L., Psarras, G.C., 2017. Thermoplastic starch modified with microfibrillated cellulose and natural rubber latex: A broadband dielectric spectroscopy study. *Carbohydr. Polym.* 157, 711–718. <https://doi.org/10.1016/j.carbpol.2016.10.036>
- Drakopoulos, S.X., Karger-Kocsis, J., Psarras, G.C., 2020. The effect of micro-fibrillated cellulose upon the dielectric relaxations and DC conductivity in thermoplastic starch bio-composites. *J. Appl. Polym. Sci.* 137, 49573. <https://doi.org/10.1002/app.49573>
- Dreux, X., 2019. Comportement viscoélastique à l'état fondu et structure d'acétates de cellulose plastifiés. Université de Lyon.
- Dubois, J., 2001. Propriétés diélectriques des plastiques. *Tech. Ing. - Plast. Compos.* 1–20. <https://doi.org/10.51257/a-v1-am3140>
- Ebrahim, Sh.M., Kashyout, A.B., Soliman, M.M., 2007. Electrical and structural properties of polyaniline/cellulose triacetate blend films. *J. Polym. Res.* 14, 423–429. <https://doi.org/10.1007/s10965-007-9125-7>
- Eesaee, M., David, E., Demarquette, N.R., Fabiani, D., 2018. Electrical breakdown properties of clay-based LDPE blends and nanocomposites. *J. Nanomater.* 2018, 7921725. <https://doi.org/10.1155/2018/7921725>
- Eichers, M., Bajwa, D., Shojaeiarani, J., Bajwa, S., 2022. Biobased plasticizer and cellulose nanocrystals improve mechanical properties of polylactic acid composites. *Ind. Crops Prod.* 183, 114981. <https://doi.org/10.1016/j.indcrop.2022.114981>
- El Assimi, T., Blažic, R., Vidović, E., Raihane, M., El Meziane, A., Baouab, M.H.V., Khouloud, M., Beniazza, R., Kricheldorf, H., Lahcini, M., 2021. Polylactide/cellulose acetate biocomposites as potential coating membranes for controlled and slow nutrients release from water-soluble fertilizers. *Prog. Org. Coat.* 156, 106255. <https://doi.org/10.1016/j.porgcoat.2021.106255>
- Elloumi, I., Koubaa, A., Kharrat, W., Bradai, C., Elloumi, A., 2021. Dielectric properties of wood-polymer composites: effects of frequency, fiber nature, proportion, and chemical composition. *J. Compos. Sci.* 5, 1–11. <https://doi.org/10.3390/jcs5060141>

- Elsawy, M.A., Saad, G.R., Sayed, A.M., 2016. Mechanical, thermal, and dielectric properties of poly(lactic acid)/chitosan nanocomposites. *Polym. Eng. Sci.* 56, 987–994. <https://doi.org/10.1002/pen.24328>
- Erdönmez, S., Güven Özdemir, Z., 2020. The mechanical and dielectric properties of polypropylene reinforced with BiSr₂CaCu₂O_{6.5} ceramic. *Polym. Bull.* 77, 1793–1812. <https://doi.org/10.1007/s00289-019-02829-5>
- European Bioplastics, 2023a. Bioplastics market data. Eur. Bioplastics EV. URL <https://www.european-bioplastics.org/market/> (accessed 2.11.24).
- European Bioplastics, 2023b. Applications for bioplastics. Eur. Bioplastics EV. URL <https://www.european-bioplastics.org/market/applications-sectors/> (accessed 2.11.24).
- Ezzeddine, I., Ghorbel, N., Ilsouk, M., Arous, M., Lahcini, M., Bouharras, F.Z., Raihane, M., Kallel, A., 2021. Dielectric and thermal characteristics of Beidellite nanoclay-reinforced poly(butylene succinate). *Mater. Chem. Phys.* 258, 123855. <https://doi.org/10.1016/j.matchemphys.2020.123855>
- Fahmy, T., Ahmed, M.T., El-kotp, A., Abdelwahed, H.G., Alshaeer, M.Y., 2016. Broadband dielectric spectroscopy and electric modulus analysis of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and related copolymers *Films. Int. J. Phys. Appl.* 8, 1–14.
- Fal, J., Bulanda, K., Oleksy, M., Sobczak, J., Shi, J., Liu, M., Boncel, S., Żyła, G., 2021. High AC and DC electroconductivity of scalable and economic graphite–diamond polylactide nanocomposites. *Materials* 14, 2835. <https://doi.org/10.3390/ma14112835>
- Fang, J., Meng, C., Zhang, G., Xu, Z., 2023. High-performance flexible PANI/PLA textiles with antibacterial, flame retardant and electromagnetic shielding for all-solid-state supercapacitors and sensors. *Fibers Polym.* 24, 1015–1028. <https://doi.org/10.1007/s12221-023-00107-w>
- Fang, L., Wu, C., Qian, R., Xie, L., Yang, K., Jiang, P., 2014. Nano–micro structure of functionalized boron nitride and aluminum oxide for epoxy composites with enhanced thermal conductivity and breakdown strength. *RSC Adv.* 4, 21010–21017. <https://doi.org/10.1039/C4RA01194E>
- Feng, Y., Peng, C., Deng, Q., Li, Y., Hu, J., Wu, Q., 2018. Annealing and stretching induced high energy storage properties in all-organic composite dielectric films. *Materials* 11, 2279. <https://doi.org/10.3390/ma11112279>
- Fernandez-Vicente, M., Calle, W., Ferrandiz, S., Conejero, A., 2016. Effect of infill parameters on tensile mechanical behavior in desktop 3D printing. *3D Print. Addit. Manuf.* 3, 183–192. <https://doi.org/10.1089/3dp.2015.0036>
- Filimon, A., Dobos, A.M., Musteata, V., 2019. New perspectives on development of polysulfones/cellulose derivatives based ionic-exchange membranes: Dielectric response and hemocompatibility study. *Carbohydr. Polym.* 226, 115300. <https://doi.org/10.1016/j.carbpol.2019.115300>
- Fischer, S., Thümmeler, K., Volkert, B., Hettrich, K., Schmidt, I., Fischer, K., 2008. Properties and applications of cellulose acetate. *Macromol. Symp.* 262, 89–96. <https://doi.org/10.1002/masy.200850210>
- Forti, V., Baldé, C.P., Kuehr, R., Bel, G., 2020. The Global E-waste Monitor 2020. United Nations University (UNU)/United Nations Institute for Training and Research (UNITAR).
- Fredin, L.A., Li, Z., Lanagan, M.T., Ratner, M.A., Marks, T.J., 2013. Sustainable high capacitance at high frequencies: metallic aluminum–polypropylene nanocomposites. *ACS Nano* 7, 396–407. <https://doi.org/10.1021/nn3044148>

- Fryń, P., Lalik, S., Górska, N., Iwan, A., Marzec, M., 2021. Comparison of the dielectric properties of Ecoflex® with L,D-poly(lactic acid) or polycaprolactone in the presence of SWCN or 5CB. *Materials* 14, 1719. <https://doi.org/10.3390/ma14071719>
- Fu, M., Chen, G., Dissado, L.A., Fothergill, J.C., Zou, C., 2007. The effect of gamma irradiation on space charge behaviour and dielectric spectroscopy of low-density polyethylene, in: 2007 IEEE International Conference on Solid Dielectrics. Presented at the 2007 IEEE International Conference on Solid Dielectrics, IEEE, Winchester, pp. 442–445. <https://doi.org/10.1109/ICSD.2007.4290846>
- Gad, M., Abualsaud, R., Rahoma, A., Al-Thobity, A.M., Alabidi, K., Akhtar, S., 2018. Effect of zirconium oxide nanoparticles addition on the optical and tensile properties of polymethyl methacrylate denture base material. *Int. J. Nanomedicine* 13, 283–292. <https://doi.org/10.2147/IJN.S152571>
- Gallot-Lavallee, O., Heux, L., 2013. Dielectric spectroscopy on a PHBV bio-polymer, in: 2013 Annual Report Conference on Electrical Insulation and Dielectric Phenomena. Presented at the 2013 IEEE Conference on Electrical Insulation and Dielectric Phenomena - (CEIDP 2013), IEEE, Chenzhen, China, pp. 559–562. <https://doi.org/10.1109/CEIDP.2013.6748275>
- Galos, J., Hu, Y., Ravindran, A.R., Ladani, R.B., Mouritz, A.P., 2021. Electrical properties of 3D printed continuous carbon fibre composites made using the FDM process. *Compos. Part Appl. Sci. Manuf.* 151, 106661. <https://doi.org/10.1016/j.compositesa.2021.106661>
- Gasmi, S., Hassan, M.K., Luyt, A.S., 2019. Crystallization and dielectric behaviour of PLA and PHBV in PLA/PHBV blends and PLA/PHBV/TiO₂ nanocomposites. *EXPRESS Polym. Lett.* 13, 199–212. <https://doi.org/10.3144/expresspolymlett.2019.16>
- Gérard, T., Budtova, T., 2011. Preparation and characterization of polyhydroxyalkanoates (PHA) and polylactide (PLA) blends, in: 27th World Congress of the Polymer Processing Society. Presented at the 27th World Congress of the Polymer Processing Society, Morocco, pp. 1–5.
- Gigante, V., Seggiani, M., Cinelli, P., Signori, F., Vania, A., Navarini, L., Amato, G., Lazzeri, A., 2021. Utilization of coffee silverskin in the production of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) biopolymer-based thermoplastic biocomposites for food contact applications. *Compos. Part Appl. Sci. Manuf.* 140, 106172. <https://doi.org/10.1016/j.compositesa.2020.106172>
- Gojayev, E.M., Aliyeva, Sh.V., Khalilova, X.S., Jafarova, G.S., Jabarov, S.H., 2019. The dielectric properties and electrical conductivity of LDPE modified by fillers of biological origin. *Int. J. Mod. Phys. B* 33, 1950309. <https://doi.org/10.1142/S0217979219503090>
- Gonzalez-Garzon, M., Shahbikian, S., Huneault, M.A., 2018. Properties and phase structure of melt-processed PLA/PMMA blends. *J. Polym. Res.* 25, 58. <https://doi.org/10.1007/s10965-018-1438-1>
- Goulas, A., Zhang, S., Cadman, D.A., Järveläinen, J., Mylläri, V., Whittow, W.G., Vardaxoglou, J. (Yiannis) C., Engstrøm, D.S., 2019. The impact of 3D printing process parameters on the dielectric properties of high permittivity composites. *Designs* 3, 50. <https://doi.org/10.3390/designs3040050>
- Gregorova, A., Hrabalova, M., Wimmer, R., Saake, B., Altaner, C., 2009. Poly(lactide acid) composites reinforced with fibers obtained from different tissue types of *Picea sitchensis*. *J. Appl. Polym. Sci.* 114, 2616–2623. <https://doi.org/10.1002/app.30819>

- Guezguez, I., Mrabet, B., Ferjani, E., 2013. XPS and contact angle characterization of surface modified cellulose acetate membranes by mixtures of PMHS/PDMS. *Desalination* 313, 208–211. <http://dx.doi.org/10.1016/j.desal.2012.11.018>
- Guinault, A., Sollogoub, C., Domenek, S., Grandmontagne, A., Ducruet, V., 2010. Influence of crystallinity on gas barrier and mechanical properties of pla food packaging films. *Int. J. Mater. Form.* 3, 603–606. <https://doi.org/10.1007/s12289-010-0842-9>
- Gunasekaran, K.N., Aravinth, V., Muthu Kumaran, C.B., Madhankumar, K., Pradeep Kumar, S., 2021. Investigation of mechanical properties of PLA printed materials under varying infill density. *Mater. Today Proc.* 45, 1849–1856. <https://doi.org/10.1016/j.matpr.2020.09.041>
- Gunduz, I.E., McClain, M.S., Cattani, P., Chiu, G.T.-C., Rhoads, J.F., Son, S.F., 2018. 3D printing of extremely viscous materials using ultrasonic vibrations. *Addit. Manuf.* 22, 98–103. <https://doi.org/10.1016/j.addma.2018.04.029>
- Guo, L.Q., Tao, J., Zhu, L.Q., Xiao, H., Gao, W.T., Yu, F., Fu, Y.M., 2018. Starch-based biopolymer electrolyte gated oxide synaptic transistors. *Org. Electron.* 61, 312–317. <https://doi.org/10.1016/j.orgel.2018.06.009>
- Hamad, K., Kaseem, M., Deri, F., Ko, Y.G., 2016. Mechanical properties and compatibility of polylactic acid/polystyrene polymer blend. *Mater. Lett.* 164, 409–412. <https://doi.org/10.1016/j.matlet.2015.11.029>
- Hamciuc, C., Serbezeanu, D., Carja, I.-D., Vlad-Bubulac, T., Musteata, V.-E., Forrat Pérez, V., Guillem López, C., López Buendia, A.M., 2013. Effect of DOPO units and of polydimethylsiloxane segments on the properties of epoxy resins. *J. Mater. Sci.* 48, 8520–8529. <https://doi.org/10.1007/s10853-013-7670-5>
- Han, B., Yin, C., Chang, J., Pang, Y., Lv, P., Song, W., Wang, X., 2020. Study on the structure and dielectric properties of zeolite/LDPE nanocomposite under thermal aging. *Polymers* 12, 2108. <https://doi.org/10.3390/polym12092108>
- He, L., Zeng, J., Huang, Y., Yang, Xiong, Li, D., Chen, Y., Yang, Xiangyu, Wang, D., Zhang, Y., Fu, Z., 2020. Enhanced thermal conductivity and dielectric properties of h-BN/LDPE composites. *Materials* 13, 4738. <https://doi.org/10.3390/ma13214738>
- Hegde, V., 2017. Dielectric study of biodegradable and/or bio-based polymeric materials (Materials). Université Grenoble Alpes, Grenoble.
- Hegde, V.J., Gallot-Lavallee, O., Heux, L., 2016. Dielectric study of polycaprolactone: a biodegradable polymer, in: 2016 IEEE International Conference on Dielectrics (ICD). Presented at the 2016 IEEE International Conference on Dielectrics (ICD), IEEE, Montpellier, France, pp. 293–296. <https://doi.org/10.1109/ICD.2016.7547602>
- Hegde, V.J., Gallot-Lavallee, O., Heux, L., 2015. Overview on thermal and electrical properties of biodegradable polymers, in: 2015 IEEE 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM). Presented at the 2015 IEEE 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM), IEEE, Sydney, Australia, pp. 540–543. <https://doi.org/10.1109/ICPADM.2015.7295328>
- Heid, T., Frechette, M., David, E., 2016. Enhanced electrical and thermal performances of nanostructured epoxy/POSS composites. *IEEE Trans. Dielectr. Electr. Insul.* 23, 1732–1742. <https://doi.org/10.1109/TDEI.2016.005531>
- Henning, C., Schmid, A., Hecht, S., Ruckmar, C., Harre, K., Bauer, R., 2019. Usability of bio-based polymers for PCB, in: 2019 42nd International Spring Seminar on Electronics Technology (ISSE). Presented at the 2019 42nd International Spring

- Seminar on Electronics Technology (ISSE), IEEE, Wroclaw, Poland, pp. 1–7. <https://doi.org/10.1109/ISSE.2019.8810257>
- Henning, C., Schmid, A., Ruckmar, C., Zink, P., Bauer, R., Harre, K., Gobel, G., 2020. Realization of double-sided wiring boards of biopolymer, in: 2020 43rd International Spring Seminar on Electronics Technology (ISSE). IEEE, Demanovska Valley, Slovakia, pp. 1–6. <https://doi.org/10.1109/ISSE49702.2020.9121011>
- Hikosaka, S., Ishikawa, H., Ohki, Y., 2008. Effects of crystallinity on thermally stimulated current and complex permittivity of poly(L-lactide), in: 2008 Annual Report Conference on Electrical Insulation and Dielectric Phenomena. Presented at the 2008 Annual Report Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), IEEE, Quebec City, QC, Canada, pp. 497–500. <https://doi.org/10.1109/CEIDP.2008.4772773>
- Hirai, Hiroto Ishikawa, Yoshimichi Ohki, 2007. Electrical conduction properties of several biodegradable polymers, in: 2007 Annual Report - Conference on Electrical Insulation and Dielectric Phenomena. Presented at the 2007 Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, IEEE, Vancouver, BC, Canada, pp. 592–595. <https://doi.org/10.1109/CEIDP.2007.4451542>
- Hirai, N., Maeno, Y., Tamura, H., Kaneko, D., Tanaka, T., Ohki, Y., Tajitsu, Y., Kohtoh, M., Okabe, S., 2004. Dielectric properties of biodegradable polylactic acid and starch ester, in: Proceedings of the 2004 IEEE International Conference on Solid Dielectrics, 2004. ICSD 2004. Presented at the Proceedings of the 2004 IEEE International Conference on Solid Dielectrics, 2004. ICSD 2004., IEEE, Toulouse, France, pp. 87–89. <https://doi.org/10.1109/ICSD.2004.1350296>
- Horvath, J., 2014. Mastering 3D Printing. Apress, Berkeley, CA. <https://doi.org/10.1007/978-1-4842-0025-4>
- Hossain, Md.A., Roy, C.K., Sarkar, S.D., Roy, H., Howlader, A.H., Firoz, S.H., 2020. Improvement of the strength of poly(acrylic acid) hydrogels by the incorporation of functionally modified nanocrystalline Cellulose. *Mater. Adv.* 1, 2107–2116. <https://doi.org/10.1039/D0MA00478B>
- Hrichi, S., Arous, M., Raihane, M., Lahcini, M., Elghoui, H., Bouharras, F.Z., Kallel, A., 2019. Dielectric and electrical properties of poly(ϵ -caprolactone)/ organomodified clay bionanocomposites prepared in open air by in situ polymerization. *J. Advances Phys.* 15, 6101–6120. <https://doi.org/10.24297/jap.v15i0.8015>
- Hsiao, K.-T., 2013. Embedded single carbon fibre to sense the thermomechanical behavior of an epoxy during the cure process. *Compos. Part Appl. Sci. Manuf.* 46, 117–121. <https://doi.org/10.1016/j.compositesa.2012.11.007>
- Huang, X., Zhi, C., Jiang, P., Golberg, D., Bando, Y., Tanaka, T., 2013. Polyhedral oligosilsesquioxane-modified boron nitride nanotube based epoxy nanocomposites: an ideal dielectric material with high thermal conductivity. *Adv. Funct. Mater.* 23, 1824–1831. <https://doi.org/10.1002/adfm.201201824>
- Ibrahim, M.I., Alsafadi, D., Alamry, K.A., Hussein, M.A., 2021. Properties and applications of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) biocomposites. *J. Polym. Environ.* 29, 1010–1030. <https://doi.org/10.1007/s10924-020-01946-x>
- Immonen, K., Willberg-Keyriläinen, P., Ropponen, J., Nurmela, A., Metsä-Kortelainen, S., Kaukonen, O.-V., Kangas, H., 2021. Thermoplastic cellulose-based compound for additive manufacturing. *Molecules* 26, 1701. <https://doi.org/10.3390/molecules26061701>

- International Standard, 2007. IEC 60085:2007 - Electrical insulation - Thermal evaluation and designation.
- Ioannou, G., Patsidis, A., Psarras, G.C., 2011. Dielectric and functional properties of polymer matrix/ZnO/BaTiO₃ hybrid composites. *Compos. Part Appl. Sci. Manuf.* 42, 104–110. <https://doi.org/10.1016/j.compositesa.2010.10.010>
- Iqhrammullah, M., Marlina, M., Khalil, H.P.S.A., Kurniawan, K.H., Suyanto, H., Hedwig, R., Karnadi, I., Olaiya, N.G., Abdullah, C.K., Abdulmajid, S.N., 2020. Characterization and performance evaluation of cellulose acetate–polyurethane film for lead II ion removal. *Polymers* 12, 1317. <https://doi.org/10.3390/polym12061317>
- Ishak, K.A., Velayutham, T.S., Annuar, M.S.M., Sirajudeen, A.A.O., 2021. Structure-property interpretation of biological polyhydroxyalkanoates with different monomeric composition: Dielectric spectroscopy investigation. *Int. J. Biol. Macromol.* 169, 311–320. <https://doi.org/10.1016/j.ijbiomac.2020.12.090>
- Ishikawa, H., Ohki, Y., 2008. Temperature dependence of complex permittivity in biodegradable polybutylene succinate. *IEEJ Trans. Fundam. Mater.* 128, 647–651. <https://doi.org/10.1541/ieejfms.128.647>
- Ishikawa, H., Omori, S., Ohki, Y., 2007. Dielectric properties of polybutylene succinate and polybutylene succinate adipate, in: 2007 IEEE International Conference on Solid Dielectrics. Presented at the 2007 IEEE International Conference on Solid Dielectrics, IEEE, Winchester, UK, pp. 635–638. <https://doi.org/10.1109/ICSD.2007.4290893>
- Islam, N., Gafur, M.A., Khan, A.H., 2021. Conduction mechanism and conductivity behaviour of pure PP and PP banana fiber (PP-B) composites. *J. Build. Mater. Sci.* 2, 16–20. <https://doi.org/10.30564/jbms.v2i2.2870>
- Izci, E., Bowler, N., 2019. Dielectric properties of isotactic polypropylene and montmorillonite nanocomposites, in: 2010 Annual Report Conference on Electrical Insulation and Dielectric Phenomena. Presented at the 2010 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, West Lafayette, IN, USA, pp. 1–4. <https://doi.org/10.1109/CEIDP.2010.5724084>
- Jacob, M., Varughese, K.T., Thomas, S., 2006. Dielectric characteristics of sisal–oil palm hybrid biofibre reinforced natural rubber biocomposites. *J. Mater. Sci.* 41, 5538–5547. <https://doi.org/10.1007/s10853-006-0298-y>
- Jariyasakoolroj, P., 2014. Silane modified starch for compatible reactive blend with poly(lactic acid). *Carbohydr. Polym.* 106, 255–263.
- Jasim, S.M., Ali, N.A., 2019. Properties characterization of plasticized polylactic acid biochar (bio carbon) nano-composites for antistatic packaging. *Iraqi J. Phys.* 17, 13–26. <https://doi.org/10.20723/ijp.17.42.13-26>
- Jeon, G.W., An, J.-E., Jeong, Y.G., 2012. High performance cellulose acetate propionate composites reinforced with exfoliated graphene. *Compos. Part B Eng.* 43, 3412–3418. <https://doi.org/10.1016/j.compositesb.2012.01.023>
- Jeszka, J.K., Pietrzak, L., Pluta, M., Boiteux, G., 2010. Dielectric properties of polylactides and their nanocomposites with montmorillonite. *J. Non-Cryst. Solids* 356, 818–821. <https://doi.org/10.1016/j.jnoncrysol.2009.06.057>
- Jilal, I., Barkany, S.E., Bahari, Z., Idrissi, A.E., Salhi, A., Abou-Salama, M., Amhamdi, H., 2018. A new equation between surface tension and solubility parameters of cellulose derivatives depending on DS: application on cellulose acetate. *Appl. J. Environ. Eng. Sci.* 4, 171–181.

- Jin, K., Tang, Y., Zhu, X., Zhou, Y., 2020. Polylactic acid based biocomposite films reinforced with silanized nanocrystalline cellulose. *Int. J. Biol. Macromol.* 162, 1109–1117. <https://doi.org/10.1016/j.ijbiomac.2020.06.201>
- Jin, S., Cao, J., Li, J., Han, J., Mei, C., Li, K., Xiao, H., 2022. Biomass-based functional film integrated with nitrogen-coordinating boronic ester and cellulose-barium titanate nanohybrids. *Ind. Crops Prod.* 189, 115765. <https://doi.org/10.1016/j.indcrop.2022.115765>
- Jirků, P., Urban, J., Müller, M., Kolář, V., Chandan, V., Svobodová, J., Mishra, R.K., Jamshaid, H., 2023. Evaluation of mechanical properties and filler interaction in the field of SLA polymeric additive manufacturing. *Materials* 16, 4955. <https://doi.org/10.3390/ma16144955>
- Johns, J., Nakason, C., 2011. Dielectric properties of natural rubber/chitosan blends: Effects of blend ratio and compatibilization. *J. Non-Cryst. Solids* 357, 1816–1821. <https://doi.org/10.1016/j.jnoncrysol.2011.01.036>
- Joseph, S., Deenadayalan, E., Mahanwar, P.A., 2015. Studies on melt processable biocomposites of polylactic acid. *J. Polym. Environ.* 23, 321–333. <https://doi.org/10.1007/s10924-014-0668-5>
- Jow, T.R., Cygan, P.J., 1992. Investigation of dielectric breakdown of polyvinylidene fluoride using AC and DC methods, in: Conference Record of the 1992 IEEE International Symposium on Electrical Insulation. Presented at the Conference Record of the 1992 IEEE International Symposium on Electrical Insulation, IEEE, Baltimore, MD, USA, pp. 181–184. <https://doi.org/10.1109/ELINSL.1992.247024>
- Junpha, J., Wisitsoraat, A., Prathumwan, R., Chaengsawang, W., Khomungkhun, K., Subannajui, K., 2020. Electronic tongue and cyclic voltammetric sensors based on carbon nanotube/polylactic composites fabricated by fused deposition modelling 3D printing. *Mater. Sci. Eng. C* 117, 111319. <https://doi.org/10.1016/j.msec.2020.111319>
- Kang, H., Li, Y., Gong, M., Guo, Y., Guo, Z., Fang, Q., Li, X., 2018. An environmentally sustainable plasticizer toughened polylactide. *RSC Adv.* 8, 11643–11651. <https://doi.org/10.1039/C7RA13448G>
- Katayama, J., Ohki, Y., Fuse, N., Kozako, M., Tanaka, T., 2013. Effects of nanofiller materials on the dielectric properties of epoxy nanocomposites. *IEEE Trans. Dielectr. Electr. Insul.* 20, 157–165. <https://doi.org/10.1109/TDEI.2013.6451354>
- Kato, F., Matsushita, M., Omori, S., Ohki, Y., 2006. Effect of endothermic reaction associated with glass transition on the breakdown strength of biodegradable polymer films, in: 2006 Annual Report Conference on Electrical Insulation and Dielectric Phenomena. pp. 241–244. <https://doi.org/10.1109/CEIDP.2006.312106>
- Kemari, Y., Teyssedre, G., Mekhaldi, A., Tegar, M., 2020. Dielectric properties and β -relaxation in cross-linked polyethylene: effect of thermal aging, in: 2020 IEEE 3rd International Conference on Dielectrics (ICD). Presented at the Valencia, Spain, IEEE, pp. 73–76. <https://doi.org/10.1109/ICD46958.2020.9341896>
- Khalaf, A., 2013. Graphite and copper nanoparticles in PVC/NBR composites. KGK Rubberpoint.
- Khan, M.Q., Kharaghani, D., Sanaullah, Shahzad, A., Saito, Y., Yamamoto, T., Ogasawara, H., Kim, I.S., 2019. Fabrication of antibacterial electrospun cellulose acetate/ silver-sulfadiazine nanofibers composites for wound dressings applications. *Polym. Test.* 74, 39–44. <https://doi.org/10.1016/j.polymertesting.2018.12.015>

- Khare, R.A., Bhattacharyya, A.R., Kulkarni, A.R., Saroop, M., Biswas, A., 2008. Influence of multiwall carbon nanotubes on morphology and electrical conductivity of PP/ABS blends. *J. Polym. Sci. Part B Polym. Phys.* 46, 2286–2295. <https://doi.org/10.1002/polb.21560>
- Khoshnevisan, K., Maleki, H., Samadian, H., Shahsavari, S., Sarrafzadeh, M.H., Larijani, B., Dorkoosh, F.A., Haghpanah, V., Khorramizadeh, M.R., 2018. Cellulose acetate electrospun nanofibers for drug delivery systems: Applications and recent advances. *Carbohydr. Polym.* 198, 131–141. <https://doi.org/10.1016/j.carbpol.2018.06.072>
- Khouaja, A., Koubaa, A., Daly, H., 2021. Dielectric properties and thermal stability of cellulose high-density polyethylene bio-based composites. *Ind. Crops Prod.* 171, 113928. <https://doi.org/10.1016/j.indcrop.2021.113928>
- Kim, H., Johnson, J., Chavez, L.A., Garcia Rosales, C.A., Tseng, T.-L.B., Lin, Y., 2018. Enhanced dielectric properties of three phase dielectric MWCNTs/BaTiO₃/PVDF nanocomposites for energy storage using fused deposition modeling 3D printing. *Ceram. Int.* 44, 9037–9044. <https://doi.org/10.1016/j.ceramint.2018.02.107>
- Koller, M., Bona, R., Braunegg, G., Hermann, C., Horvat, P., Kroutil, M., Martinz, J., Neto, J., Pereira, L., Varila, P., 2005. Production of polyhydroxyalkanoates from agricultural waste and surplus materials. *Biomacromolecules* 6, 561–565. <https://doi.org/10.1021/bm049478b>
- Kortaberria, G., Marieta, C., Jimeno, A., Arruti, P., Mondragon, I., 2006. Crystallization of poly(L-lactid acid) monitored by dielectric relaxation spectroscopy and atomic force microscopy. *J. Microsc.* 224, 277–289. <https://doi.org/10.1111/j.1365-2818.2006.01701.x>
- Kosbar, L.L., Gelorme, J.D., Japp, R.M., Fotorny, W.T., 2000. Introducing biobased materials into the electronics industry. *J. Ind. Ecol.* 3, 93–105. <https://doi.org/10.1162/108819800300106401>
- Kotp, A.E., 2010. Effect of conductive relaxation on dielectric relaxation in Poly (3-hydroxy butyrate) PHB semi-crystalline polymer. *Int. J. Basic Appl. Sci.* 10, 28–38.
- Koubaa, A., Perré, P., Hutcheon, R.M., Lessard, J., 2008. Complex dielectric properties of the sapwood of aspen, white birch, yellow birch, and sugar maple. *Dry. Technol.* 26, 568–578. <https://doi.org/10.1080/07373930801944762>
- Kumar, V., Kumar, R., 2012. Dielectric and mechanical properties of alkali- and silane-treated bamboo-epoxy nanocomposites. *J. Compos. Mater.* 46, 3089–3101. <https://doi.org/10.1177/0021998311435831>
- Kundu, M., Mandal, A., 2022. Additive manufacturing process (3D printing): “a critical review of techniques, applications & future scope.” *Int. J. Eng. Res.* 11, 171–193.
- Kuzmanić, I., Vujović, I., Petković, M., Šoda, J., 2023. Influence of 3D printing properties on relative dielectric constant in PLA and ABS materials. *Prog. Addit. Manuf.* 8, 703–710. <https://doi.org/10.1007/s40964-023-00411-0>
- Labet, M., Thielemans, W., 2009. Synthesis of polycaprolactone: a review. *Chem. Soc. Rev.* 38, 3484. <https://doi.org/10.1039/b820162p>
- Ladhar, A., Arous, M., Kaddami, H., Ayadi, Z., Kallel, A., 2017. Correlation between the dielectric and the mechanical behavior of cellulose nanocomposites extracted from the rachis of the date palm tree. *IOP Conf. Ser. Mater. Sci. Eng.* 258, 012001. <https://doi.org/10.1088/1757-899X/258/1/012001>
- Lajewski, S., Mauch, A., Geiger, K., Bonten, C., 2021. Rheological characterization and modeling of thermally unstable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). *Polymers* 13, 2294. <https://doi.org/10.3390/polym13142294>

- Lamberti, P., Spinelli, G., Kuzhir, P.P., Guadagno, L., Naddeo, C., Romano, V., Kotsilkova, R., Angelova, P., Georgiev, V., 2018. Evaluation of thermal and electrical conductivity of carbon-based PLA nanocomposites for 3D printing. *AIP Conf. Proc.* 1981, 20158. <https://doi.org/10.1063/1.5046020>
- Laput, O., Vasenina, I., Salvadori, M.C., Savkin, K., Zuza, D., Kurzina, I., 2019. Low-temperature plasma treatment of polylactic acid and PLA/HA composite material. *J. Mater. Sci.* 54, 11726–11738. <https://doi.org/10.1007/s10853-019-03693-4>
- Larguech, S., Triki, A., Ramachandran, M., Kallel, A., 2021. Dielectric properties of jute fibers reinforced poly(lactic acid)/poly(butylene succinate) blend matrix. *J. Polym. Environ.* 29, 1240–1256. <https://doi.org/10.1007/s10924-020-01927-0>
- Lau, K.Y., Piah, M.A.M., Ching, K.Y., 2017. Correlating the breakdown strength with electric field analysis for polyethylene/silica nanocomposites. *J. Electrostat.* 86, 1–11. <https://doi.org/10.1016/j.elstat.2016.12.021>
- Lay, M., Thajudin, N.L.N., Hamid, Z.A.A., Rusli, A., Abdullah, M.K., Shuib, R.K., 2019. Comparison of physical and mechanical properties of PLA, ABS and nylon 6 fabricated using fused deposition modeling and injection molding. *Compos. Part B Eng.* 176, 107341. <https://doi.org/10.1016/j.compositesb.2019.107341>
- Lecoublet, M., Ragoubi, M., Leblanc, N., Koubaa, A., 2023. Dielectric and rheological performances of cellulose acetate, polylactic acid and polyhydroxybutyrate-co-valerate biobased blends. *Polymer* 285, 126358. <https://doi.org/10.1016/j.polymer.2023.126358>
- Lee, D.-H., Park, H., Cho, W.-J., 2023. Synaptic Transistors Based on PVA: Chitosan Biopolymer Blended Electric-Double-Layer with High Ionic Conductivity. *Polymers* 15, 896. <https://doi.org/10.3390/polym15040896>
- Lee, D.-M., Rubab, N., Hyun, I., Kang, W., Kim, Y.-J., Kang, M., Choi, B.O., Kim, S.-W., 2022. Ultrasound-mediated triboelectric nanogenerator for powering on-demand transient electronics. *Sci. Adv.* 8, 1–8. <https://doi.org/10.1126/sciadv.abl8423>
- Lee, W., Kim, J., 2021. highly thermal conductive and electrical insulating epoxy composites with a three-dimensional filler network by sintering silver nanowires on aluminum nitride surface. *Polymers* 13, 1–12. <https://doi.org/10.3390/polym13050694>
- Li, F., Luo, S., Zhang, J., Yu, J., 2013. Temperature dependences of solid structure and properties of biodegradable poly(butylene succinate-co-terephthalate) (PBST) copolyester. *J. Therm. Anal. Calorim.* 113, 915–921. <https://doi.org/10.1007/s10973-012-2772-x>
- Li, G., Wang, L., Lei, X., Peng, Z., Wan, T., Maganti, S., Huang, M., Murugadoss, V., Seok, I., Jiang, Q., Cui, D., Alhadhrami, A., Ibrahim, M.M., Wei, H., 2022. Flexible, yet robust polyaniline coated foamed polylactic acid composite electrodes for high-performance supercapacitors. *Adv. Compos. Hybrid Mater.* 5, 853–863. <https://doi.org/10.1007/s42114-022-00501-7>
- Li, H., Liu, H., Li, J., Wei, D., Wang, Y., Song, B., 2015. Dielectric behaviors of carbon nanotube/silicone elastomer composites. *Sci. Eng. Compos. Mater.* 22, 215–221. <https://doi.org/10.1515/secm-2013-0280>
- Li, J., Chen, J.-L., Tang, X.-H., Cai, J.-H., Liu, J.-H., Wang, M., 2020. Constructing nanopores in poly(oxymethylene)/multi-wall carbon nanotube nanocomposites via poly(l-lactide) assisting for improving electromagnetic interference shielding. *J. Colloid Interface Sci.* 565, 536–545. <https://doi.org/10.1016/j.jcis.2020.01.057>
- Li, J., Guo, P., Kong, X., Wang, Y., Li, F., Du, B., 2022. Curing degree dependence of dielectric properties of bisphenol-a-based epoxy resin cured with methyl

- hexahydrophthalic anhydride. *IEEE Trans. Dielectr. Electr. Insul.* 29, 2072–2079. <https://doi.org/10.1109/TDEI.2022.3212970>
- Li, M., Kim, I.-H., Jeong, Y.G., 2010. Cellulose acetate/multiwalled carbon nanotube nanocomposites with improved mechanical, thermal, and electrical properties. *J. Appl. Polym. Sci.* 118, 2475–2481. <https://doi.org/10.1002/app.32591>
- Li, X.-R., Guo, J., Li, W.-D., Zhang, L.-Y., Wang, C., Guo, B.-H., Zhang, G.-J., 2018. Analysis of morphology and electrical insulation of 3D printing parts, in: 2018 IEEE International Conference on High Voltage Engineering and Application (ICHVE). Presented at the 2018 IEEE International Conference on High Voltage Engineering and Application (ICHVE), IEEE, ATHENS, Greece, pp. 1–4. <https://doi.org/10.1109/ICHVE.2018.8642096>
- Li, Z., Cao, W., Sheng, G., Jiang, X., Danikas, M.G., 2016. Experimental study on space charge and electrical strength of MgO nano-particles/polypropylene composite. *IEEE Trans. Dielectr. Electr. Insul.* 23, 1812–1819. <https://doi.org/10.1109/TDEI.2016.005181>
- Li, Z., Li, Y., 2022. 16 - All-solid-state batteries, in: Letcher, T.M. (Ed.), *Storing Energy* (Second Edition). Elsevier, pp. 343–361. <https://doi.org/10.1016/B978-0-12-824510-1.00007-6>
- Liang, G.D., Tjong, S.C., 2006. Electrical properties of low-density polyethylene/multiwalled carbon nanotube nanocomposites. *Mater. Chem. Phys.* 100, 132–137. <https://doi.org/10.1016/j.matchemphys.2005.12.021>
- Liang, J.-Z., Zou, S.-Y., Du, Q., 2018. Impact and flexural properties of polypropylene composites reinforced with multi-walled carbon nanotubes. *Polym. Test.* 70, 434–440. <https://doi.org/10.1016/j.polymertesting.2018.07.029>
- Liao, Y., Liu, C., Coppola, B., Barra, G., Di Maio, L., Incarnato, L., Lafdi, K., 2019. Effect of porosity and crystallinity on 3D printed PLA properties. *Polymers* 11, 1487. <https://doi.org/10.3390/polym11091487>
- Lin, T.-H., Putranto, A., Wang, Y.-T., 2021. Smart sensor tags for seepage sensing protected by 3D-printed case for embedding in concrete structures. *Constr. Build. Mater.* 284, 122784. <https://doi.org/10.1016/j.conbuildmat.2021.122784>
- Liu, C.-F., Sun, R.-C., 2010. Chapter 5 - Cellulose, in: *Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels*, Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose.
- Liu, X., Zou, Q., Wang, T., Zhang, L., 2018. Electrically conductive graphene-based biodegradable polymer composite films with high thermal stability and flexibility. *Nano* 13, 1850033. <https://doi.org/10.1142/S1793292018500339>
- Luo, J., Zhu, M., Wang, L., Zhou, H., Wen, B., Wang, X., Zhang, Y., 2022. CO₂-based fabrication of biobased and biodegradable poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/graphene nanoplates nanocomposite foams: toward EMI shielding application. *Polymer* 253, 125034. <https://doi.org/10.1016/j.polymer.2022.125034>
- Luo, S., Li, F., Yu, J., Cao, A., 2012. Aggregation structure development and mechanical properties of biodegradable poly(butylene succinate-co-terephthalate) fibers. *J. Appl. Polym. Sci.* 125, 2426–2432. <https://doi.org/10.1002/app.36506>
- Ma, C., Gao, S., Gao, X., Wu, M., Wang, R., Wang, Y., Tang, Z., Fan, F., Wu, Wenxuan, Wan, H., Wu, Wenzhuo, 2019. Chitosan biopolymer-derived self-powered triboelectric sensor with optimized performance through molecular surface engineering and data-driven learning. *InfoMat* 1, 116–125. <https://doi.org/10.1002/inf2.12008>

- Ma, X., Hu, Q., Dai, Y., He, P., Zhang, X., 2022. Disposable sensors based on biodegradable polylactic acid piezoelectret films and their application in wearable electronics. *Sens. Actuators Phys.* 346, 113834. <https://doi.org/10.1016/j.sna.2022.113834>
- Ma, Y., Liu, Y., Su, H., Wang, L., Zhang, J., 2018. Relationship between hydrogen bond and viscosity for a series of pyridinium ionic liquids: molecular dynamics and quantum chemistry. *J. Mol. Liq.* 255, 176–184. <https://doi.org/10.1016/j.molliq.2018.01.121>
- Madbouly, S.A., Mansour, A.A., Abdou, N.Y., 2007. Molecular dynamics of amorphous/crystalline polymer blends studied by broadband dielectric spectroscopy. *Eur. Polym. J.* 43, 1892–1904. <https://doi.org/10.1016/j.eurpolymj.2007.03.004>
- Maeno, Y., Kino, H., Omori, S., Hirai, N., Tanaka, T., Ohki, Y., Tajitsu, Y., Kohtoh, M., Okabe, S., 2005. Dipolar polarization and depolarization currents in biodegradable polymers, in: *Proceedings of 2005 International Symposium on Electrical Insulating Materials, 2005. (ISEIM 2005)*. Presented at the Proceedings of 2005 International Symposium on Electrical Insulating Materials, 2005. (ISEIM 2005)., IEEE, Kitakyushu, Japan, pp. 417–420. <https://doi.org/10.1109/ISEIM.2005.193577>
- Magazine, R., van Bochove, B., Borandeh, S., Seppälä, J., 2022. 3D inkjet-printing of photo-crosslinkable resins for microlens fabrication. *Addit. Manuf.* 50, 102534. <https://doi.org/10.1016/j.addma.2021.102534>
- Maiza, M., Benaniba, M.T., Quintard, G., Massardier-Nageotte, V., 2015. Biobased additive plasticizing polylactic acid (PLA). *Polímeros* 25, 581–590. <https://doi.org/10.1590/0104-1428.1986>
- Mano, J.F., Niarova, D.K., 2003. Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. *J. Mater. Sci. Mater. Med.* 14, 127–135. <https://doi.org/10.1023/a:1022015712170>
- Masarra, N.-A., Batistella, M., Quantin, J.-C., Regazzi, A., Pucci, M.F., El Hage, R., Lopez-Cuesta, J.-M., 2022. Fabrication of PLA/PCL/Graphene Nanoplatelet (GNP) Electrically Conductive Circuit Using the Fused Filament Fabrication (FFF) 3D Printing Technique. *Ecole Nationale Supérieure des Mines d'Alès*.
- Mathew, A.P., Oksman, K., Sain, M., 2005. Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). *J. Appl. Polym. Sci.* 97, 2014–2025. <https://doi.org/10.1002/app.21779>
- Matsushita, M., Maeno, Y., Kino, H., Fujita, S., Hirai, N., Tanaka, T., Ohki, Y., Tajitsu, Y., Kohtoh, M., Okabe, S., 2005. Effects of glass transition on the dielectric breakdown and electrical conduction in several biodegradable polymers, in: *Proceedings of 2005 International Symposium on Electrical Insulating Materials, 2005. (ISEIM 2005)*. Presented at the Proceedings of 2005 International Symposium on Electrical Insulating Materials, 2005. (ISEIM 2005)., IEEE, Kitakyushu, Japan, pp. 413–416. <https://doi.org/10.1109/ISEIM.2005.193576>
- Mattana, G., Briand, D., Marette, A., Vásquez Quintero, A., de Rooij, N.F., 2015. Polylactic acid as a biodegradable material for all-solution-processed organic electronic devices. *Org. Electron.* 17, 77–86. <https://doi.org/10.1016/j.orgel.2014.11.010>
- Maurel, A., Courty, M., Fleutot, B., Tortajada, H., Prashantha, K., Armand, M., Grugeon, S., Panier, S., Dupont, L., 2018. Highly loaded graphite–polylactic acid composite-based filaments for lithium-ion battery three-dimensional printing. *Chem. Mater.* 30, 7484–7493. <https://doi.org/10.1021/acs.chemmater.8b02062>

- Mazur, K., Singh, R., Friedrich, R.P., Genç, H., Unterweger, H., Sałasińska, K., Bogucki, R., Kuciel, S., Cicha, I., 2020. The effect of antibacterial particle incorporation on the mechanical properties, biodegradability, and biocompatibility of PLA and PHBV composites. *Macromol. Mater. Eng.* 305, 2000244. <https://doi.org/10.1002/mame.202000244>
- Meereboer, K.W., Pal, A.K., Misra, M., Mohanty, A.K., 2020. Sustainable PHBV/cellulose acetate blends: effect of a chain extender and a plasticizer. *ACS Omega* 5, 14221–14231. <https://doi.org/10.1021/acsomega.9b03369>
- Meng, X., Yang, J., Liu, Z., Lu, W., Sun, Y., Dai, Y., 2020. Non-contact, fibrous cellulose acetate/aluminum flexible electronic-sensor for humidity detecting. *Compos. Commun.* 20, 100347. <https://doi.org/10.1016/j.coco.2020.04.013>
- Meynial-Salles, I., Dorotyn, S., Soucaille, P., 2008. A new process for the continuous production of succinic acid from glucose at high yield, titer, and productivity. *Biotechnol. Bioeng.* 99, 129–135. <https://doi.org/10.1002/bit.21521>
- Mhmood, T.R., Al-Karkhi, N.K., 2023. A review of the stereolithography 3D printing process and the effect of parameters on quality. *Al-Khwarizmi Eng. J.* 19, 82–94. <https://doi.org/10.22153/kej.2023.04.003>
- Mierzwa, M., Floudas, G., Dorgan, J., Knauss, D., Wegner, J., 2002. Local and global dynamics of polylactides. A dielectric spectroscopy study. *J. Non-Cryst. Solids* 307–310, 296–303. [https://doi.org/10.1016/S0022-3093\(02\)01480-1](https://doi.org/10.1016/S0022-3093(02)01480-1)
- Mike Chung, T., 2012. Functionalization of polypropylene with high dielectric properties: applications in electric energy storage. *Green Sustain. Chem.* 2, 29–37. <https://doi.org/10.4236/gsc.2012.22006>
- Misenan, M.S.M., Ali, E.S., Khair, A.S.A., 2018. Conductivity, dielectric and modulus study of chitosan-methyl cellulose – BMIMTFSI polymer electrolyte doped with cellulose nano crystal, in: *Proceedings of the International Conference on Recent Advancements in Science and Technology 2017 (ICoRAST2017)*. Presented at the RECENT ADVANCEMENT ON APPLIED PHYSICS, INDUSTRIAL CHEMISTRY AND CHEMICAL TECHNOLOGY: Proceedings of the International Conference on Recent Advancements in Science and Technology 2017 (ICoRAST2017), Melaka, Malaysia, p. 030010. <https://doi.org/10.1063/1.5041231>
- Mishra, S., Sahoo, R., Unnikrishnan, L., Ramadoss, A., Mohanty, S., Nayak, S.K., 2021. Enhanced structural and dielectric behaviour of PVDF-PLA binary polymeric blend system. *Mater. Today Commun.* 26, 101958. <https://doi.org/10.1016/j.mtcomm.2020.101958>
- Mofokeng, J.P., Luyt, A.S., 2015a. Morphology and thermal degradation studies of melt-mixed PLA/PHBV biodegradable polymer blend nanocomposites with TiO₂ as filler. *J. Appl. Polym. Sci.* 132, 42138. <https://doi.org/10.1002/app.42138>
- Mofokeng, J.P., Luyt, A.S., 2015b. Dynamic mechanical properties of PLA/PHBV, PLA/PCL, PHBV/PCL blends and their nanocomposites with TiO₂ as nanofiller. *Thermochim. Acta* 613, 41–53. <https://doi.org/10.1016/j.tca.2015.05.019>
- Mohamed, R.M., Yusoh, K., 2015. A Review on the Recent Research of Polycaprolactone (PCL). *Adv. Mater. Res.* 1134, 249–255. <https://doi.org/10.4028/www.scientific.net/AMR.1134.249>
- Mohit, Hashmi, S.A., 2023. Biodegradable poly-ε-caprolactone based porous polymer electrolytes for high performance supercapacitors with carbon electrodes. *J. Power Sources* 557, 232548. <https://doi.org/10.1016/j.jpowsour.2022.232548>

- Mohiuddin, M., Sadasivuni, K.K., Mun, S., Kim, J., 2015. Flexible cellulose acetate/graphene blueprints for vibrotactile actuator. *RSC Adv.* 5, 34432–34438. <https://doi.org/10.1039/C5RA03043A>
- Molefi, J.A., Luyt, A.S., Krupa, I., 2010. Comparison of the influence of copper micro- and nano-particles on the mechanical properties of polyethylene/copper composites. *J. Mater. Sci.* 45, 82–88. <https://doi.org/10.1007/s10853-009-3894-9>
- Monika, Pal, A.K., Bhasney, S.M., Bhagabati, P., Katiyar, V., 2018. Effect of dicumyl peroxide on a poly(lactic acid) (PLA)/poly(butylene succinate) (PBS)/functionalized chitosan-based nanobiocomposite for packaging: a reactive extrusion study. *ACS Omega* 3, 13298–13312. <https://doi.org/10.1021/acsomega.8b00907>
- Montanheiro, T.L. do A., Cristóvan, F.H., Machado, J.P.B., Tada, D.B., Durán, N., Lemes, A.P., 2015. Effect of MWCNT functionalization on thermal and electrical properties of PHBV/MWCNT nanocomposites. *J. Mater. Res.* 30, 55–65. <https://doi.org/10.1557/jmr.2014.303>
- Mullaveetil, F.N., Dauksevicius, R., Wakjira, Y., 2021. Strength and elastic properties of 3D printed PVDF-based parts for lightweight biomedical applications. *J. Mech. Behav. Biomed. Mater.* 120, 104603. <https://doi.org/10.1016/j.jmbbm.2021.104603>
- Müller, A.J., Ávila, M., Saenz, G., Salazar, J., 2014. Chapter 3. Crystallization of PLA-based Materials, in: Jiménez, A., Peltzer, M., Ruseckaite, R. (Eds.), *Polymer Chemistry Series*. Royal Society of Chemistry, Cambridge, pp. 66–98. <https://doi.org/10.1039/9781782624806-00066>
- Musto, P., Russo, P., Cimino, F., Acierno, D., Lupò, G., Petrarca, C., 2015. Dielectric behavior of biopolymer based composites containing multi wall carbon nanotubes: Effect of filler content and aspect ratio. *Eur. Polym. J.* 64, 170–178. <https://doi.org/10.1016/j.eurpolymj.2015.01.010>
- Nabiyev, A.A., Maharramov, A.M., Baulin, A.A., 2014. Frequency dispersion of dielectric losses in the HDPE/ZrO₂ micro- and nanocomposites, in: VII Eurasian Conference “Nuclear Science and Its Application”. Presented at the VII Eurasian Conference “Nuclear science and its application”, Unpublished, Baku, Azerbaijan, pp. 121–122. <https://doi.org/10.13140/RG.2.2.31321.01122>
- Nainggolan, I., Nasution, T.I., Putri, S.R.E., Azdena, D., Balyan, M., Agusnar, H., 2018. Study on chitosan film properties as a green dielectric. *IOP Conf. Ser. Mater. Sci. Eng.* 309, 012081. <https://doi.org/10.1088/1757-899X/309/1/012081>
- Nakatsuka, T., 2011. Polylactic acid-coated cable. *Fujikura Tech. Rev.* 40, 39–46.
- Nassajfar, M.N., Deviatkin, I., Leminen, V., Horttanainen, M., 2021. Alternative materials for printed circuit board production: an environmental perspective. *Sustainability* 13, 12126. <https://doi.org/10.3390/su132112126>
- Nemoto, Y., Kato, F., Hirai, N., Ohki, Y., Kaneko, S., Okabe, S., 2008. Effects of blending various biodegradable polymer plasticizers on the conduction current and AC breakdown strength in starch ester, in: 2008 International Symposium on Electrical Insulating Materials (ISEIM 2008). Presented at the 2008 International Symposium on Electrical Insulating Materials (ISEIM), IEEE, Yokkaichi, pp. 542–545. <https://doi.org/10.1109/ISEIM.2008.4664524>
- Newman, D., Laredo, E., Bello, A., Grillo, A., Feijoo, J.L., Müller, A.J., 2009. Molecular mobilities in biodegradable poly(D,L-lactide)/Poly(ε-caprolactone) blends. *Macromolecules* 42, 5219–5225. <https://doi.org/10.1021/ma9007303>
- Ngo, T.D., Kashani, A., Imbalzano, G., Nguyen, K.T.Q., Hui, D., 2018. Additive manufacturing (3D printing): a review of materials, methods, applications and

- challenges. *Compos. Part B Eng.* 143, 172–196. <https://doi.org/10.1016/j.compositesb.2018.02.012>
- Noroozi, Nazbanoo, Thomson, J.A., Noroozi, Nader, Schafer, L.L., Hatzikiriakos, S.G., 2012. Viscoelastic behaviour and flow instabilities of biodegradable poly (ϵ -caprolactone) polyesters. *Rheol. Acta* 51, 179–192. <https://doi.org/10.1007/s00397-011-0586-6>
- Norshamira, A., Mariatti, M., 2014. Dielectric properties of inorganic fillers filled epoxy thin film, in: *Proceedings of the 23rd Scientific Conference of Microscopy Society Malaysia (SCMSM 2014)*. Tronoh, Malaysia, p. 20021. <https://doi.org/10.1063/1.4919159>
- Nuchanong, P., Seadan, M., Khankrua, R., Suttiruengwong, S., 2021. Thermal stability enhancement of poly(hydroxybutyrate-co-hydroxyvalerate) through in situ reaction. *Des. Monomers Polym.* 24, 113–124. <https://doi.org/10.1080/15685551.2021.1914406>
- Nuriev, M.A., Magerramov, A.M., Shukyurova, A.A., 2018. Electrical conductivity of nanocomposites based on low-density polyethylene and Cu₂S nanoparticles. *Surf. Eng. Appl. Electrochem.* 54, 32–37. <https://doi.org/10.3103/S1068375518010118>
- Nurul, M., Mariatti, M., 2013. Effect of thermal conductive fillers on the properties of polypropylene composites. *J. Thermoplast. Compos. Mater.* 26, 627–639. <https://doi.org/10.1177/0892705711427345>
- Ogura, I., 1999. Low dielectric constant epoxy resins, in: *Handbook of Low and High Dielectric Constant Materials and Their Applications*. Elsevier, pp. 213–240. <https://doi.org/10.1016/B978-012513905-2/50007-8>
- Ohki, Y., Fuse, N., Hikosaka, S., Takemura, Y., Mizuno, M., Fukunaga, K., 2009. Complex permittivity spectra of several insulating polymers at electrical and THz frequencies, in: *2009 IEEE Conference on Electrical Insulation and Dielectric Phenomena*. Presented at the 2009 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), IEEE, Virginia Beach, VA, USA, pp. 7–10. <https://doi.org/10.1109/CEIDP.2009.5377894>
- Ohki, Y., Hirai, N., 2007. Electrical conduction and breakdown properties of several biodegradable polymers. *IEEE Trans. Dielectr. Electr. Insul.* 14, 1559–1566. <https://doi.org/10.1109/TDEI.2007.4401240>
- Ohki, Y., Hirai, N., 2006. Dielectric properties of biodegradable polymers, in: *2006 IEEE Conference on Electrical Insulation and Dielectric Phenomena*. Presented at the 2006 IEEE Conference on Electrical Insulation and Dielectric Phenomena, IEEE, Kansas, MO, USA, pp. 668–671. <https://doi.org/10.1109/CEIDP.2006.312020>
- Oi, T., Shinyama, K., Fujita, S., 2012. Electrical properties of heat-treated polylactic acid. *Electr. Eng. Jpn.* 180, 1–8. <https://doi.org/10.1002/ej.21272>
- Olmedo-Martínez, J.L., Porcarelli, L., Guzmán-González, G., Calafel, I., Forsyth, M., Mecerreyes, D., Müller, A.J., 2021. Ternary poly(ethylene oxide)/Poly(L,L-lactide) PEO/PLA blends as high-temperature solid polymer electrolytes for lithium batteries. *ACS Appl. Polym. Mater.* 3, 6326–6337. <https://doi.org/10.1021/acsapm.1c01093>
- Omnexus, 2022. Dielectric strength: units, test methods & material table [WWW Document]. URL <https://omnexus.specialchem.com/polymer-properties/properties/dielectric-strength> (accessed 3.29.22).
- Ong, C.J., Price, F.P., 2007. Blends of poly(ϵ -caprolactone) with poly(vinyl chloride). I. morphology. *J. Polym. Sci. Polym. Symp.* 63, 45–58. <https://doi.org/10.1002/polc.5070630108>

- Ophardt, C.E., 2003. Polarity of organic compounds [WWW Document]. Virtual Chembook. URL <http://chemistry.elmhurst.edu/vchembook/213organicfcgp.html> (accessed 3.20.22).
- Öteyaka, M.Ö., Aybar, K., Öteyaka, H.C., 2021. Effect of infill ratio on the tensile and flexural properties of unreinforced and carbon fiber-reinforced polylactic acid manufactured by fused deposition modeling. *J. Mater. Eng. Perform.* 30, 5203–5215. <https://doi.org/10.1007/s11665-021-05694-4>
- Ouellette, R.J., Rawn, J.D., 2015. 1 - Structure of organic compounds, in: Ouellette, R.J., Rawn, J.D. (Eds.), *Principles of Organic Chemistry*. Elsevier, Boston, pp. 1–32. <https://doi.org/10.1016/B978-0-12-802444-7.00001-X>
- Pachekoski, W.M., Dalmolin, C., Agnelli, J.A.M., 2012. The influence of the industrial processing on the degradation of poly(hydroxybutyrate) - PHB. *Mater. Res.* 16, 237–332. <https://doi.org/10.1590/S1516-14392012005000180>
- Pantani, R., Sorrentino, A., 2013. Influence of crystallinity on the biodegradation rate of injection-moulded poly(lactic acid) samples in controlled composting conditions. *Polym. Degrad. Stab.* 98, 1089–1096. <https://doi.org/10.1016/j.polymdegradstab.2013.01.005>
- Paragkumar N, T., Edith, D., Six, J.-L., 2006. Surface characteristics of PLA and PLGA films. *Appl. Surf. Sci.* 253, 2758–2764. <https://doi.org/10.1016/j.apsusc.2006.05.047>
- Parangusan, H., Bhadra, J., Ahmad, Z., Mallick, S., Touati, F., Al-Thani, N., 2021. Humidity sensor based on poly(lactic acid)/PANI–ZnO composite electrospun fibers. *RSC Adv.* 11, 28735–28743. <https://doi.org/10.1039/D1RA02842A>
- Park, S., Shou, W., Makatura, L., Matusik, W., Fu, K. (Kelvin), 2022. 3D printing of polymer composites: materials, processes, and applications. *Matter* 5, 43–76. <https://doi.org/10.1016/j.matt.2021.10.018>
- Pascual-Jose, B., Badia, J.D., Múgica, A., Addiego, F., Müller, A.J., Ribes-Greus, A., 2021. Analysis of plasticization and reprocessing effects on the segmental cooperativity of polylactide by dielectric thermal spectroscopy. *Polymer* 223, 123701. <https://doi.org/10.1016/j.polymer.2021.123701>
- Patibandla, S., Mian, A., 2021. Layer-to-layer physical characteristics and compression behavior of 3D printed polymer metastructures fabricated using different process parameters. *J. Elastomers Plast.* 53, 386–401. <https://doi.org/10.1177/0095244320939995>
- Pei, W., Shang, W., Liang, C., Jiang, X., Huang, C., Yong, Q., 2020. Using lignin as the precursor to synthesize Fe₃O₄@lignin composite for preparing electromagnetic wave absorbing lignin-phenol-formaldehyde adhesive. *Ind. Crops Prod.* 154, 112638. <https://doi.org/10.1016/j.indcrop.2020.112638>
- Peidavosi, N., Azami, M., Beheshtizadeh, N., Ramazani Saadatabadi, A., 2022. Piezoelectric conductive electrospun nanocomposite PCL/polyaniline/barium titanate scaffold for tissue engineering applications. *Sci. Rep.* 12, 20828. <https://doi.org/10.1038/s41598-022-25332-w>
- Pentek, A., Nyitrai, M., Schiffer, A., Abraham, H., Bene, M., Molnar, E., Told, R., Maroti, P., 2020. The Effect of printing parameters on electrical conductivity and mechanical properties of PLA and ABS based carbon composites in additive manufacturing of upper limb prosthetics. *Crystals* 10, 398. <https://doi.org/10.3390/cryst10050398>
- Perumal Ramasamy, R., Yang, K., Rafailovich, M.H., 2014. Polypropylene-graphene - a nanocomposite that can be converted into a meta-material at desired frequencies. *RSC Adv.* 4, 44888–44895. <https://doi.org/10.1039/C4RA05814C>

- Petrov, I., Kalinkevich, O., Pogorielov, M., Kalinkevich, A., Stanislavov, A., Sklyar, A., Danilchenko, S., Yovcheva, T., 2016. Dielectric and electric properties of new chitosan-hydroxyapatite materials for biomedical application: dielectric spectroscopy and corona treatment. *Carbohydr. Polym.* 151, 770–778. <https://doi.org/10.1016/j.carbpol.2016.05.110>
- Phuong, V.T., Verstiche, S., Cinelli, P., Anguillesi, I., Coltelli, M.-B., Lazzeri, A., 2014. Cellulose acetate blends - effect of plasticizers on properties and biodegradability. *J. Renew. Mater.* 2, 35–41. <https://doi.org/10.7569/JRM.2013.634136>
- Platnieks, O., Gaidukovs, S., Barkane, A., Sereda, A., Gaidukova, G., Grase, L., Thakur, V.K., Filipova, I., Fridrihsone, V., Skute, M., Laka, M., 2020. Biobased poly(butylene succinate)/microcrystalline cellulose/nanofibrillated cellulose-based sustainable polymer composites: thermo-mechanical and biodegradation studies. *Polymers* 12, 1472. <https://doi.org/10.3390/polym12071472>
- Pluta, M., Galeski, A., 2007. Plastic deformation of amorphous poly(L/DL-lactide): structure evolution and physical properties. *Biomacromolecules* 8, 1836–1843. <https://doi.org/10.1021/bm061229v>
- Poh, L., Wu, Q., Chen, Y., Narimissa, E., 2022. Characterization of industrial low-density polyethylene: a thermal, dynamic mechanical, and rheological investigation. *Rheol. Acta* 61, 701–720. <https://doi.org/10.1007/s00397-022-01360-1>
- Pratt, G.J., Smith, M.J.A., 1999. Dielectric relaxation spectroscopy of a commercial poly(β -hydroxybutyrate-co- β -hydroxyvalerate). *Eur. Polym. J.* 35, 909–914. [https://doi.org/10.1016/S0014-3057\(98\)00053-6](https://doi.org/10.1016/S0014-3057(98)00053-6)
- Pratt, G.J., Smith, M.J.A., 1997. Dielectric relaxation spectroscopy of a poly hydroxybutyrate homopolymer. *Eur. Polym. J.* 33, 857–861. [https://doi.org/10.1016/S0014-3057\(96\)00285-6](https://doi.org/10.1016/S0014-3057(96)00285-6)
- Psarras, G.C., 2018. 2 - Fundamentals of dielectric theories, in: *Dielectric Polymer Materials for High-Density Energy Storage*. Elsevier, pp. 11–57. <https://doi.org/10.1016/B978-0-12-813215-9.00002-6>
- Puls, J., Wilson, S.A., Hölter, D., 2011. Degradation of cellulose acetate-based materials: a review. *J. Polym. Environ.* 19, 152–165. <https://doi.org/10.1007/s10924-010-0258-0>
- Qi, X., Tong, X., You, S., Mao, R., Cai, E., Pan, W., Zhang, C., Hu, R., Shen, J., 2022. Mild hyperthermia-assisted ROS scavenging hydrogels achieve diabetic wound healing. *ACS Macro Lett.* 11, 861–867. <https://doi.org/10.1021/acsmacrolett.2c00290>
- Qian, S., Sheng, K., Yu, K., Xu, L., Fontanillo Lopez, C.A., 2018. Improved properties of PLA biocomposites toughened with bamboo cellulose nanowhiskers through silane modification. *J. Mater. Sci.* 53, 10920–10932. <https://doi.org/10.1007/s10853-018-2377-2>
- Quintana, R., Persenaire, O., Lemmouchi, Y., Bonnaud, L., Dubois, P., 2014. Grafted D/L-lactide to cellulose acetate by reactive melt processing: Its role as CA/PLA blend compatibilizer. *Eur. Polym. J.* 57, 30–36. <https://doi.org/10.1016/j.eurpolymj.2014.05.003>
- Quintana, R., Persenaire, O., Lemmouchi, Y., Sampson, J., Martin, S., Bonnaud, L., Dubois, P., 2013. Enhancement of cellulose acetate degradation under accelerated weathering by plasticization with eco-friendly plasticizers. *Polym. Degrad. Stab.* 98, 1556–1562. <https://doi.org/10.1016/j.polymdegradstab.2013.06.032>
- Rafiqah, S.A., Khalina, A., Harmaen, A.S., Tawakkal, I.A., Zaman, K., Asim, M., Nurrazi, M.N., Lee, C.H., 2021. A review on properties and application of

- biobased poly(butylene succinate). *Polymers* 13, 1436. <https://doi.org/10.3390/polym13091436>
- Rathnayake, W.S.M., Karunanayake, L., Samarasekara, A.M.P.B., Amarasinghe, D.A.S., 2020. Sunflower oil-based MCC surface modification to achieve improved thermomechanical properties of a polypropylene composite. *Cellulose* 27, 4355–4371. <https://doi.org/10.1007/s10570-020-03053-5>
- Ravikumar, R., Ganesh, M., Ubaidulla, U., Young Choi, E., Tae Jang, H., 2017. Preparation, characterization, and in vitro diffusion study of nonwoven electrospun nanofiber of curcumin-loaded cellulose acetate phthalate polymer. *Saudi Pharm. J.* 25, 921–926. <https://doi.org/10.1016/j.jsps.2017.02.004>
- Reddy, N.V., Kumar, C.R., Rao, V.V.R.N., 1993. Dielectric properties of amorphous cellulose acetate-butyrate polymer films. *Polym. Int.* 32, 381–384. <https://doi.org/10.1002/pi.4990320408>
- Ren, G., Yu, Z., Xiong, R., 2015. Dielectric, optical and thermal properties of LDPE/ZnO hybrid film. *J. Wuhan Univ. Technol.-Mater Sci Ed* 30, 37–42. <https://doi.org/10.1007/s11595-015-1096-7>
- Ren, J., Urakawa, O., Adachi, K., 2003. Dielectric and Viscoelastic Studies of Segmental and Normal Mode Relaxations in Undiluted Poly(D,L-lactic acid). *Macromolecules* 36, 210–219. <https://doi.org/10.1021/ma0212341>
- Rezvani Ghomi, E.R., Khosravi, F., Saedi Ardahaei, A.S., Dai, Y., Neisiany, R.E., Foroughi, F., Wu, M., Das, O., Ramakrishna, S., 2021. The Life Cycle Assessment for Polylactic Acid (PLA) to Make It a Low-Carbon Material. *Polymers* 13, 1854. <https://doi.org/10.3390/polym13111854>
- Rhim, J.-W., Park, H.-M., Ha, C.-S., 2013. Bio-nanocomposites for food packaging applications. *Prog. Polym. Sci.* 38, 1629–1652. <https://doi.org/10.1016/j.progpolymsci.2013.05.008>
- Roumy, L., Touchard, F., Marchand, D., Truong Hoang, T.Q., Martinez-Hergueta, F., 2023. Durability of Joule effect of 3D printed carbon black/polylactic acid: electrical cyclic tests and analytical modelling. *Int. J. Fatigue* 173, 107677. <https://doi.org/10.1016/j.ijfatigue.2023.107677>
- Rubio-Valle, J.F., Sánchez, M.C., Valencia, C., Martín-Alfonso, J.E., Franco, J.M., 2022. Production of lignin/cellulose acetate fiber-bead structures by electrospinning and exploration of their potential as green structuring agents for vegetable lubricating oils. *Ind. Crops Prod.* 188, 115579. <https://doi.org/10.1016/j.indcrop.2022.115579>
- Russo, P., Patti, A., Petrarca, C., Acierno, S., 2018. Thermal conductivity and dielectric properties of polypropylene-based hybrid compounds containing multiwalled carbon nanotubes. *J. Appl. Polym. Sci.* 135, 46470. <https://doi.org/10.1002/app.46470>
- Rytöluoto, I., Niittymäki, M., Seri, P., Naderiallaf, H., Lahti, K., Saarimäki, E., Flyktman, T., Paajanen, M., 2022. Biaxially oriented silica–polypropylene nanocomposites for HVDC film capacitors: morphology-dielectric property relationships, and critical evaluation of the current progress and limitations. *J. Mater. Chem. A* 10, 3025–3043. <https://doi.org/10.1039/D1TA10336A>
- Saad, G.R., Botros, M.G., Nessim, R.I., 1992. Dielectric study of acetylated cotton cellulose and saponified cellulose acetate. *Angew. Makromol. Chem.* 197, 23–39. <https://doi.org/10.1002/apmc.1992.051970102>
- Sahoo, S., Misra, M., Mohanty, A.K., 2011. Enhanced properties of lignin-based biodegradable polymer composites using injection moulding process. *Compos.*

- Part Appl. Sci. Manuf. 42, 1710–1718.
<https://doi.org/10.1016/j.compositesa.2011.07.025>
- Sahu, P., Gupta, M.K., 2021. Eco-friendly treatment and coating for improving the performance of sisal composites. *Polym. Test.* 93, 106923.
<https://doi.org/10.1016/j.polymertesting.2020.106923>
- Salaeh, S., Thitithammawong, A., Salae, A., 2020. Highly enhanced electrical and mechanical properties of methyl methacrylate modified natural rubber filled with multiwalled carbon nanotubes. *Polym. Test.* 85, 106417.
<https://doi.org/10.1016/j.polymertesting.2020.106417>
- Salehi, S., Bahners, T., Gutmann, J.S., Gao, S.-L., Mäder, E., Fuchsluger, T.A., 2014. Characterization of structural, mechanical and nano-mechanical properties of electrospun PGS/PCL fibers. *RSC Adv.* 4, 16951–16957.
<https://doi.org/10.1039/C4RA01237B>
- Samykan, M., 2021. Mechanical property and prediction model for FDM-3D printed polylactic acid (PLA). *Arab. J. Sci. Eng.* 46, 7875–7892.
<https://doi.org/10.1007/s13369-021-05617-4>
- Sang, Z.-H., Xie, X.-L., Zhou, S.-Y., Li, Y., Yan, Z., Xu, L., Zhong, G.-J., Li, Z.-M., 2017. Gradient structure of crystalline morphology in injection-molded polylactide parts tuned by oscillation shear flow and its influence on thermomechanical performance. *Ind. Eng. Chem. Res.* 56, 6295–6306.
<https://doi.org/10.1021/acs.iecr.7b00930>
- Santos, B., Rozsa, Ch., Galego, N., Michels, A.F., Behar, M., Zawislak, F.C., 2011. Hydrophilic transformations in polyhydroxyalkanoates. *Int. J. Polym. Anal. Charact.* 16, 431–441. <https://doi.org/10.1080/1023666X.2011.598269>
- Saravanamoorthy, S., Chandra Bose, A., Velmathi, S., 2015. Facile fabrication of polycaprolactone/h-MoO₃ nanocomposites and their structural, optical and electrical properties. *RSC Adv.* 5, 99074–99083.
<https://doi.org/10.1039/C5RA17733B>
- Sata, H., Murayama, M., Shimamoto, S., 2004. 5.4 Properties and applications of cellulose triacetate film. *Macromol. Symp.* 208, 323–334.
<https://doi.org/10.1002/masy.200450413>
- Scaffaro, R., Maio, A., Nostro, A., 2020. Poly(lactic acid)/carvacrol-based materials: preparation, physicochemical properties, and antimicrobial activity. *Appl. Microbiol. Biotechnol.* 104, 1823–1835. <https://doi.org/10.1007/s00253-019-10337-9>
- Schönhals, A., 2010. Broadband dielectric spectroscopy and its relationship to other spectroscopic techniques.
- Seghier, T., Benabed, F., 2015. Dielectric proprieties determination of high density polyethylene (HDPE) by dielectric spectroscopy. *Int. J. Mater. Mech. Manuf.* 3, 121–124. <https://doi.org/10.7763/IJMMM.2015.V3.179>
- Shafee, E.E., 2001. The influence of semicrystalline morphology on the dielectric relaxation properties of poly(3-hydroxybutyrate). *Eur. Polym. J.* 37, 1677–1684.
[https://doi.org/10.1016/S0014-3057\(01\)00034-9](https://doi.org/10.1016/S0014-3057(01)00034-9)
- Shahdan, D., Ahmad, S., Chen, R.S., Omar, A., Zailan, F.D., Abu Hassan, N.A., 2020. Mechanical performance, heat transfer and conduction of ultrasonication treated polyaniline bio-based blends. *Int. Commun. Heat Mass Transf.* 117, 104742.
<https://doi.org/10.1016/j.icheatmasstransfer.2020.104742>
- Shaikh, H.M., Anis, A., Poulouse, A.M., Al-Zahrani, S.M., Madhar, N.A., Alhamidi, A., Aldeligan, S.H., Alsubaie, F.S., 2022. Synthesis and characterization of cellulose

- triacetate obtained from date palm (*Phoenix dactylifera* L.) trunk mesh-derived cellulose. *Molecules* 27, 1434. <https://doi.org/10.3390/molecules27041434>
- Shang, L., Fei, Q., Zhang, Y.H., Wang, X.Z., Fan, D.-D., Chang, H.N., 2012. Thermal properties and biodegradability studies of poly(3-hydroxybutyrate-co-3-hydroxyvalerate). *J. Polym. Environ.* 20, 23–28. <https://doi.org/10.1007/s10924-011-0362-9>
- Shinyama, K., 2018. Mechanical and electrical properties of polylactic acid with aliphatic-aromatic polyester. *J. Eng.* 2018, 6597183. <https://doi.org/10.1155/2018/6597183>
- Shinyama, K., Fujita, S., 2005. Electrical conduction and dielectric properties of biodegradable plastics. *IEEJ Trans. Fundam. Mater.* 125, 204–208. <https://doi.org/10.1541/IEEJFMS.125.204>
- Shuai, C., Wang, C., Qi, F., Peng, S., Yang, W., He, C., Wang, G., Qian, G., 2020. Enhanced crystallinity and antibacterial of PHBV scaffolds incorporated with zinc oxide. *J. Nanomater.* 2020, 6014816. <https://doi.org/10.1155/2020/6014816>
- Shukur, M.F., Ithnin, R., Kadir, M.F.Z., 2014. Electrical characterization of corn starch-LiOAc electrolytes and application in electrochemical double layer capacitor. *Electrochimica Acta* 136, 204–216. <https://doi.org/10.1016/j.electacta.2014.05.075>
- Sics, I., Tupureina, V., Kalnins, M., Ezquerro, T.A., Baltá-Calleja, F.J., 1998. Dielectric relaxation of poly-(β -hydroxybutyrate) relating to microstructure. *J. Macromol. Sci. Part B* 37, 851–862. <https://doi.org/10.1080/00222349808212421>
- Silva, M.J., Sanches, A.O., Cena, C.R., Nagashima, H.N., Medeiros, E.S., Malmonge, J.A., 2021. Study of the electrical conduction process in natural rubber-based conductive nanocomposites filled with cellulose nanowhiskers coated by polyaniline. *Polym. Compos.* 42, 1519–1529. <https://doi.org/10.1002/pc.25920>
- Sivanjineyulu, V., Behera, K., Chang, Y.-H., Chiu, F.-C., 2018. Selective localization of carbon nanotube and organoclay in biodegradable poly(butylene succinate)/polylactide blend-based nanocomposites with enhanced rigidity, toughness and electrical conductivity. *Compos. Part Appl. Sci. Manuf.* 114, 30–39. <https://doi.org/10.1016/j.compositesa.2018.08.009>
- Snell, K.D., Singh, V., Brumbley, S.M., 2015. Production of novel biopolymers in plants: recent technological advances and future prospects. *Curr. Opin. Biotechnol.* 32, 68–75. <https://doi.org/10.1016/j.copbio.2014.11.005>
- Solazzo, M., O'Brien, F.J., Nicolosi, V., Monaghan, M.G., 2019. The rationale and emergence of electroconductive biomaterial scaffolds in cardiac tissue engineering. *APL Bioeng.* 3, 041501. <https://doi.org/10.1063/1.5116579>
- Souza, D., Castillo, T.E., Rodríguez, R.J.S., 2012. Effects of hydroxyvalerate contents in thermal degradation kinetic of cellulose acetate propionate/poly(3-hydroxyalkanoates) blends. *J. Therm. Anal. Calorim.* 109, 1353–1364. <https://doi.org/10.1007/s10973-011-2152-y>
- Spinelli, G., Kotsilkova, R., Ivanov, E., Georgiev, V., Ivanova, R., Naddeo, C., Romano, V., 2020. Dielectric spectroscopy and thermal properties of polylactic acid reinforced with carbon-based particles: experimental study and design theory. *Polymers* 12, 2414. <https://doi.org/10.3390/polym12102414>
- Stancu, C., Notingher, P.V., Panaitescu, D., Marinescu, V., 2013. Electrical conductivity of polyethylene-neodymium composites, in: 2013 8th International Symposium on Advanced Topics in Electrical Engineering (ATEE). Presented at the 2013 8th International Symposium on Advanced Topics in Electrical Engineering (ATEE),

- IEEE, Bucharest, Romania, pp. 1–6.
<https://doi.org/10.1109/ATEE.2013.6563458>
- Su, A., Al'Aref, S.J., 2018. History of 3D Printing, in: 3D Printing Applications in Cardiovascular Medicine. Elsevier, pp. 1–10. <https://doi.org/10.1016/B978-0-12-803917-5.00001-8>
- Su, J., Xiao, Y., Ren, M., 2013. Enhanced thermal conductivity in epoxy nanocomposites with hybrid boron nitride nanotubes and nanosheets: enhanced thermal conductivity in insulating epoxy nanocomposites. *Phys. Status Solidi Appl. Mater.* 210, 2699–2705. <https://doi.org/10.1002/pssa.201330213>
- Sui, G., Jana, S., Zhong, W.H., Fuqua, M.A., Ulven, C.A., 2008. Dielectric properties and conductivity of carbon nanofiber/semi-crystalline polymer composites. *Acta Mater.* 56, 2381–2388. <https://doi.org/10.1016/j.actamat.2008.01.034>
- Supeno, S., Daik, R., El-Sheikh, S.M., 2014. The synthesis of a macro-initiator from cellulose in a zinc-based ionic liquid. *BioResources* 9, 1267–1275. <https://doi.org/10.15376/biores.9.1.1267-1275>
- Tabriz, A.G., Kuofie, H., Scoble, J., Boulton, S., Douroumis, D., 2023. Selective laser sintering for printing pharmaceutical dosage forms. *J. Drug Deliv. Sci. Technol.* 86, 104699. <https://doi.org/10.1016/j.jddst.2023.104699>
- Taga, N., Tanaka, K., Ishizaki, A., 1997. Effects of rheological change by addition of carboxymethylcellulose in culture media of an air-lift fermentor on poly-D-3-hydroxybutyric acid productivity in autotrophic culture of hydrogen-oxidizing bacterium, *Alcaligenes eutrophus*. *Biotechnol. Bioeng.* 53, 529–533. [https://doi.org/10.1002/\(SICI\)1097-0290\(19970305\)53:5<529::AID-BIT11>3.0.CO;2-B](https://doi.org/10.1002/(SICI)1097-0290(19970305)53:5<529::AID-BIT11>3.0.CO;2-B)
- Tagami, N., Okada, M., Hirai, N., Ohki, Y., Tanaka, T., Imai, T., Harada, M., Ochi, M., 2008. Dielectric properties of epoxy/clay nanocomposites - effects of curing agent and clay dispersion method. *IEEE Trans. Dielectr. Electr. Insul.* 15, 24–32. <https://doi.org/10.1109/T-DEI.2008.4446733>
- Takala, M., Ranta, H., Nevalainen, P., Pakonen, P., Pelto, J., Karttunen, M., Virtanen, S., Koivu, V., Pettersson, M., Sonerud, B., Kannus, K., 2010. Dielectric properties and partial discharge endurance of polypropylene-silica nanocomposite. *IEEE Trans. Dielectr. Electr. Insul.* 17, 1259–1267. <https://doi.org/10.1109/TDEI.2010.5539698>
- TechSci Research, 2023. Electronic materials market size and trends 2028.
- Tejada-Oliveros, R., Balart, R., Ivorra-Martinez, J., Gomez-Caturla, J., Montanes, N., Quiles-Carrillo, L., 2021. Improvement of impact strength of polylactide blends with a thermoplastic elastomer compatibilized with biobased maleinized linseed oil for applications in rigid packaging. *Molecules* 26, 240. <https://doi.org/10.3390/molecules26010240>
- Ten, E., Bahr, D.F., Li, B., Jiang, L., Wolcott, M.P., 2012. Effects of cellulose nanowhiskers on mechanical, dielectric, and rheological properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskey composites. *Ind. Eng. Chem. Res.* 51, 2941–2951. <https://doi.org/10.1021/ie2023367>
- Thomassin, J.-M., Pagnouille, C., Bednarz, L., Huynen, I., Jerome, R., Detrembleur, C., 2008. Foams of polycaprolactone/MWNT nanocomposites for efficient EMI reduction. *J. Mater. Chem.* 18, 792–796. <https://doi.org/10.1039/b709864b>
- Tomano, N., Boondamnoen, O., Aumnate, C., Potiyaraj, P., 2022. Enhancing impact resistance and biodegradability of PHBV by melt blending with ENR. *Sci. Rep.* 12, 22633. <https://doi.org/10.1038/s41598-022-27246-z>

- Torğut, G., Gürler, N., 2021. Nanofiller reinforced biodegradable PHA/PLA composites: physico-chemical, thermal and dielectric properties. *J. Polym. Res.* 28, 452. <https://doi.org/10.1007/s10965-021-02816-3>
- Truman, L., Whitwam, E., Nelson-Cheeseman, B.B., Koerner, L.J., 2020. Conductive 3D printing: resistivity dependence upon infill pattern and application to EMI shielding. *J. Mater. Sci. Mater. Electron.* 31, 14108–14117. <https://doi.org/10.1007/s10854-020-03965-9>
- Tsuji, H., 2016. Poly(lactic acid) stereocomplexes: a decade of progress. *Adv. Drug Deliv. Rev.* 107, 97–135. <https://doi.org/10.1016/j.addr.2016.04.017>
- Uyor, U., Popoola, A., Popoola, O., Aigbodion, V., 2022. Thermal, mechanical and dielectric properties of functionalized sandwich BN-BaTiO₃-BN/polypropylene nanocomposites. *J. Alloys Compd.* 894, 162405. <https://doi.org/10.1016/j.jallcom.2021.162405>
- Veranitisagul, C., Wattanathana, W., Wannapaiboon, S., Hanlumyuang, Y., Sukthavorn, K., Nootsuwan, N., Chotiwan, S., Phuthong, W., Jongrungruangchok, S., Laobuthee, A., 2019. Antimicrobial, conductive, and mechanical properties of AgCB/PBS composite system. *J. Chem.* 2019, 3487529. <https://doi.org/10.1155/2019/3487529>
- Vesely, P., Tichý, T., Šefl, O., Horynová, E., 2018. Evaluation of dielectric properties of 3D printed objects based on printing resolution. *IOP Conf. Ser. Mater. Sci. Eng.* 461, 012091. <https://doi.org/10.1088/1757-899X/461/1/012091>
- Vieira, L., Montagna, L.S., Marini, J., Passador, F.R., 2021. Influence of particle size and glassy carbon content on the thermal, mechanical, and electrical properties of PHBV/glassy carbon composites. *J. Appl. Polym. Sci.* 138, 49740. <https://doi.org/10.1002/app.49740>
- Virtanen, S., Vaughan, A.S., Yang, L., Saiz, F., Quirke, N., 2016. Dielectric breakdown strength and electrical conductivity of low density polyethylene octylnanosilica composite, in: 2016 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP). Presented at the 2016 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), IEEE, Toronto, ON, Canada, pp. 58–61. <https://doi.org/10.1109/CEIDP.2016.7785608>
- Virtanen, S., Vaughan, A.S., Yang, S., Saiz, F., Quirke, N., 2017. Electrical conductivity and moisture uptake studies of low density polyethylene octylnanosilica composite, in: Proceedings of the Nordic Insulation Symposium. pp. 1–5. <https://doi.org/10.5324/nordis.v0i25.2368>
- Vivaldi, F., Sebechlebská, T., Vaněčková, E., Biagini, D., Bonini, A., Kolivoška, V., 2022. Electric conductivity measurements employing 3D printed electrodes and cells. *Anal. Chim. Acta* 1203, 339600. <https://doi.org/10.1016/j.aca.2022.339600>
- Volpe, V., De Feo, G., De Marco, I., Pantani, R., 2018. Use of sunflower seed fried oil as an ecofriendly plasticizer for starch and application of this thermoplastic starch as a filler for PLA. *Ind. Crops Prod.* 122, 545–552. <https://doi.org/10.1016/j.indcrop.2018.06.014>
- Wan, M., Srivastava, A.K., Dhawan, P.K., Yadav, R.R., Sant, S.B., Kripal, R., Lee, J.-H., 2015. High dielectric response of 2D-polyaniline nanoflake based epoxy nanocomposites. *RSC Adv.* 5, 48421–48425. <https://doi.org/10.1039/C5RA05660H>
- Wang, Guilong, Wang, L., Mark, L.H., Shaayegan, V., Wang, Guizhen, Li, H., Zhao, G., Park, C.B., 2018. Ultralow-threshold and lightweight biodegradable porous PLA/MWCNT with segregated conductive networks for high-performance

- thermal insulation and electromagnetic interference shielding applications. *ACS Appl. Mater. Interfaces* 10, 1195–1203. <https://doi.org/10.1021/acsami.7b14111>
- Wang, H., Ji, J., Zhang, W., Zhang, Y., Jiang, J., Wu, Z., Pu, S., Chu, P., 2009. Biocompatibility and bioactivity of plasma-treated biodegradable poly(butylene succinate). *Acta Biomaterialia* 5, 279–287. <https://doi.org/10.1016/j.actbio.2008.07.017>
- Wang, H., Yang, L., 2023. Dielectric constant, dielectric loss, conductivity, capacitance and model analysis of electronic electroactive polymers. *Polym. Test.* 120, 107965. <https://doi.org/10.1016/j.polymertesting.2023.107965>
- Wang, H., Yang, X., Fu, Z., Zhao, X., Li, Y., Li, J., 2017. Rheology of nanosilica-compatible immiscible polymer blends: formation of a “heterogeneous network” facilitated by interfacially anchored hybrid nanosilica. *Macromolecules* 50, 9494–9506. <https://doi.org/10.1021/acs.macromol.7b02143>
- Wang, K., Xie, X., Wang, J., Zhao, A., Peng, Y., Rao, Y., 2020. Effects of infill characteristics and strain rate on the deformation and failure properties of additively manufactured polyamide-based composite structures. *Results Phys.* 18, 103346. <https://doi.org/10.1016/j.rinp.2020.103346>
- Wang, Q., Ji, C., Sun, J., Zhu, Q., Liu, J., 2020. Structure and properties of polylactic acid biocomposite films reinforced with cellulose nanofibrils. *Molecules* 25, 3306. <https://doi.org/10.3390/molecules25143306>
- Wang, Q., Wang, Y., Meng, Q., Wang, T., Guo, W., Wu, G., You, L., 2017. Preparation of high antistatic HDPE/polyaniline encapsulated graphene nanoplatelet composites by solution blending. *RSC Adv.* 7, 2796–2803. <https://doi.org/10.1039/C6RA26458A>
- Wang, W., Zhang, W., Liang, B., 2021. The influences of multiple factors for flexural performance of polypropylene: crystallization, crystal evolution, nanoparticles. *J. Mater. Sci.* 56, 15667–15683. <https://doi.org/10.1007/s10853-021-06243-z>
- Wang, Y., Zhu, L., Zhou, J., Jia, B., Jiang, Y., Wang, J., Wang, M., Cheng, Y., Wu, K., 2019. Dielectric properties and thermal conductivity of epoxy resin composite modified by Zn/ZnO/Al₂O₃ core-shell particles. *Polym. Bull.* 76, 3957–3970. <https://doi.org/10.1007/s00289-018-2581-x>
- Warnakulasooriya, L., 2022. Bio-polymeric materials for electrical insulation applications (Electrical and Computer Engineering). University of Manitoba, Department of Electrical and Computer Engineering University of Manitoba Winnipeg, Manitoba, Canada.
- Wibowo, A., Vyas, C., Cooper, G., Qulub, F., Suratman, R., Mahyuddin, A.I., Dirgantara, T., Bartolo, P., 2020. 3D printing of polycaprolactone–polyaniline electroactive scaffolds for bone tissue engineering. *Materials* 13, 1–17. <https://doi.org/10.3390/ma13030512>
- Wohlert, T., Gornet, T., 2015. History of additive manufacturing.
- Wong, P.-Y., Phang, S.-W., Baharum, A., 2020. Effects of synthesised polyaniline (PAni) contents on the anti-static properties of PAni-based polylactic acid (PLA) films. *RSC Adv.* 10, 39693–39699. <https://doi.org/10.1039/D0RA07076A>
- Wsoo, M.A., Shahir, S., Mohd Bohari, S.P., Nayan, N.H.M., Razak, S.I.A., 2020. A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: A new perspective. *Carbohydr. Res.* 491, 107978. <https://doi.org/10.1016/j.carres.2020.107978>
- Wu, H., Rogalski, M., Kessler, M.R., 2013. Zirconium tungstate/epoxy nanocomposites: effect of nanoparticle morphology and negative thermal expansivity. *ACS Appl. Mater. Interfaces* 5, 9478–9487. <https://doi.org/10.1021/am402242g>

- Wu, W., Liu, T., Zhang, D., Sun, Q., Cao, K., Zha, J., Lu, Y., Wang, B., Cao, X., Feng, Y., Roy, V.A.L., Li, R.K.Y., 2019. Significantly improved dielectric properties of polylactide nanocomposites via TiO₂ decorated carbon nanotubes. *Compos. Part Appl. Sci. Manuf.* 127, 105650. <https://doi.org/10.1016/j.compositesa.2019.105650>
- Xia, W., Zhou, J., Hu, T., Ren, P., Zhu, G., Yin, Y., Li, J., Zhang, Z., 2020. Enhanced magnetoelectric coefficient and interfacial compatibility by constructing a three-phase CFO@BT@PDA/P(VDF-TrFE) core-shell nanocomposite. *Compos. Part Appl. Sci. Manuf.* 131, 105805. <https://doi.org/10.1016/j.compositesa.2020.105805>
- Xiang, Y., Qi, X., Cai, E., Zhang, C., Wang, J., Lan, Y., Deng, H., Shen, J., Hu, R., 2023. Highly efficient bacteria-infected diabetic wound healing employing a melanin-reinforced biopolymer hydrogel. *Chem. Eng. J.* 460, 141852. <https://doi.org/10.1016/j.cej.2023.141852>
- Xing, C., Wang, H., Hu, Q., Xu, F., Cao, X., You, J., Li, Y., 2013. Mechanical and thermal properties of eco-friendly poly(propylene carbonate)/cellulose acetate butyrate blends. *Carbohydr. Polym.* 92, 1921–1927. <https://doi.org/10.1016/j.carbpol.2012.11.058>
- Xu, J., Guo, B.-H., 2010. Microbial succinic acid, its polymer poly(butylene succinate), and applications, in: Chen, G.G.-Q. (Ed.), *Plastics from Bacteria*, Microbiology Monographs. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 347–388. https://doi.org/10.1007/978-3-642-03287-5_14
- Xu, P., Huang, B., Tang, R., Wang, Z., Tu, J., Ding, Y., 2022. Improved mechanical and EMI shielding properties of PLA/PCL composites by controlling distribution of PIL-modified CNTs. *Adv. Compos. Hybrid Mater.* 5, 991–1002. <https://doi.org/10.1007/s42114-021-00406-x>
- Xu, W., Tan, L., Qin, S., He, Y., Wu, T., Qu, J., 2021. Efficient fabrication of highly exfoliated and evenly dispersed high-density polyethylene/expanded graphite nanocomposite with enhanced dielectric constant and extremely low dielectric loss. *Compos. Part Appl. Sci. Manuf.* 142, 106242. <https://doi.org/10.1016/j.compositesa.2020.106242>
- Yakubu, A., Abbas, Z., Abdullahi, S., 2020. Mechanical, dielectric and shielding performance of rice husk/polycaprolactone composites enhanced via rice husk particles inclusion. *Open Access Libr. J.* 7, 1–12. <https://doi.org/10.4236/oalib.1106514>
- Yan, C., Wei, J., Guan, J., Shao, Z., Lv, S., 2023. Highly foldable and free-standing supercapacitor based on hierarchical and hollow MOF-anchored cellulose acetate carbon nanofibers. *Carbon* 213, 118187. <https://doi.org/10.1016/j.carbon.2023.118187>
- Yang, H., Hu, B., Chang, F., Chen, L., Cao, X., He, G., 2023. Improved compatibility of PLA/starch blends with Binary functional monomers through UV-induced reactive extrusion. *Ind. Crops Prod.* 197, 116635. <https://doi.org/10.1016/j.indcrop.2023.116635>
- Yang, L., Li, S., Zhou, X., Liu, J., Li, Y., Yang, M., Yuan, Q., Zhang, W., 2019. Effects of carbon nanotube on the thermal, mechanical, and electrical properties of PLA/CNT printed parts in the FDM process. *Synth. Met.* 253, 122–130. <https://doi.org/10.1016/j.synthmet.2019.05.008>
- Yang, S., Wang, Y.-Y., Song, Y.-N., Jia, L.-C., Zhong, G.-J., Xu, L., Yan, D.-X., Lei, J., Li, Z.-M., 2021. Ultrathin, flexible and sandwich-structured PHBV/silver

- nanowire films for high-efficiency electromagnetic interference shielding. *J. Mater. Chem. C* 9, 3307–3315. <https://doi.org/10.1039/D0TC05266C>
- Yang, S., Wu, Z.-H., Yang, W., Yang, M.-B., 2008. Thermal and mechanical properties of chemical crosslinked polylactide (PLA). *Polym. Test.* 27, 957–963. <https://doi.org/10.1016/j.polymertesting.2008.08.009>
- Yang, S.-L., Wu, Z.-H., Meng, B., Yang, W., 2009. The effects of dioctyl phthalate plasticization on the morphology and thermal, mechanical, and rheological properties of chemical crosslinked polylactide: effects of dioctyl phthalate plasticization. *J. Polym. Sci. Part B Polym. Phys.* 47, 1136–1145. <https://doi.org/10.1002/polb.21716>
- Yatigala, N.S., Bajwa, D.S., Bajwa, S.G., 2018. Compatibilization improves physico-mechanical properties of biodegradable biobased polymer composites. *Compos. Part Appl. Sci. Manuf.* 107, 315–325. <https://doi.org/10.1016/j.compositesa.2018.01.011>
- Yeole, P., Alwekar, S., Veluswamy, N.K.P., Kore, S., Hiremath, N., Vaidya, U., Theodore, M., 2021. Characterization of textile-grade carbon fiber polypropylene composites. *Polym. Polym. Compos.* 29, 652–659. <https://doi.org/10.1177/0967391120930109>
- Yeung, C., Vaughan, A., 2016. On the effect of nanoparticle surface chemistry on the electrical characteristics of epoxy-based nanocomposites. *Polymers* 8, 1–16. <https://doi.org/10.3390/polym8040126>
- You, S., Huang, Y., Mao, R., Xiang, Y., Cai, E., Chen, Y., Shen, J., Dong, W., Qi, X., 2022. Together is better: poly(tannic acid) nanorods functionalized polysaccharide hydrogels for diabetic wound healing. *Ind. Crops Prod.* 186, 115273. <https://doi.org/10.1016/j.indcrop.2022.115273>
- Young, C.S., Weigland, R.J., 2002. An efficient approach to column selection in HPLC method development.
- Yu, C.-R., Wu, D.-M., Liu, Y., Qiao, H., Yu, Z.-Z., Dasari, A., Du, X.-S., Mai, Y.-W., 2011. Electrical and dielectric properties of polypropylene nanocomposites based on carbon nanotubes and barium titanate nanoparticles. *Compos. Sci. Technol.* 71, 1706–1712. <https://doi.org/10.1016/j.compscitech.2011.07.022>
- Yu, J., Huo, R., Wu, C., Wu, X., Wang, G., Jiang, P., 2012. Influence of interface structure on dielectric properties of epoxy/alumina nanocomposites. *Macromol. Res.* 20, 816–826. <https://doi.org/10.1007/s13233-012-0122-2>
- Yu, J., Xu, S., Liu, B., Wang, H., Qiao, F., Ren, X., Wei, Q., 2023. PLA bioplastic production: From monomer to the polymer. *Eur. Polym. J.* 193, 112076. <https://doi.org/10.1016/j.eurpolymj.2023.112076>
- Yu, L., Ke, S., Zhang, Y., Shen, B., Zhang, A., Huang, H., 2011. Dielectric relaxations of high-k poly(butylene succinate) based all-organic nanocomposite films for capacitor applications. *J. Mater. Res.* 26, 2493–2502. <https://doi.org/10.1557/jmr.2011.271>
- Yu, W., Zhou, C., 2012. Rheology of miscible polymer blends with viscoelastic asymmetry and concentration fluctuation. *Polymer* 53, 881–890. <https://doi.org/10.1016/j.polymer.2011.12.025>
- Yuan, Q., Chen, M., Zhan, S., Li, Y., Lin, Y., Yang, H., 2022. Ceramic-based dielectrics for electrostatic energy storage applications: Fundamental aspects, recent progress, and remaining challenges. *Chem. Eng. J.* 446, 136315. <https://doi.org/10.1016/j.cej.2022.136315>

- Yuen, J.D., Shriver-Lake, L.C., Walper, S.A., Zabetakis, D., Breger, J.C., Stenger, D.A., 2020. Microbial nanocellulose printed circuit boards for medical sensing. *Sensors* 20, 2047. <https://doi.org/10.3390/s20072047>
- Zhang, B., Liu, Y., Liu, J., Sun, L., Cong, L., Fu, F., Mauger, A., Julien, C.M., Xie, H., Pan, X., 2021. “Polymer-in-ceramic” based poly(ϵ -caprolactone)/ceramic composite electrolyte for all-solid-state batteries. *J. Energy Chem.* 52, 318–325. <https://doi.org/10.1016/j.jechem.2020.04.025>
- Zhang, H., Wei, X., Qu, J.-P., 2021. Microstructure evolution and mechanism of PLA/PVDF hybrid dielectrics fabricated under elongational flow. *Polymer* 224, 123719. <https://doi.org/10.1016/j.polymer.2021.123719>
- Zhang, J., Zou, F., Tao, H., Gao, W., Guo, L., Cui, B., Yuan, C., Liu, P., Lu, L., Wu, Z., Fang, Y., 2023. Effects of different sources of cellulose on mechanical and barrier properties of thermoplastic sweet potato starch films. *Ind. Crops Prod.* 194, 116358. <https://doi.org/10.1016/j.indcrop.2023.116358>
- Zhang, K., Yu, H.-O., Shi, Y.-D., Chen, Y.-F., Zeng, J.-B., Guo, J., Wang, B., Guo, Z., Wang, M., 2017. Morphological regulation improved electrical conductivity and electromagnetic interference shielding in poly(L-lactide)/poly(ϵ -caprolactone)/carbon nanotube nanocomposites via constructing stereocomplex crystallites. *J. Mater. Chem. C* 5, 2807–2817. <https://doi.org/10.1039/C7TC00389G>
- Zhang, P., You, P., Feng, J., Xie, R., Chen, L., Xiong, Y., Song, P., 2023. Vitrimer-like, mechanically Robust, healable and recyclable biobased elastomers based on epoxy natural Rubbers, polylactide and layered double hydroxide. *Compos. Part Appl. Sci. Manuf.* 171, 107575. <https://doi.org/10.1016/j.compositesa.2023.107575>
- Zhang, S., Arya, R.K., Pandey, S., Vardaxoglou, Y., Whittow, W., Mittra, R., 2016. 3D-printed planar graded index lenses. *IET Microw. Antennas Propag.* 10, 1411–1419. <https://doi.org/10.1049/iet-map.2016.0013>
- Zhao, J., Yu, D., Zhang, W., Wang, Z., Wang, Y., 2023. Fabrication and output performance of triboelectric nanogenerator from helical structure of biodegradable polylactic acid by 3D printing. *Curr. Appl. Phys.* 51, 44–52. <https://doi.org/10.1016/j.cap.2023.04.018>
- Zhao, Y., Wang, Z., Wang, J., Mai, H., Yan, B., Yang, F., 2004. Direct synthesis of poly(D,L-lactic acid) by melt polycondensation and its application in drug delivery. *J. Appl. Polym. Sci.* 91, 2143–2150. <https://doi.org/10.1002/app.13354>
- Zhou, Y., Wang, F., Yang, Z., Hu, X., Pan, Y., Lu, Y., Jiang, M., 2022. 3D printing of polyurethane/nanocellulose shape memory composites with tunable glass transition temperature. *Ind. Crops Prod.* 182, 114831. <https://doi.org/10.1016/j.indcrop.2022.114831>
- Ziemath, E.C., Escanhoela, C.A., Braunger, M.L., 2017. Comparison of activation energies for the electrical conductivity of silicate glasses obtained by DC and AC techniques. *Solid State Ion.* 301, 146–151. <https://doi.org/10.1016/j.ssi.2017.01.025>
- Zion Market Research, 2023. Dielectric Material Market Size, Share, Growth & Trends by 2030 [WWW Document]. Zion Mark. Res. URL <https://www.zionmarketresearch.com/report/dielectric-material-market-size> (accessed 5.3.24).

Résumé en français

Dans un contexte de développement durable et de sensibilisation du public envers les problématiques environnementales, les polymères biosourcés représentent une niche d'avenir dans le secteur industriel avec une forte dynamique de croissance. C'est un contexte favorable au développement de nouvelles structures biosourcées et/ou biodégradables adaptées à de nombreuses applications diélectriques, mais de nombreuses limitations existent encore pour bénéficier pleinement des performances diélectriques des polymères biosourcés. Cette thèse s'intègre dans cette logique de promotion des matériaux biosourcés dans le domaine diélectrique en proposant une étude avancée des propriétés multiphysiques, notamment diélectriques, des polymères biosourcés pour identifier les applications dans les domaines diélectriques adaptées pour de tels matériaux. Dans la première phase de la thèse, une étude de la littérature avancée nous a permis d'identifier trois polymères biosourcés avec un fort potentiel pour le domaine diélectrique, à savoir l'acide polylactique (PLA), le polyhydroxybutyrate-co-valérate (PHBV) et l'acétate de cellulose (CA). Leurs performances diélectriques étaient similaires à certains polymères synthétiques conventionnels utilisés dans le domaine de l'isolation électrique comme le polyéthylène, le polypropylène et la résine époxy. De plus, l'analyse de la littérature nous a permis d'identifier trois stratégies permettant de davantage favoriser l'intégration de polymères biosourcés dans le domaine de l'isolation électrique, à savoir la création de mélanges polymériques, la création de bio(nano)composites à base de charges cellulose et l'utilisation de nouvelles techniques de mise en œuvre comme l'impression 3D. La troisième phase de la thèse propose l'utilisation combinée de la création de mélanges polymériques et de l'impression 3D pour l'obtention de matériaux imprimés en 3D pour une application en isolation électrique. Les résultats préliminaires du Chapitre 4 ont démontré que les mélanges de PLA:CA étaient les plus prometteurs pour la suite du projet et sont donc choisis pour l'étape d'impression 3D. L'ajout de CA a amélioré la stabilité mécanique du PLA lorsque ce dernier est en état caoutchoutique, mais diminue également légèrement la capacité d'isolation électrique du PLA. Une étape d'optimisation via un plan de

Taguchi a permis la fabrication de mélanges polymériques imprimés en 3D présentant une rigidité mécanique et une capacité d'isolation électrique comparable au polyéthylène basse densité. La dernière phase de la thèse propose de combiner l'utilisation de bio(nano)composites à base de cellulose et d'impression 3D pour l'obtention de matériaux à base de PLA imprimés en 3D pour une application en isolation électrique. Deux charges différentes ont été utilisées et comparées : les microcristaux de cellulose et les nanocristaux de cellulose. Les résultats ont montré que l'ajout de charges cellulosiques améliorait la rigidité mécanique des matériaux, mais diminuait également légèrement leur capacité d'isolation électrique. Une étape d'optimisation via un plan factoriel a permis de fabriquer des biocomposites à charges cellulosiques imprimés en 3D dont la rigidité mécanique et la capacité d'isolation électrique sont comparables à celles du polyéthylène haute densité et au polypropylène et poly(chlorure de vinyle). Cette thèse propose ainsi des alternatives biosourcées, voire compostables au polyéthylène et polypropylène dans les domaines d'isolation électrique, grâce à l'utilisation combinée de différentes stratégies faciles à appliquer à l'échelle industrielle, démarche s'inscrivant dans le cycle de développement durable.

Abstract

In a context of sustainable development and public awareness of environmental issues, biobased polymers represent a promising niche in the industrial sector, with a strong growth potential. This is a favorable context for the development of new biobased and/or biodegradable structures suitable for a wide range of dielectric applications, but many limitations still exist to fully benefit from the dielectric performance of biobased polymers. This thesis is part of a broader effort to promote the use of biobased materials in the dielectric field, proposing an advanced study of the multiphysical properties, particularly dielectric properties, of biobased polymers to identify applications in dielectric fields suitable for such materials. In the first phase of the thesis, an advanced literature review identified three biobased polymers with high potential for the dielectric field, i.e. polylactic acid (PLA), polyhydroxybutyrate-co-valerate (PHBV) and cellulose acetate (CA). Their dielectric performances were comparable to conventional synthetic polymers used in electrical insulation, such as polyethylene, polypropylene and epoxy resin. In addition, the literature review also identified three potential strategies to encourage the use of bio-based polymers in electrical insulation, i.e. the development of polymer blends, the creation of bio(nano)composites based on cellulosic fillers, and the use of new processing techniques such as 3D printing. The second phase of the thesis proposes the creation of polymer blends and 3D printing to obtain 3D-printed PLA-based materials for application in electrical insulation. Preliminary results showed that PLA : CA blends were the most promising for the continuation of the project and were therefore chosen for the 3D printing step. The addition of CA improved the mechanical stability of PLA in a rubbery state, but also slightly reduced their electrical insulation capacity. An optimization step using a Taguchi design resulted in 3D-printed polymer blends samples with mechanical rigidity and electrical insulation capacity comparable to low-density polyethylene. The final phase of the thesis proposes to combine the use of cellulose-based bio(nano)composites and 3D printing to obtain 3D-printed PLA-based materials for application in electrical insulation. Two different fillers were used and compared: cellulose microcrystals (MCC) and cellulose nanocrystals (NCC). The results showed that

the addition of cellulose fillers improved the mechanical rigidity of the materials, but also slightly reduced their electrical insulation capacity. An optimization step using a factorial design resulted in 3D-printed cellulose-reinforced biocomposites samples with mechanical rigidity and electrical insulation capacity comparable to high-density polyethylene, polypropylene and PVC. This thesis therefore proposes biobased and even compostable alternatives to polyethylene and polypropylene in the electrical insulation field, through the combined use of different strategies easily applicable on an industrial scale, in line with a sustainable development approach.

Titre : Propriétés diélectriques des matériaux biosourcés

Mots clés : polymères biosourcés, propriétés diélectriques, propriétés mécaniques, mélanges polymériques, biocomposites, impression 3D, isolation électrique