



HAL
open science

Chemical modification of lignin for the elaboration of novel biobased aromatic polymers and additives

Pietro Buono

► **To cite this version:**

Pietro Buono. Chemical modification of lignin for the elaboration of novel biobased aromatic polymers and additives. Material chemistry. Université de Strasbourg, 2017. English. NNT : 2017STRAE015 . tel-01778018

HAL Id: tel-01778018

<https://theses.hal.science/tel-01778018v1>

Submitted on 25 Apr 2018

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.

ÉCOLE DOCTORALE physique et chimie physique (ED 182)

UMR CNRS 7515 ICPEES

THÈSE présentée par :

Buono Pietro

Soutenue le : **25 Septembre 2017**

Pour obtenir le grade de : **Docteur de l'université de Strasbourg**

Discipline/ Spécialité : Chimie des matériaux

Modification chimique de lignines pour l'élaboration de nouveaux polymères et additifs aromatiques biosourcés

THÈSE dirigée par :

Luc Avérous

Professeur des Universités, Université de Strasbourg

RAPPORTEURS :

Sylvain Caillol

Chargé de recherche, HdR, ENSCM à Montpellier

Naceur Belgacem

Professeur des Universités, INP Grenoble

AUTRES MEMBRES DU JURY :

Youssef Habibi

Scientifique Senior, Luxembourg Institute of Science and Technology

Anne Hébraud

Maître de Conférences, HdR, Université de Strasbourg

Cette thèse de doctorat a été rédigée en utilisant pour chaque chapitre le format habituellement adopté pour la rédaction d'articles scientifiques paraissant dans les revues à comité de lecture. C'est pourquoi, l'indulgence du lecteur est sollicitée pour les répétitions et redites inhérentes à la forme de rédaction choisie.

Le présent mémoire de thèse a ainsi été partiellement rédigé en langue anglaise, conformément à l'autorisation délivrée par le Professeur Jean-Pierre Bucher, professeur des universités à l'Institut de Physique et Chimie des Matériaux de Strasbourg et directeur de l'Ecole Doctorale de Physique et Chimie-Physique

The authors of the scientific articles presented in this thesis are grateful to the Luxembourg National Research Fond (FNR) for financial support (AFR-FNR no. 9903572).

The authors are also thankful to Green Value SA (Switzerland) for providing freely lignin Protobin 1000.

Regis Vaudemont and Benoit Marcolini (LIST) are thanked for their help with DMA, DSC and TGA measurements.

Chheng Ngov (ICPEES) is thanked for her help with SEC measurements.

COMMUNICATIONS LIEES AUX TRAVAUX DE THESE

Publications :

Les résultats présentés dans cette thèse font l'objet de trois articles et d'une revue bibliographique.

Articles publiés:

- P. Bueno, A. Duval, P. Verge, L. Averous and Y. Habibi. New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation, *ACS Sustainable Chem. Eng.*, **2016**, 4 (10), 5212–5222.
- P. Bueno, A. Duval, L. Averous and Y. Habibi. Lignin-based Materials Through Thiol - Maleimide “click” Polymerization, *ChemSusChem* **2017**, 10 (5), 984–992.

Articles soumis :

- P. Bueno, A. Duval, L. Averous and Y. Habibi. Thermally Healable and Remendable Lignin-Based Materials through Diels – Alder Click Polymerization, *under review in ACS Sus. Chem. Eng.*

Article qui sera soumis ultérieurement:

- P. Bueno, A. Duval, L. Averous and Y. Habibi. “Clicking” biobased polyphenols: A sustainable platform for aromatic polymeric materials

Conférences:

P. Bueno, A. Duval, P. Verge, L. Averous and Y. Habibi. Synthesis of novel silylated lignin and its incorporation in low density polyethylene matrix. Warwik Polymer Conference, 11-14th July 2016. Warwik, UK. *Oral Presentation*

P. Bueno, A. Duval, P. Verge, L. Averous and Y. Habibi. New functional lignin-based polymeric materials: synthesis, processing and characterization. 15th International Symposium on Biopolymer (ISBP2016), Sep 26th-29th 2016, Madrid-Spain. *Oral Presentation*

P. Bueno, A. Duval, L. Averous and Y. Habibi. New functional lignin-based polymers: Synthesis and characterisation. 251st ACS National Meeting, San Diego, CA, March 13-17, 2016. *Oral Presentation*

LISTE DES ABREVIATIONS

11-MUA	11-maleimidoundecylenic acid
11-MUC	11-maleimido undecenoyl chloride
Ac-SL	Acetylated soda lignin
ATR	Attenuated total reflection
BTX	Benzene toluene xylene
CNSL	Cashew nut shell liquid
CTs	Condensed tannins
D-A	Diels-Alder
DAC	Diallyl carbonate
DCM	Dichloromethane
DMA	Dynamic mechanical analysis
DMAP	Dimethyl amino pyridine
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential scanning calorimetry
<i>E</i>	Young modulus
<i>E'</i>	Storage modulus
<i>E''</i>	Loss modulus
FA	Ferulic acid
FGE	Furfuryl Glycidyl ether
FTIR	Fourier transformed infrared
HRMS	High resolution mass spectrometry
HTs	Hydrolyzable tannins
MALDI	Matrix assisted laser desorption ionisation
Mal-SL	Maleimide soda lignin
MMA	Methyl methacrylate
NMR	Nuclear magnetic resonance
PAA	Polyacetylamino pentyl acrylate
PCA	<i>para</i> -coumaric acid
PCL	Polycaprolactone
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PFB	Pentafluorobenzaldehyde

PhTs	Phloro tannins
PLA	Polylactic acid
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethanes
PVAc	Polyvynyl acetate
PVC	Polyvynyl chloride
ROP	Ring opening polymerization
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
Si-SL	Silylated soda lignin
SL	Soda lignin
S _N 2	Bimolecular nucleophilic substitution
TBAB	Tetrabutylammonium bromide
TBAC	Tetrabutylammonium chloride
TBAF	Tetrabutylammonium fluoride
TBDMS	<i>tert</i> -butyldimethylsilyl
TBDMSCl	<i>tert</i> -butyldimethylsilyl chloride
TEA	Triethylamine
T_g	Glass transition temperature
TGA	Thermo-gravimetric analysis
THF	Tetrahydrofuran
T_m	Melting temperature
TPP	Triphenylphosphine
T_α	Transition temperature (DMA)
VEC	Vinyl ethylene carbonate
X_c	Degree of crystallinity
ϵ	Elongation at break
σ	Tensile strength
ΔH_m	Melting enthalpy
ΔH_{cc}	Cold crystallization enthalpy

LISTE DES TABLEAUX, SCHEMAS ET FIGURES

Tableaux:

Chapitre 1

Table 1.1: Commercial production of lignin.

Table 1.2: Tannins precursors.

Table 1.3: Comparison of the different procedures reporting the grafting of vinyl and internal alkenes groups onto lignin, tannins and CNSL.

Table 1.4: Comparison of the different procedures reporting the grafting of acrylic and methacrylic groups onto lignin, tannins and CNSL.

Chapitre 2

Table 2.1: Content in maleimide groups of the derivatized lignins.

Table 2.2: Swelling tests in H₂O and methanol and main DMA results.

Annexe du chapitre 2

Table S2.1: Thermal properties (TGA, DSC) of the thiol-maleimide lignin-based materials.

Table S2.2: Uniaxial tensile properties of the thiol-maleimide lignin-based materials.

Chapitre 3

Table 3.1: T_{95%} of the lignin based D-A materials measured by TGA.

Annexe du chapitre 3

Table S3.1: Content of maleimide groups in Mal-SL.

Table S3.2: Furan content calculation within the polyfunctional furan linkers.

Table S3.3: Thermo-mechanical properties of the lignin based D-A materials.

Chapitre 4

Table 4.1: Results of Tensile Tests and Izod Impact Tests for LDPE–Lignin Blend (10% Lignin Content).

Table 4.2: Results of DSC and DMA Measurements for LDPE–Lignin Blends (10 wt % of Lignin).

Annexe du chapitre 4

Table S4.1: Quantification of the functional groups in the silylated lignins by ³¹P (mmol g⁻¹) and ¹H NMR (mmol g⁻¹).

Table S4.2: Quantification of the functional groups in the acetylated lignins by ³¹P (mmol g⁻¹) and ¹H NMR (mmol g⁻¹).

Table S4.3: Solubility test for neat SL, acetylated SL (Ac-SL_06) and silylated SL (Si-SL_05).

Schèmes:

Chapitre 1

Scheme 1.1: Huisgen 1,3-dipolar cycloaddition of alkynes and azides yielding 1,2,3-triazoles.

Scheme 1.2: Thermally reversible furan – maleimide adduct.

Scheme 1.3: Thiol–ene free-radical addition to electron-rich / electron-poor carbon–carbon double bonds, and the catalyzed thiol-Michael addition to electron-deficient carbon–carbon double bonds.

Scheme 1.4: Mechanism of the thiol-yne radical reaction.

Scheme 1.5: Synthetic pathway used to introduce azide groups on lignin.

Scheme 1.6: Lignin and tannins furan derivatization using furfuryl glycidyl ether.

Scheme 1.7: Esterification of soda lignin (SL) with 11-MUA to yield maleimido-modified soda.

Scheme 1.8: Lignin's oxidations pathways generating *o*-quinones and *p*-quinones groups.

Scheme 1.9: Schematic representation of the click reaction between the propargylated lignin and microcrystalline cellulose derivatized with azide groups.

Scheme 1.10: a) Lignin's phenolic hydrogen abstraction by a radical initiator b) reaction between the radical initiator and the generated lignin free radical.

Scheme 1.11: Synthetic pathway for vanillin allylation and further functionalization through thiol – ene.

Chapitre 2

Scheme 2.1: Esterification of soda lignin (SL) with 11-MUA to yield maleimido-modified soda lignin (Mal-SL).

Scheme 2.2: Polymerization of Mal-SL with the corresponding polyfunctional thiols linkers.

Chapitre 3

Scheme 3.1: Esterification of soda lignin (SL) with 11-MUA to yield maleimido-modified soda lignin (Mal-SL).

Scheme 3.2: Synthesis of polyfunctional furan linkers from the corresponding thiols.

Scheme 3.3: Thermo-reversible D-A polymerization of Mal-SL with the polyfunctional furan linkers.

Annexe du chapitre 3

Scheme S3.1: a) Epoxy ring opening by fluoride anion and further formation of thiolate anion b) thio-ether linkage formation.

Chapitre 4

Scheme 4.1: Lignin Silylation (a) and Acetylation (b)

Scheme 4.2: Details of the Silylation mechanism via N-tert-Butyldimethylsilylimidazole intermediate (a) and Acetylation mechanism via N-Acetylpyridinium intermediate (b)

Figures:

Chapitre 1

Figure 1.1: Hypothetical chemical structure of lignin.

Figure 1.2: Chemical structure of CNSL principal components.

Figure 1.3: Naturally occurring phenolic compounds from various biological origins obtained from lignin.

Figure 1.4: Chemical structure of the main tocols in nature.

Figure 1.5: Possible chemical modification strategies applicable to natural polyphenols.

Figure 1.6: Illustration of the flavan-ols unit present in CTs.

Figure 1.7: Schematic representation of the main “click” reaction.

Figure 1.8: Synthetic strategies which have been applied to graft alkyne moieties onto lignin macromers

Figure 1.9: 1,3 Huisgen cycloaddition between propargylated lignin, lignin-PCL and lignin PCL/PLA chain extended with azidated lignin.

Figure 1.10: Polymerization of maleimide soda lignin with the corresponding polyfunctional thiols linkers.

Figure 1.11: Thermo-reversible Diels-Alder polymerization of maleimide functionalized lignin with polyfunctional furan linkers.

Figure 1.12: Lignin based Diels-Alder material a) initially b) after the cut c) after the self-healing.

Chapitre 2

Figure 2.1: Conversions of aliphatic and phenolic OH groups of SL during the reaction with 11-MUC.

Figure 2.2: a) ¹H NMR and b) FTIR spectra of SL and Mal-SL_1.1.

Figure 2.3: a) Size-exclusion chromatograms (CHCl₃, polystyrene calibration) of SL and Mal-SL prepared from different amounts of 11-MUC. b) UV/Vis spectra of Mal-SL_1.1 at the two elution times indicated by the arrows in part (a).

Figure 2.4: a) Variation of T_g of the materials prepared with Mal-SL_1.1 with linker functionality. b) Variation of T_g of the materials prepared with the 4-SH linker with the amount of 11-MUC employed in the synthesis of Mal-SL.

Figure 2.5: Variation of T_g of the thiol-maleimide lignin-based materials depending on a) the linker functionality and b) the amount of 11-MUC employed in the synthesis of Mal-SL.

Figure 2.6: Variation of the mechanical properties of the materials prepared with Mal-SL_1.1 with linker functionality: a) Young's modulus E , b) tensile strengths, and c) elongation at break e . Variation of the mechanical properties of the materials based on the 4-SH linker with the amount of 11-MUC: d) Young's modulus E , e) tensile strength s , and f) elongation at break e .

Annexe du chapitre 2

Figure S2.1: ^{31}P NMR of SL and Mal-SL. IS = internal standard (cholesterol).

Figure S2.2: ^1H NMR of SL and Mal-SL in DMSO- d_6 . IS = internal standard (2,3,4,5,6-pentafluorobenzaldehyde).

Figure S2.3: FTIR spectra of the materials prepared with Mal-SL_1.1 (a) Mal-SL_0.7 (b) and Mal-SL_1.3

(c). 2-SH-Mal_SL0.7, 3-SH-Mal-SL_1.3 and 4-SH-Mal-SL_1.3 were not washed prior to analysis because of their partial solubility in methanol, unlike all other materials.

Figure S2.4: Swelling and mass loss in methanol of the materials prepared with Mal-SL_1.1 depending on the linker functionality.

Figure S2.5: Swelling and mass loss in methanol of the materials prepared with 4-SH linker (a) and 2- ϕ -SH linker (b) depending on the amount of 11-MUC used to derivatize the lignin.

Figure S2.6: Swelling and mass loss in water of the materials prepared with Mal-SL_1.1 depending on the linker functionality.

Figure S2.7: Swelling and mass loss in water of the materials prepared with 4-SH linker (a) and 2- ϕ -SH linker (b) depending on the amount of 11-MUC used to derivatize the lignin.

Figure S2.8: DMA of the materials prepared with Mal-SL_0.7: storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature.

Figure S2.9: DMA of the materials prepared with Mal-SL_1.1: storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature.

Figure S2.10: DMA of the materials prepared with Mal-SL_1.3: storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature.

Chapitre 3

Figure 3.1: (a) ^1H NMR spectra of the mixture of Mal-SL and FGE after 0 and 24 h at 60 °C, (b) evolution of the conversion and percentage of *endo* structures with the reaction time at 60 °C.

Figure 3.2: Thermograms of the four monomers mixtures from -30 to 130 °C.

Figure 3.3: FTIR spectrum for 2 D-A after its monomers homogenization, 24h at 60 °C, and after DSC analysis carried out in isothermal at 110 and 130 °C.

Figure 3.4: T_g (a), T_α (b) and cross linking density ν_e (c) of the lignin based D-A materials depending on the linker's functionality.

Figure 3.5: Mechanical properties of the lignin based D-A materials related to the linker's functionality a) Young's modulus E , b) elongation at break ϵ , and c) tensile strengths σ .

Figure 3.6: Lignin based D-A materials a) recovered after the first processing b) after the reprocessing and c) cut in bone shape for tensile measurements.

Figure 3.7: Thermo-mechanical properties of the lignin based D-A materials related to the number of reprocessing a) T_g b) T_α c) Young's modulus E d) elongation at break ϵ and e) tensile strengths σ .

Figure 3.8: Optical microscope picture of a) 2 D-A after scratch b) 2 D-A after curing at 60 °C for 1h c) 2 D-A after curing at 60 °C for 1h with additional 20 min at 110 °C d) 4 D-A after scratch e) 4 D-A after curing at 60 °C for 1h f) D-A after curing at 60 °C for 1h with additional 20 min at 130 °C g) reference material after scratch h) reference material after curing at 60 °C for 1h i) reference material after curing at 60 °C for 1h with additional 20 min at 130 °C.

Figure 3.9: 2 S-Fur-Mal-SL a) before the cut b) after the cut c) after the self-healing.

Figure 3.10: Stress - elongation curves of 2 D-A before and after the healing process.

Annexe du chapitre 3

Figure S3.1: a) ^1H NMR of SL and Mal-SL in DMSO-d_6 . IS = internal standard (2,3,4,5,6-pentafluorobenzaldehyde). b) ^{31}P NMR of SL and Mal-SL. IS = internal standard (cholesterol).

Figure S3.2: a) ^1H NMR and b) FTIR spectrum of polyfunctional furan linkers.

Figure S3.3: ^1H NMR of Furfuryl Glycidyl Ether (FGE).

Figure S3.4: ^1H NMR interpretation for of 2 S – Fur.

Figure S3.5: ^{13}C NMR interpretation for of 2 S – Fur.

Figure S3.6: HRMS analysis of 2 S – Fur.

Figure S3.7: FTIR spectrum of 2 S – Fur.

Figure S3.8: ^1H NMR interpretation for of 2 ϕ S – Fur.

Figure S3.9: ^{13}C NMR interpretation of 2 S – Fur.

Figure S3.10: HRMS analysis of 2 ϕ S – Fur.

Figure S3.11: FTIR spectrum of 2 ϕ S – Fur.

Figure S3.12: ^1H NMR interpretation for of 3 S – Fur.

Figure S3.13: ^{13}C NMR interpretation of 3 S – Fur.

Figure S3.14: HRMS analysis of 3 S – Fur.

Figure S3.15: FTIR spectrum of 3 S – Fur.

Figure S3.16: ^1H NMR interpretation for of 4 S – Fur.

Figure S3.17: ^{13}C NMR interpretation of 4 S – Fur.

Figure S3.18: HRMS analysis of 4 S – Fur.

Figure S3.19: FTIR spectrum of 4 S – Fur.

Figure S3.20: FTIR spectrum of the monomers mixture a t=0 and after 24h at 60° C a) 2 D-A b) 2 ϕ D-A c) 3 D-A and d) 4 D-A.

Figure S3.21: FTIR spectrum of the D-A materials before and after DSC analysis performed at 110 and 130 °C a) 2 D-A b) 2 ϕ D-A c) 3 D-A and d) 4 D-A.

Figure S3.22: TGA analysis of the lignin based D-A materials.

Figure S3.23: Storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature.

Figure S3.24: TGA curves before and after reprocessing of the D-A lignin based materials.

Figure S3.25: Storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature before and after reprocessing of the D-A lignin based materials.

Figure S3.26: Optical microscope picture of a) 2 ϕ D-A after scratch b) 2 D-A after curing at 60 °C for 1h c) 2 ϕ D-A after curing at 60 °C for 1h with additional 20 min at 110 °C d) 3 D-A after scratch e) 3 D-A after curing at 60 °C for 1h f) 3 D-A after curing at 60 °C for 1h with additional 20 min at 130 °C.

Figure S3.27: 4 D-A a) before the cut b) after the cut c) after the self-healing.

Chapitre 4

Figure 4.1: Evolution of the OH content (measured by quant ^{31}P NMR) with reaction time during silylation with 1.2 or 2.5 equiv. TBDMSCl: aliphatic OH groups (a), phenolic OH groups (b).

Figure 4.2: Influence of the amount of reagent used for the derivatization on the OH content measured by ^{31}P NMR (18 h reaction at room temperature): silylation with TBDMSCl (a), acetylation with Ac_2O (b).

Figure 4.3: ^1H NMR (a) and FTIR (b) spectra of neat (SL), acetylated (Ac-SL_06), and silylated (Si-SL_05) lignins. ^1H NMR were recorded in DMSO-d_6 .

Figure 4.5: Molar mass distributions of fully acetylated (Ac-SL_06) and silylated lignins (Si-SL_05), measured by SEC in chloroform (calibration with PS standards).

Figure 4.6: (a) Water contact angle of silicon wafer reference, neat SL, and fully acetylated (Ac-SL_06) or silylated (Si-SL_05) lignins. (b) Evolution of the contact angle with the percentage of derivatized OH groups (calculated by ^{31}P NMR).

Figure 4.7: TGA (a) and DTG (b) curves of the neat SL and fully acetylated (Ac-SL_06) or silylated (Si-SL_05) lignins.

Figure 4.8: SEM images of cryo-fractures of LDPE (a), LDPE–neat SL blend (b), LDPE–acetylated SL (Ac-SL_06) blend (c), and LDPE–silylated SL (Si-SL_05) blend (d). All the blends contain 10 wt % of lignin.

Annexe du chapitre 4

Figure S4.1: TGA coupled to MS of neat soda lignin (SL).

Figure S4.2: TGA coupled to MS of acetylated lignin (Ac-SL_06).

Figure S4.3: TGA coupled to MS of silylated lignin (Si-SL_05).

Figure S4.4: TGA coupled to MS of silylated lignin (Si-SL_05) (following)

Figure S4.5: DSC traces of the neat (SL), acetylated (Ac-SL_06) and silylated lignins (Si-SL_05).

Figure S4.6: Dynamic mechanical analysis: storage E' and loss moduli E'' (a) and loss factor $\tan \delta$ (b) of LDPE and its blends with neat (SL), acetylated (Ac-SL_06) and silylated lignins (Si-SL_05).

SOMMAIRE

COMMUNICATIONS LIEES AUX TRAVAUX DE THESE.....	iii
LISTE DES ABREVIATIONS.....	vii
LISTE DES TABLEAUX, SCHEMAS ET FIGURES.....	xiii
SOMMAIRE.....	xxii
INTRODUCTION GENERALE.....	i
	3
Chapitre 1 : La chimie "Click": un outil utile pour la synthèse contrôlée de matériaux polymères aromatiques biosourcés.....	8
Introduction du chapitre 1.....	9
1. Introduction.....	11
2. Main aromatic biomolecules and building blocks.....	13
2.1 Lignins.....	14
2.2 Tannins.....	16
2.3 Cashew Nut Shell Liquid (CNSL).....	19
2.4 Others bio-based aromatic macromers.....	21
2.5 Strategies for the chemical modification of bio-based aromatic polyphenols.....	23
3. Click Chemistry.....	25
3.1 Huisgen 1,3 dipolar cycloaddition.....	25
3.2 Furan Maleimide Diels – Alder cycloadditions.....	26
3.3 Thiol – ene reactions.....	27
3.4 Thiol – yne reaction.....	28
4. Addition of “clickable” groups onto aromatic macromers.....	29
4.1 Introduction of vinyl and enes groups.....	30
4.2 Introduction of acrylate and methacrylate groups.....	34
4.3 Introduction of alkyne groups.....	36
4.4 Introduction of alkyl azide groups.....	38
4.5 Introduction of furan groups.....	39
4.6 Introduction of maleimide groups.....	40
4.7 Naturally occurring clickable groups.....	41
5. Synthesis of aromatic polymeric materials through “click” reactions.....	42
5.1 Azide – alkyne cycloaddition.....	43
5.2 Thiol – ene reactions.....	45
5.3 Furan – Maleimide D-A.....	48
6. Conclusions and perspectives.....	50

Conclusion et perspectives du chapitre 1.....	52
Références du chapitre 1.....	53
Chapitre 2 : Matériaux à base de lignines obtenues par polymérisation « clic » thiol-maléimide.....	68
Introduction du chapitre 2.....	69
1. Introduction.....	71
2. Experimental section.....	73
2.1 Reagents and materials.....	73
2.2 Synthesis and materials processing.....	73
2.3 Characterization.....	75
3. Results and discussions.....	78
3.1 Synthesis of maleimido functionalized solda lignin (Mal-SL).....	78
3.2 Synthesis of thiol-maleimide lignin-based polymeric materials.....	81
3.3 Evaluation of the structure of the thiol-maleimide networks.....	83
3.4 Thermal and mechanical properties of the thiol-maleimide lignin-based materials.....	85
4. Conclusions.....	87
Conclusion et perspectives du chapitre 2.....	89
Références du chapitre 2.....	90
Chapitre 3 : Matériaux thermoréversibles et auto-réparants à base de lignines obtenues par polymérisation à base de réactions Diels-Alder	95
Introduction du chapitre 3.....	96
1. Introduction.....	98
2. Experimental section.....	99
2.1 Reagents and materials.....	99
2.2 Synthesis and materials processing.....	100
2.3 Characterization.....	102
3. Results and discussions.....	104
3.1 Synthesis of maleimido functionalized solda lignin (Mal-SL).....	104
3.2 Model reaction between Mal-SL and FGE.....	106
3.3 D-A polymerization and retro D-A of Mal-SL.....	108
3.4 Characterization of the lignin based D-A materials.....	110
3.5 Reprocessing of the lignin based D-A materials.....	112
3.6 Self-healing properties.....	114

4. Conclusions.....	117
Conclusion et perspectives du chapitre 3.....	119
Références du chapitre 3.....	120
Chapitre 4: Modification chimique de la lignine: acétylation versus silylation.....	124
Introduction du chapitre 4.....	125
1. Introduction.....	127
2. Experimental section.....	128
2.1 Reagents and materials.....	128
2.2 Syntheses and materials processing.....	129
2.3 Characterization.....	130
3. Results and discussions.....	134
3.1 Comparison on lignin reactivity toward silylation and acetylation.....	134
3.2 Physico-chemical properties of silylated and acetylated lignins.....	139
3.3 Thermal properties of silylated and acetylated lignins.....	142
3.4 Blends of lignins derivates with low-density polyethylene (LDPE).....	144
4. Conclusions.....	147
Conclusion et perspectives du chapitre 4.....	149
Références du chapitre 4.....	150
CONCLUSION GENERALE & PERSPECTIVES.....	156
ANNEXES.....	
Annexe I: Supporting information du chapitre 2.....	162
Annexe II: Supporting information du chapitre 3.....	168
Annexe III: Supporting information du chapitre 4.....	188
LISTE COMPLETE DES REFERENCES BIBLIOGRAPHIQUES.....	196

INTRODUCTION GENERALE

Bien que leurs développements soient relativement récents pour le domaine des matériaux, les polymères sont devenus omniprésents. Depuis le boom de l'industrie pétrochimique du milieu des années soixante, le marché des polymères a connu une croissance exponentielle atteignant une production de plus de 300 millions de tonnes en 2015. Les tendances montrent qu'au cours des 20 prochaines années, cette valeur devrait doubler et presque quadrupler d'ici 2050. Cependant, la limitation de certaines fractions fossiles et les évolutions des tendances sociétales poussent les industriels à mettre sur le marché des produits plus respectueux de l'environnement et biosourcés. En effet, les bioplastiques sont en pleine croissance (10 à 20% par an) et représentent environ 4 millions de tonnes en 2016. Ce chiffre devrait augmenter jusqu'à plus de 6 millions de tonnes en 2021.

Dans cette évolution vers les polymères biosourcés, la lignine, de par ses unités aromatiques et une production annuelle de 50 millions de tonnes, est un macromère très intéressant pour la synthèse de nouveaux polymères. En effet, Les polymères aromatiques, représentent actuellement 15 à 20% de la production des thermoplastiques. Le squelette rigide de par les cycles aromatiques donne des propriétés uniques en termes de résistance aux chocs, de résistance à la chaleur, de faible retrait et de résistance chimique. Malgré une grande quantité de lignine générée dans l'industrie papetière, seule une petite quantité (2%) est exploitée dans l'industrie chimique, le reste est utilisée comme combustible dans ces unités de bioraffinerie. La variabilité de la ressource, la présence de soufre et la grande diversité d'architectures sont les principaux obstacles pour l'utilisation de la lignine comme composant de base pour la production de produits de grande masse. Lors la dernière décennie, de nombreux succès ont été obtenus pour la valorisation de ce biopolymère abondant ou macromère. Mais de forts investissements en recherche sont encore nécessaires pour une exploitation pérenne de cette bioressource et synthons à différents niveaux de la chaîne de valeur créée.

Dans le contexte d'une collaboration entre l'Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé (ICPEES / UMR CNRS 7515) à l'Université de Strasbourg (UniStra) à

Strasbourg et le Luxembourg Institute of Science and Technology, un projet, intitulé « Modification chimique de lignines pour l'élaboration de nouveaux polymères et additifs aromatiques et biosourcés » a été lancé. Ce projet a notamment été financé par le Fonds National de la Recherche du Luxembourg (AFR_PhD bourse n° 9903572).

L'objectif désigné a été réalisé au travers de diverses modifications chimiques de la lignine, avec l'élaboration de nouveaux polymères et additifs biosourcés, qui ont été évalués et caractérisés par diverses approches.

Les stratégies de synthèse développées ont été en relation avec les principes d'une chimie « verte », en évitant l'utilisation de solvants et catalyseurs toxiques (quand c'était possible) et en utilisant des réactions « clic », caractérisée pour être rapides avec des rendements quantitatifs sans production de sous-produits.

Ce manuscrit s'articulera en quatre chapitres organisés autour de différents articles scientifiques rédigés en anglais qui seront encadrés par des textes d'introduction et de conclusion en français.

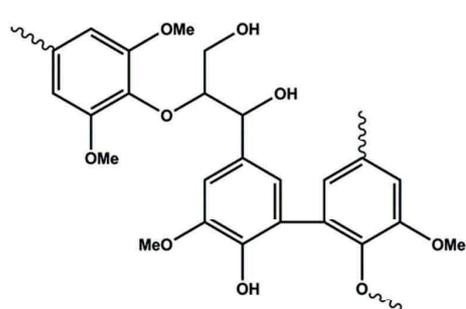
Tout d'abord, le chapitre 1 s'attachera à faire un état de l'art des principaux polymères biosourcés aromatiques, leurs bioressources, leurs localisations, leurs structures et réactivités chimiques, et leurs utilisations réelles ou potentielles. Le chapitre présente notamment les matériaux à base de lignine synthétisés en utilisant une « clic » polymérisation. Cette première partie est l'objet d'une review prochainement soumise.

Le deuxième chapitre présente les résultats relatifs à la synthèse et à l'étude des relations « structure-propriété » des polymères obtenus par polymérisation thiol – ene. Dans cette étude, des macromères de lignine ont été greffé par une réaction d'estérification avec l'acide 11-maleimide-undecenoic (obtenu à partir de l'huile de ricin), sans l'utilisation de solvants et de catalyseurs. Les dérivés de lignine à base de fonctions maléimides ont été ensuite polymérisés par une réaction thiol-ene avec différents thiols aliphatique et aromatiques polyfonctionnels

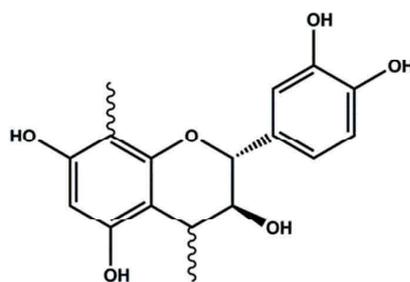
Le troisième chapitre, présente les résultats portant sur la synthèse de matériaux à base de lignine thermo-réversibles et auto-réparant, élaborés avec succès pour la première fois grâce à une polymérisation de type Diels-Alder (D-A) thermo-réversible. Différents réseaux polymériques ont été synthétisés par cycloaddition D-A à partir de dérivés maleimide de lignine et de furanes polyfonctionnels. La polymérisation a été conduite sans l'utilisation de solvants à 60 °C. Les réseaux polymères correspondants présentent des propriétés d'auto-réparation lorsqu'ils sont coupés ou rayés et réparés à 110/130 °C, indiquant la réversibilité des liaisons D-A développées.

Le quatrième et dernier chapitre de ce travail est dédié à la synthèse d'un nouveau dérivé de lignine à base de groupes tert-butyldiméthylsilyle. Les groupes hydroxyles phénoliques et aliphatiques portés par la lignine ont été modifiés avec du chlorure de tert-butyldiméthylsilyle (TBDMSCl) pour produire les liaisons éthers silyliques correspondantes. La lignine silylée est soluble dans une large gamme de solvants organiques et montre un caractère hydrophobe plus important en comparaison avec la lignine non modifiée. Pour évaluer le potentiel de ce nouveau produit comme additif dans des matrices polymériques, il a été mélangé avec du polyéthylène basse densité (PEBD). La lignine silylée a montré une bonne compatibilité, avec une dispersion homogène dans cette matrice polyoléfine en comparaison de la lignine non modifiée.

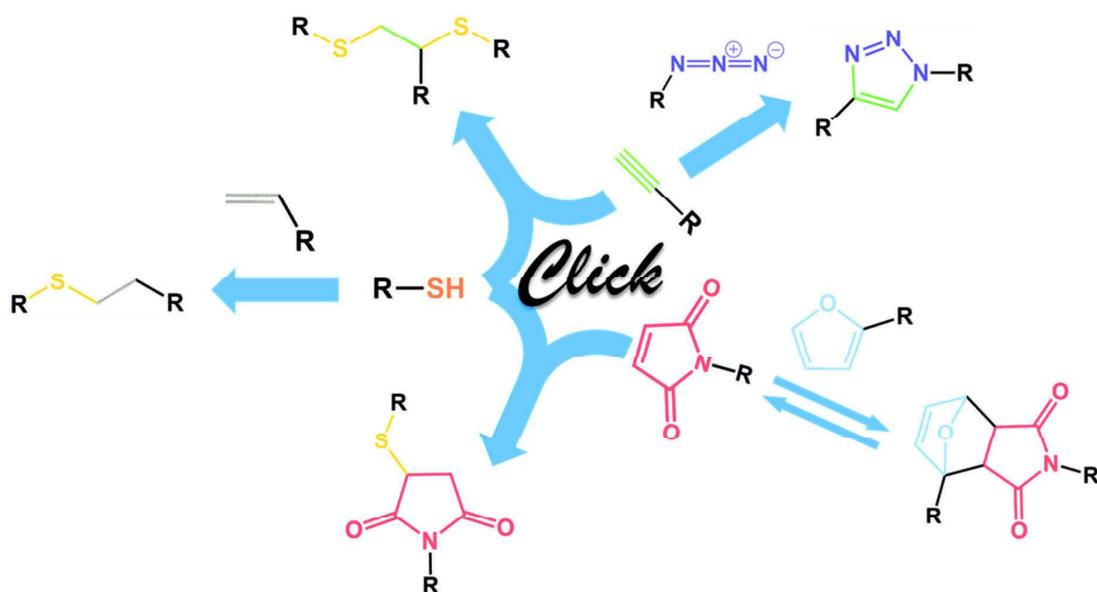
Chapitre 1 : La chimie "Click": un outil utile pour la synthèse contrôlée de matériaux polymères aromatiques biosourcés



Lignins



Tannins



Introduction

La synthèse bibliographique présentée dans ce chapitre décrira l'application de la chimie « click » pour l'élaboration de polymères aromatiques biosourcés. Cette synthèse présentée sous la forme d'une revue intitulée « Click chemistry: an useful tool for the controlled synthesis of bio-based aromatic polymeric materials » expose dans un premier temps les principaux polymères biosourcés aromatiques, leurs bioressources, leurs localisations, leurs structures et réactivités chimiques, ainsi que leurs disponibilités et utilisations réelles ou potentielles. Ensuite, les principes sur lesquels repose la chimie clic, les réactions principales impliquées et leurs mécanismes de réaction seront décrits. La deuxième partie de la publication présente les principales modifications chimiques ayant pour objectif l'introduction de groupes fonctionnels cliquables sur les principaux biopolymères aromatiques. Enfin, les polymères et les matériaux aromatiques biosourcés obtenus par une polymérisation clic seront discutés avec les potentielles applications connexes. Dans cette deuxième partie de l'article une attention particulière sera accordée aux aspects qui restent encore inexplorés avec de potentielles contributions académiques et industrielles.

“Click” chemistry: a useful tool for the controlled synthesis of bio-based aromatic polymeric materials

Pietro Buono,^[a] Antoine Duval,^[b] Luc Averous^[b] and Youssef Habibi*^[a]

^a Department of Materials Research and Technology (MRT), Luxembourg Institute of Science and Technology (LIST), 5 avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

^b BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, Strasbourg Cedex 2 67087, France

*e-mail: youssef.habibi@list.lu

Abstract

Lignin, tannins and cashew nut shell liquid are considered the main sources of aromatic based macromers, representing an abundant alternative feedstock for the elaboration of aromatic chemicals and polymers in view to replace some fossil-based fractions. Located in different tissues of plants, these compounds with a large diversity and structural complexity are till now considered as by-products derived from fractionation-separation industrial processes with low added values. In the last decade, the use of the so-called “click chemistry” as a tool for the synthesis of controlled macromolecular architectures has seen a large development in fundamental and applied research for a wide range of applications. It could represent a valid solution to overcome the main limitations encountered in the chemical modification of natural source of chemicals, with an environmentally friendly approach to create new substrates for the development of innovative polymers and materials.

After a quick description of the main aromatic biopolymers, including the main extraction techniques along with the structure and their properties, this review article describes the chemical

modifications that have been mainly focused on natural polyphenols aiming to the introduction of “clickable” groups, and its further use for the synthesis of bio-based materials and additives. Special stress will be laid on several still unexplored chemical features that could contribute to further fundamental and applied materials science research.

1. Introduction

According to the latest market data compiled by European Bioplastics,¹ bio-based and biodegradable polymers represent only about 1-2% of the over 300 million tons of thermoset and thermoplastics produced annually. However, the demand is rising and the market is growing by about 10 to 20% per year, on average. The current production, around 4.2 million tons in 2016, should increase up to approximately 6.1 million tons in 2021. Bio-based and non-biodegradable polymers such as bio-based polyurethanes (PUR),^{2,3} bio-based polyethylene (PE)^{4,5} or polyethylene terephthalate (PET),⁶⁻⁸ are the main drivers of this growth. Biodegradable and bio-based polymers, such as poly(lactic acid) (PLA),⁹⁻¹¹ polyhydroxyalkanoates,^{12,13} and starch blends,¹⁴⁻¹⁶ are also becoming more and more demanding with an increase of the worldwide production.

Aromatic polymers like polystyrene or PET incorporating aromatic architectures are widely spread for all type of applications including packaging, building, automotive. These aromatic based materials represent 15-20% of total polymers demand.¹⁷ The rigid backbone provided by aromatic rings included in the macromolecular architecture gives unique properties in terms of stiffness, impact resistance, heat and fire resistance, low shrinkage and chemical resistance.¹⁸⁻²⁰

To find new aromatic resources is nowadays a strong necessity since the availability of aromatic or BTX fractions (for Benzene, Toluene and Xylene) from fossil resources are more and more limited, due to different factors such as the evolutions of the refineries toward the treatment of gas, the strong demand of some emerging countries. Shale gas and in a lower amplitude shale oil are rapidly emerging as a new fossil feedstock given new available technologies, however their productions are

based on light fractions mainly from C1 to C3 or to C4 to produce e.g., ethylene/propylene with only very limited aromatic fractions.

Our society is facing global challenges regarding the high CO₂ emissions, pollution, global warming and limited suitable fossil reserves overtime. Therefore, new bio-based production routes need to be designed and put in practice urgently, in order to address the ecological and economic challenges that humanity and industry are facing.

Despite recent advances in the development of value added bio-aromatics materials, some drawback could remain, such as their cost compared to fossil based equivalents, their availability and the variability of the renewable resource. Lignins, tannins and cashew nut shell liquid (CNSL) are the most abundant aromatic bio(macro)molecules with an annual production of 50 Mt, 100 kt and 450 kt, respectively,²¹⁻²⁴ representing an extremely abundant alternative feedstock for the elaboration of aromatic chemicals and polymers.

The exploitation of renewable materials feedstock is an essential but not a sufficient to promote a sustainable and “green” chemistry.²⁵ The use of safe, environmentally benign substances, the design of energy efficient processes aiming to avoid waste production should also be considered for the design of chemical products. In addition, in order to satisfy the materials market’s requirements, controlled polymeric structure and kinetics of the polymerization path are needed, characteristics that still represent a limitation for the use of raw biopolymers as feedstock for the production of valuable products.

In the last decade, the use of the so-called “click chemistry”²⁶ as a tool for the synthesis of controlled macromolecular architectures has seen a large development in fundamental and applied research for a wide range of applications.²⁷⁻²⁹ “Click” reactions are characterized by stereo and regio-specific mechanisms, leading to controlled chemical structures. Furthermore, this set of reactions provides quick and quantitative yields under mild conditions, producing inoffensive byproducts easily removable by non-chromatographic methods, according to the “green” chemistry principles.

Despite the recent huge development in polymer chemistry, the use of “click” chemistry for the design of bio-based aromatic polymers has been only scarce. The application of “click” polymerizations could potentially lead to circumvent the abovementioned limitations related to the use of biopolymers in materials science.

In this review article, we will illustrate the “click” synthetic strategies and the chemical modification aiming to introduce clickable functional groups which have been applied to aromatic bio(macro)molecules, mainly but not only lignins and tannins, the most important renewable sources of aromatic structures. Our purpose is to underline the fact that the synergetic combination of click synthetic strategies and a green approach using bio-based macromers could lead to the development of environmentally friendly and renewable polymeric materials based on aromatic units. Beyond the presentation of the different synthetic pathways, special stress will be laid on the unexplored chemical features that could contribute to further fundamental and applied researches.

2. Main aromatic biomolecules and building blocks

Earlier, the waste products such as wheat straw, bagasse, shell, seeds and fruit benches, generated by industries involved into the agriculture and the pulping sectors, were principally used as a source of low-cost energy for machineries or alternatively as natural fertilizers by the local populations. Nowadays, the increasing demand of renewable feedstock for the industry to develop chemicals and materials led to the reevaluation of such waste products, particularly for market of the aromatic polymers. For instance, the large and partially unexploited woody biomass is very rich in aromatic based units, *e.g.* cresol, catechol, guaiacols, syringol, eugenol, and potentially lignin etc., which can be used to develop new chemical architectures.

This section describes the main bio-based aromatic macromers, with a particular focus on lignins and tannins, which have received great academic and industrial interests in the last decades.

2.1 Lignins

The term lignin was coined for the first time by the Swiss botanist A. P. de Candolle, who depicted it as a “fibrous, tasteless material insoluble in water and alcohol but soluble in weak alkaline solutions, and which can be precipitated from solution using acid”.³⁰ The name “lignin” he gave to this material, derived from the Latin word *lignum*, meaning wood.

Lignin originate from phenolic based precursors, which undergo polymerization through esterification, oxidative coupling or condensation reactions to form an apparently unordered and hyperbranched material (Figure 1.1).³¹

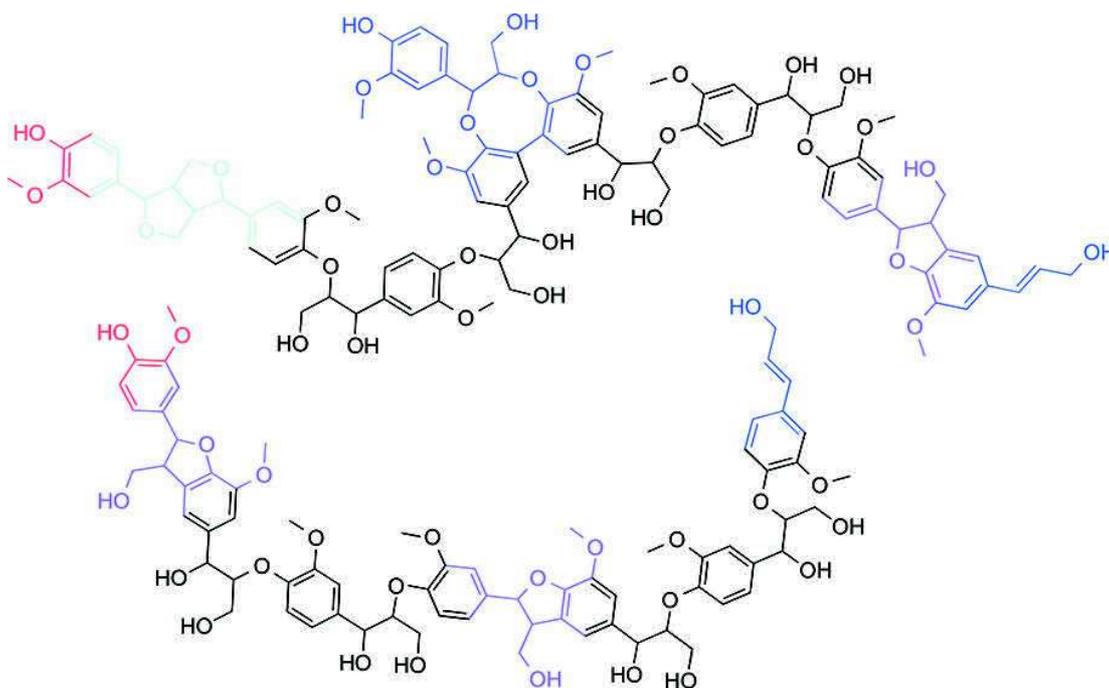


Figure 1.1 Some hypothetical chemical structure of lignin.³²

The lignin's precursors are based on three carbon side chain providing a basic nine carbon structure usually called C₉ unit and/or phenyl propane unit. A primary hydroxyl (OH) group on the C_γ terminates the side chain, while a double bond connects the C_α and C_β; the phenolic ring has

methoxide groups to various degree in *ortho* positions, depending of the monomer: *p*-coumaryl has none, conyferyl one and sinapyl two.³³

Lignin can be obtained from various sources, such as wood, sugarcane bagasse or cereals, using a variety of extraction methods. The localization, source from which it is extracted as well as the extraction processes can strongly influence its chemical structure and composition, molar mass, physico-chemical and mechanical properties (Table 1.1). During lignin extraction, the polymeric structure is degraded into smaller fragments. The corresponding processes are divided into sulfur and sulfur-free, depending on the presence or the absence of sulfur components in the extraction media.^{22,34–36} For instance, sulfide, sulfite and hydroxide anions are employed to fragment the lignin polymeric structure in the Kraft, Sulfite, and Soda processes respectively.

Among the main types of industrial chemical pulping processes, sulfite lignins (or lignosulfonates) are the largest commercially available for applications including dispersants, surfactants, and binders markets.³⁵ However, commercial lignosulfonates contain significant levels of impurities, such as hemicellulose sugars and inorganic spent pulping chemicals.

The soda process is mostly used on annual plants feedstock such as sugarcane bagasse, flax, or wheat straw, while kraft, and sulphite pulping are predominantly used on soft and hardwood.

Kraft and soda lignins may be recovered in higher purity by controlled acidification of the pulping media, since at low pH these lignin's water solubility decrease, while hemicellulose sugars and ash remain soluble in the solution. The isolated kraft and soda lignins are characterized by lower molecular weight and poorer solubility in water than lignosulfonates.

Aside these main three extraction processes, organic solvents can also be used for the extraction of soluble low molar mass lignin macromers providing the so-called *organosolv* lignin, characterized by higher purity and absence of sulfur, making them attractive for a wide range of technical applications with their more or less controlled structures. However and till now, organosolv lignin are mainly produced at small scale (Table 1).

Table 1.1 Main types of lignin with their commercial producers and productions^{22,34,36}

Type of Lignin	Capacity (kTons year ⁻¹)	Producers	Average Molar Mass (M _n – g mol ⁻¹)
Kraft	90	MeadWestvaco Domtar Ingevity West Fraser	1000-3000
Lignosulfonate	7000	Lignotech Tembec Nippon paper Cartiere Burgo	15000-50000
Soda	5-10	Green Value	800-3000
Organosolv	~3	CIMV Lignol Innovations DECHEMA/Fraunhofer Dedini	500-5000

Whatever the extraction process, hydroxyl groups, either phenolic or aliphatic, are the most common chemical functions present in lignin (Figure 1). They can be detected and quantified by various techniques, including potentiometric titration, UV spectroscopy,³⁷ ¹H NMR,^{38,39} ¹³C NMR⁴⁰ and nowadays most commonly ³¹P NMR.^{41,42} The latter allows a quick and precise quantification of carboxyl, aliphatic and phenolic OH groups. It also allows distinguishing *para*-hydroxyphenyl, guaiacyl and syringyl units as well as condensed structures.

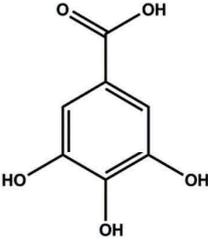
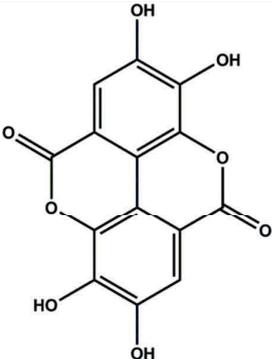
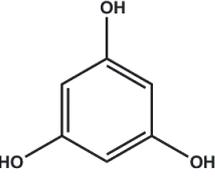
However, the content in phenolic and aliphatic OH groups differs according to the extraction process. For instance, Kraft lignin contains the highest amount of phenolic groups, due to extensive cleavage of β-O-4 bonds during its extraction. In contrary, *organosolv* lignin possess a relatively low amount of free phenolic units, because only limited bond ruptures occur during the extraction process with organic solvents. Furthermore, lignin possesses also a relatively high amount of carboxylic acid groups (more particularly in Soda lignin) and carbonyls, while other groups are present in sulfur-based lignin such as thiols (Kraft lignin) and sulfonates (Lignosulfonate lignin).

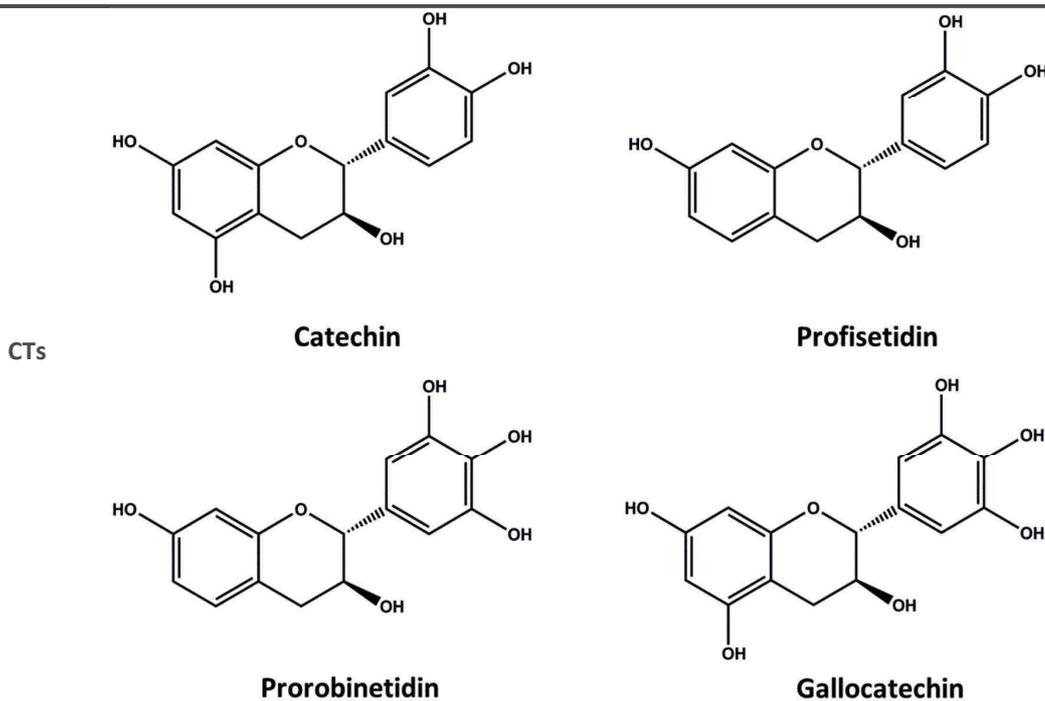
2.2 Tannins

Tannins are after lignin the second natural source of phenolic structures. The term tannin comes from *tanna*, an old German word indicating fir-trees. In the past, this word has been used to identify the plant's extract material employed to convert animal hides into leather through the so called "tanning" treatment.⁴³ Nowadays, tannins represent a large variety of water soluble polyphenolic compounds having a molar mass between 500 and 3000 g mol⁻¹ able to complex other classes of macromolecules including proteins, amino acids and alkaloids.⁴⁴

Tannins can be classified into three categories depending on their precursors: condensed tannins (CTs), hydrolysable tannins (HTs) and phlorotannins (PhTs). HTs are based on gallic and ellagic ester derivatives of sugar-type polyols, mainly D-glucose (Table 1.2); PhTs, found in red-brown algae, are essentially derived from oligomers of phloroglucinol (Table 1.2), formed through its dehydrogenative oxidative coupling; CTs are derived from the oligomerization of flavan-3-ol units such as catechin, epicatechin, epigallocatechin, and fisetinidol (Table 1.2).

Table 1.2. Tannins precursors.

HsTs	 <p data-bbox="558 813 662 835">Gallic Acid</p>	 <p data-bbox="965 873 1077 896">Ellagic Acid</p>
PhTs	 <p data-bbox="750 1160 917 1187">Phloroglucinol</p>	



Tannins extraction from plants may consist in fresh plants treatment, or most used pre-treatments in which the biomass is first frozen or dried.⁴⁵⁻⁴⁷

Tannins are basically extracted by solvents and unmodified chemical structures are obtained. Boiling water is the most used extraction method in industries, providing an extraction yield of around 60-65% from most common sources.⁴⁸ Organic solvents as ethanol, methanol, acetone, ethyl acetate or formic acid, can be used with an improvement of the extraction effectiveness. However, large solvent's volume together with longer time extraction affects the costs and the process sustainability.

HsTs are mainly used for leather tanning, given their high performances in terms of clarity of color and light resistance. Their structures, the low level of phenol substitution as well as the low nucleophilicity, limit the interest of this class of tannins for materials chemistry.

CTs tannins constitute more than 90% of the total world production of commercial tannins (242 000 tons per year), with Mimosa and Quebracho as the main species. Their higher chemical reactivity

brought interest for their use in the preparation of adhesives, resins and other applications apart from leather tanning.

2.3 Cashew nut shell liquid (CNSL)

Cashew nut shell liquid (CNSL) is a brownish viscous liquid obtained from cashew trees, which are typically spread along the coastal Asian and African regions, Mozambique, India and Brazil. India is the largest producer of CNSL and exports annually around 14 million tons of such a biomass. The production is esteemed to increase by 7-10% on annual basis.⁴⁹

CNSL contains substituted phenolic compounds in which the substituents are long unsaturated alkyl side chains that are responsible for its oily texture.⁵⁰ CNSL is located in the spongy mesocarp of the cashew nut shell of the tree *Anacardium occidentale* L and is considered a by-product obtained by the cashew nut industries during the cashew processing.

The CNSL is a mixture of anacardic acid (71.7%), cardol (18.7%), cardanol (4.7%), traces of 2-methylcardol (2.7%)⁵¹ and the remaining 2.2% is a polymeric material not well defined yet. The components, as shown in Fig. 1.2 possess a long hydrocarbon chains based on 15 C which can be saturated or mono, di or tri-unsaturated.

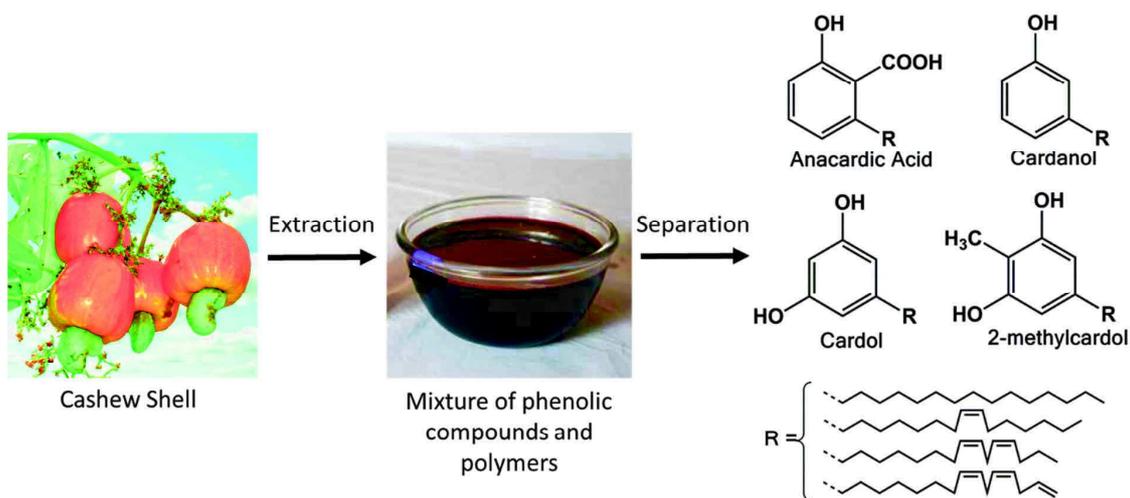


Figure 1.2. Chemical structure of the principal components of CNSL.²³

The particular chemical structure of these components is comparable to the one of fatty acids, in which a phenolic or resorcinolic ring can substitute the carboxylic acid. They have been exploited

chemically unmodified and/or modified for application including plasticizers,^{52–54} adhesives,⁵⁵ fuel additives,⁵⁶ surfactants^{57,58} and resin additives.^{59–61} Furthermore, the presence of phenol moieties also imparts antioxidant properties, therefore opening the possibilities to be used as additives to increase the stability of polymeric matrices.^{23,62}

The extraction of CNSL from cashew nutshell followed by the fractionation of every component is carried out by techniques such as solvent extraction, pyrolysis, heat and supercritical carbon dioxide extraction. Depending on the kind of process utilized and the degree of purity obtained, CNSL is commercially available under two grades: (i) natural grade, in which CNSL is cold-processed through solvent extraction of cashew nutshells, obtaining a mixture of anacardic acids (60–70%) and cardols (20–25%) as major components;⁶³ and (ii) technical grade, in which the CNSL is trickled out from the shells during the time period of the nuts roasting, essential for separation of the kernels. This hot-processed/heat-extracted CNSL contains cardanols (60–70%) and cardols (20–25%) with additional low amount of 2-methylcardols.

Definitely CNSL can be considered as sustainable, at low cost and largely available around the world. Its phenolic compounds present interesting functional structural features allowing chemical modifications to synthesize a range of useful monomers.

2.4 Others bio-based aromatic macromers

Except these different major sources of natural aromatic macromers, others aromatic compounds can be isolated from biomass either by extraction or by pyrolysis or fragmentation. For instance, by cleavage of aryl ethers and aryl–alkyl linkages from lignin, a large variety of aromatic based low molecular weight monomers can be obtained possessing different chemical functions. In particular, hydroxybenzoic acids such *para*-hydroxybenzoic, 3,4-dihydrobenzoic, syringic, vanillic, ferulic (FA), *para*-coumaric (PCA), sinapic, cinnamic, caffeic acids and their corresponding hydroxybenzaldehydes and hydroxyacetophenones such as 4-hydroxybenzaldehyde, 4-hydroxyacetophenone, vanillin, acetovanillone, syringaldehyde and acetosyringone (Figure 1.3).²⁴

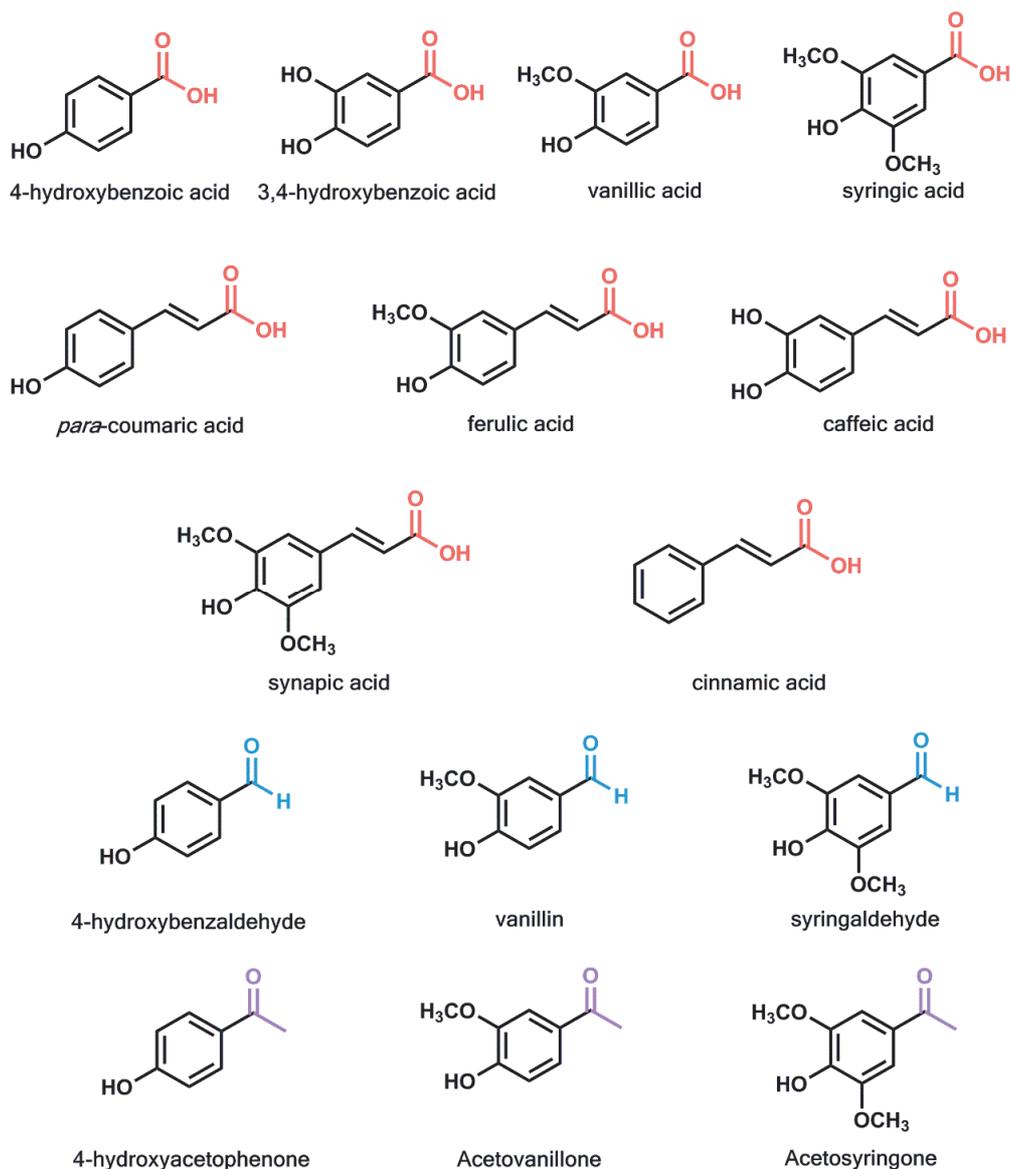


Figure 1.3. Naturally occurring phenolic compounds from various biological origins obtained from lignin.

Among the above listed compounds, definitely vanillin has been the greatest subject of interest in material science,^{64,65} since it is largely available as a by-product from the sulfite pulping paper industry.^{66,67}

In addition, long chains (either saturated or unsaturated) substituted phenols called tocols, can be found for instance in maize, sunflower, palm, soybean, or rapeseed, with excellent antioxidant properties (Figure 1.4).^{68,69}

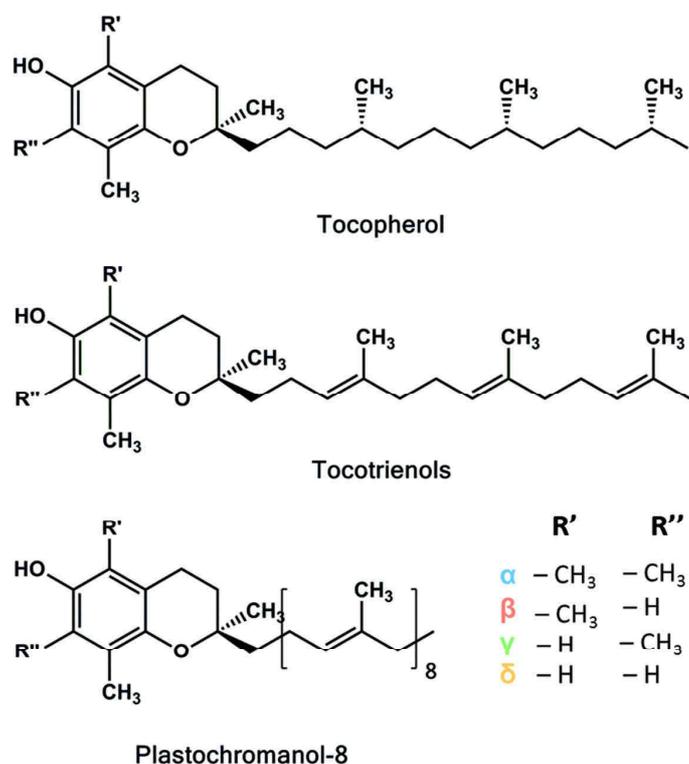


Figure 1.4. Chemical structures of the main naturally occurring tocols.

2.5 Strategies for the chemical modification of bio-based aromatic polyphenols

Natural aromatic macromers possess many different reactive groups, as detailed above, which give plenty of opportunities for chemical modifications. Given their high amounts, OH groups (phenolic or aliphatic) are the most commonly exploited to prepare chemically modified derivatives. Still, the reactivity of the aromatic ring is also exploited.

The modification of OH groups generally aims to increase the chemical reactivity, the solubility in organic solvents, or to improve the processing.

Two main strategies can be applied to obtain new bio-based aromatic building blocks: (i) modifying the OH reactive sites to introduce new chemically active groups or (ii) increasing the reactivity of the

OH groups by chain extension (Figure 1.5). A combination of both strategies is also possible, by first introducing new OH groups of high reactivity through chain extension, and then converting them into new reactive sites.

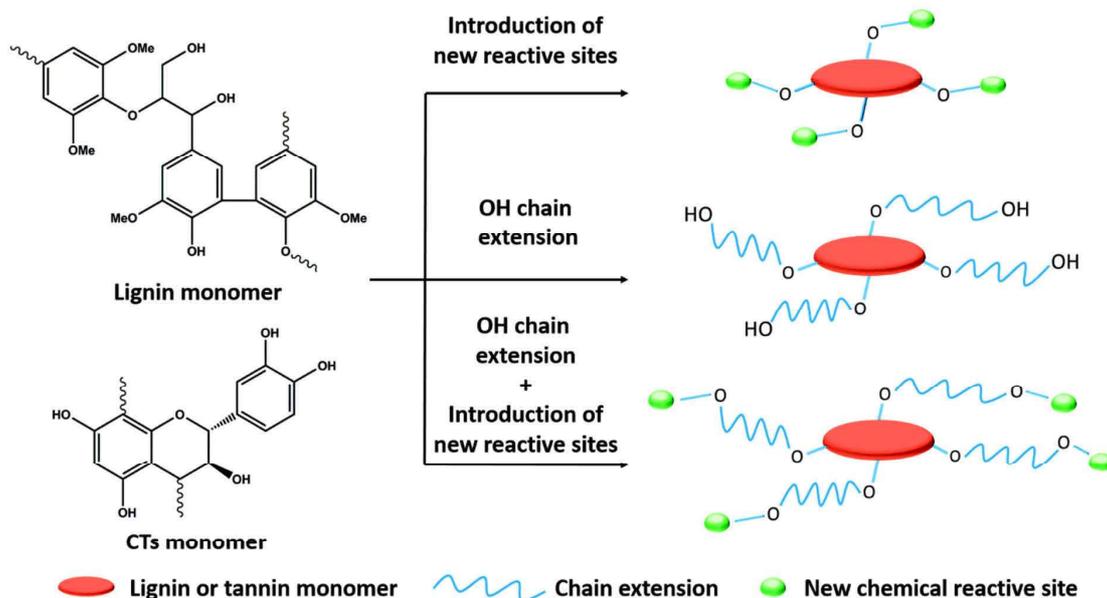


Figure 1.5. Possible chemical modification strategies applicable to natural polyphenols.

Different chemical reactions have been reported and investigated for the modification of biobased phenolic compounds such as lignin or tannins involving phenolic and aliphatic OH groups, such as acylation, etherification, and reactions with epoxy groups, ring opening polymerization (ROP) and alkoxylation.^{70–72}

The aromatic monomers activated by electron donating groups may act as nucleophiles towards electrophilic aromatic substitution. This reactivity has been used in the production of lignin, tannins and cardanol based phenol-formaldehyde type resins, but also to introduce new functional groups on CTs.

The flavan-ols unit present in CTs is composed by three rings, two of them aromatic, depicted in Figure 1.6 as A, B and C respectively.⁷³ Generally, the A ring is more nucleophile as compared to the B ring, with the carbons C-8 and C-6 the most reactive sites. This is due to the vicinal OH

substituents, which cause general activation in the B-ring without any localized effects such as those found in the A-ring.

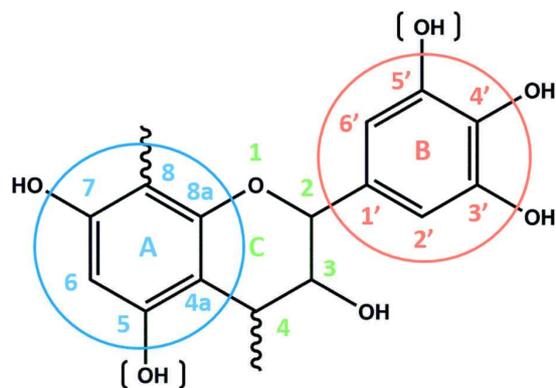


Figure 1.6. Illustration of the flavan-ols unit present in CTs.

3. Click chemistry

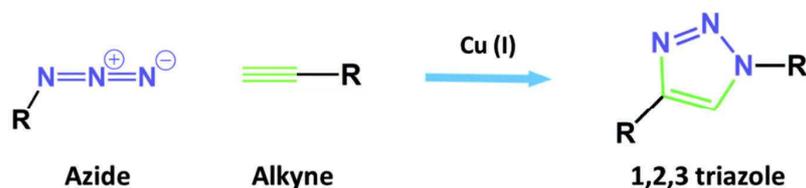
The concept of click chemistry was conceived to convey chemical reactions to a wide range of processes and demands.²⁶ Reactions should be simple, efficient, possibly stereoselective and regioselective, yield a single product, suitable to be performed at temperature and atmospheric conditions in “green” solvents or in bulk. Additionally, reactions should require simple or no work up avoiding expensive purification techniques. By critically overviewing the chemical reactions that have been developed and perfected since the 20th century, it is possible to list chemical reactions that fulfill many features of the ideal “click” prerequisites. In the following section, we will outline the most common click reactions; for a deeper mechanistic view we invite the readers to recent literature.^{27–29,74–81}

3.1 Huisgen 1,3 dipolar cycloaddition

Among all the reactions falling into the ‘click’ concept, the Huisgen 1,3-dipolar cycloaddition of alkynes and azides to yield 1,2,3-triazoles is undoubtedly the most common example of a click reaction (Scheme 1.1). Generally, alkyne and azide functionalities can be introduced easily into molecules through mild conditions and close to quantitative yields. In addition, their kinetic stability

and tolerance to a wide variety of functional groups and reaction conditions make these complementary coupling partners particularly attractive. However, organic azides can decompose explosively with production of N_2 and then should be treated with due care. Typically, aliphatic azides having a C/N ratio > 3 have a particular high kinetic stability. Despite these potential hazards, different works have shown that azides can be prepared, stored and used with controlled risk.⁸²

Sharpless⁸³ and Meldal⁸⁴ independently reported a Cu^I -catalysed version of the Huisgen 1,3 dipolar cycloaddition of azides and alkynes leading to higher regioselectivity, affording 1,4-regioisomer exclusively, and increasing the reaction rate up to 10^7 times, thus avoiding high temperatures. This high-yielding reaction tolerates a variety of functional groups and affords the 1,2,3-triazole product with minimal work-up and purification. In addition, it was demonstrated that water not only is tolerated in the reaction media but also has an additional beneficial kinetic effect. Since the discovery of Cu(I)-catalyzed alkyne – azide coupling a myriad of substrates were reported employing this powerful reaction for applications in materials science, biomedical research, drug design and biotechnology fields.



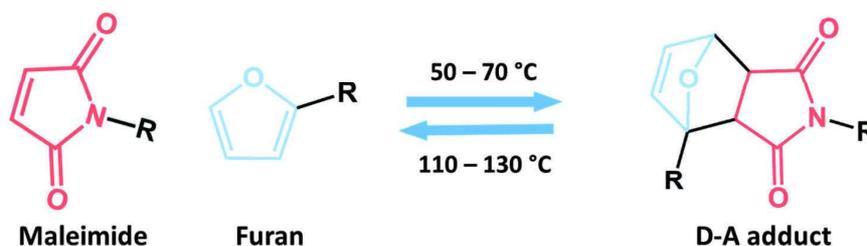
Scheme 1.1. Huisgen 1,3-dipolar cycloaddition of alkynes and azides yielding 1,2,3-triazoles.

3.2 Furan Maleimide Diels – Alder cycloadditions

The Diels–Alder (D-A) reaction is a [4+2] cycloaddition between a conjugated diene and a substituted alkene-bearing electron withdrawing groups – commonly called dienophile –, leading to the formation of substituted cyclohexene systems (Scheme 1.2). Described for the first time by Otto Diels and Kurt Alder in 1928,⁸⁵ awarded further for their efforts with the Nobel Prize in Chemistry in 1950, the Diels–Alder reaction is particularly utilized in synthetic organic chemistry as an effective path for the production of six-membered unsaturated rings with good control over regio and

stereochemical properties (add refs). The D-A adduct can be reversible under certain conditions and the reverse reaction is known as retro D-A. This attractive feature has been exploited in polymer chemistry in designing temperature-controlled reversible polymer networks, particularly in switchable materials and self-healing applications.^{81,86–88}

Furan – Maleimide D-A has been particularly exploited for its relatively mild conditions in which it is possible to perform an on-demand depolymerisation – repolymerisation. The straightforward formation of the D-A adduct occurs at around 50-70 °C, and its disassembly at 110-150 °C (retro D-A reaction) (Scheme 1.2). In this reaction, furans behave as a diene and maleimide as a dienophile. Furthermore, furan derivatives can be obtained from renewable resources and are therefore likely to play a growing role in sustainable approaches to green chemistry and materials science. Recently, Gandini largely reviewed the use of the Furan – Maleimide D-A in designing thermo-reversible macromolecular architectures.⁸¹ A wide range of A-A, B-B, A-B and multifunctional monomers have been prepared including furan and maleimide moieties, and further polymerized. Alternatively, furans and maleimides groups have been incorporated in various polymer matrices such as PE, PLA, PUR, PS, acrylic copolymers in order to expose pendant “clickable” groups providing a more efficient recyclability of polymer networks.^{89–92}



Scheme 1.2. Thermally reversible furan – maleimide adduct.

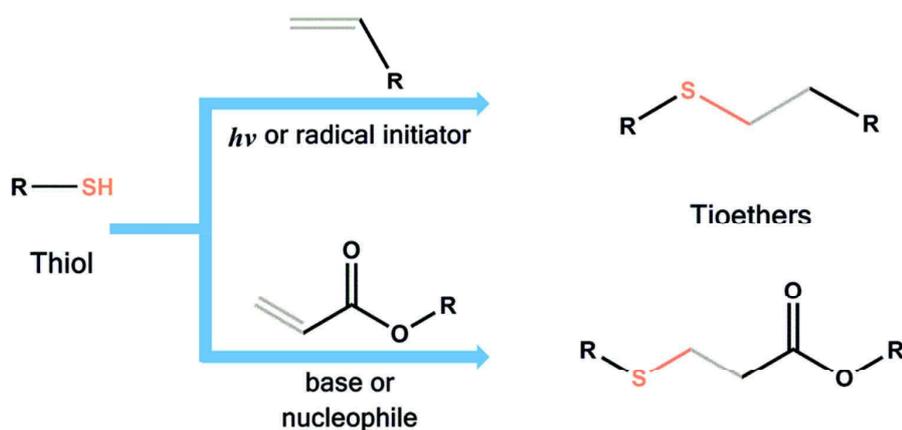
3.3 Thiol – ene click reactions

The relatively weak sulphur–hydrogen bonds of thiols paves the way for a range of chemical reactions with nearly quantitative yields, possessing the ability to be carried out by a variety of methods under mild conditions.^{76,78} Highly performing reactions of thiols with compounds bearing

double bonds (or simply “enes”), were already well known at the beginning of the 20th Century.⁹³ Two in particular emerged: (i) the thiol–ene free-radical addition to electron-rich / electron-poor carbon–carbon double bonds, and (ii) the catalysed thiol-Michael addition to electron-deficient carbon–carbon double bonds (Scheme 1.3). Both bases and nucleophiles may catalyze the Michael addition between thiols and electron-poor vinyl groups such as acrylates, maleimides, and vinyl sulfones.

The reactions between thiols and enes (radical thiol–ene or anionic/nucleophile Michael addition) possess many of the characteristics of click reactions. In addition, they are unaffected by the presence of water and the radical-mediated reaction shows good oxygen inhibition resistance,⁹⁴ unlike the conventional radical-mediated reactions that are severely inhibited by the presence of oxygen.⁹⁵

Definitely, the thiol – ene reaction has been demonstrated to be a robust click tool in material science capable of bulk polymerization, polymers post-modification, dendrimer synthesis and conjugation of different classes of polymers.

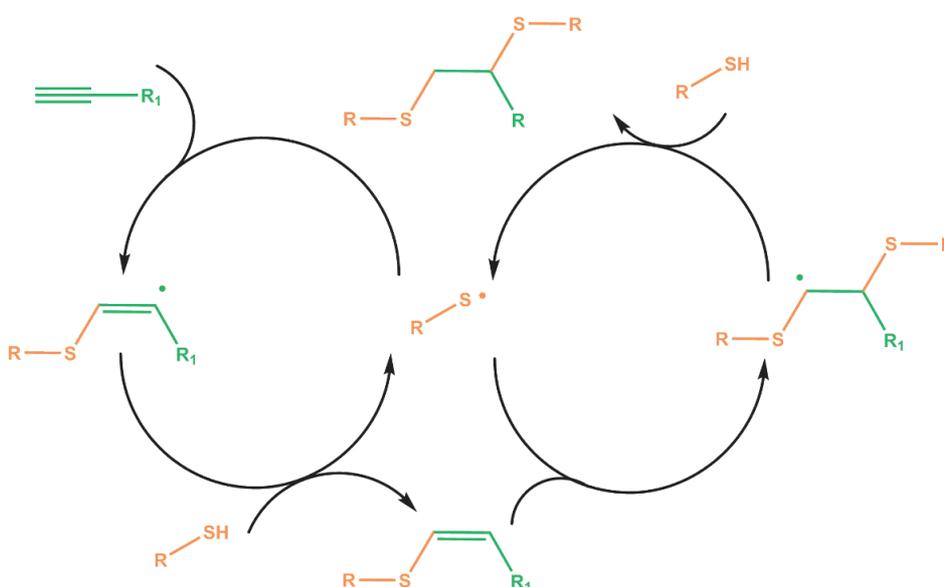


Scheme 1.3. Thiol–ene free-radical addition to electron-rich / electron-poor carbon–carbon double bonds, and the catalyzed thiol-Michael addition to electron-deficient carbon–carbon double bonds.

3.4 Thiol – yne click reactions

Bowman et al.,⁹⁶ showed that the radical-mediated thiol-ene mechanism can be complemented by the thiol-yne mechanism in which a thiyl radical is able to react twice with alkynes, forming two thio-

ether linkages and thus saturating the alkyne triple bond in a way that after the reaction termination, each alkyne functional group is combined with two thiols to produce a dithioether (Scheme 1.4). Mechanistically, the reaction is exactly equivalent to the thiol-ene one. The monothiol-yne addition product is a vinyl sulphide that is generally at least as reactive to thiyl radical addition as the initial alkyne. However, no second thiol addition occurs for particular cyclic alkynes such as cyclooctynes. The difunctional thiol addition onto alkynes results in an increased cross-linking network obtained by thiol-yne polymerizations when compared with thiol-ene ones, offering interesting pathway to create multifunctional polymer structures.^{97,98}



Scheme 1.4. Mechanism of the thiol-yne radical reaction.

4. Introduction of “clickable” groups onto aromatic macromers

The concise description of some of the most popular ‘click’ reactions (previous section) reveals that several chemical functions are particularly attractive, since they can be engaged in more than one type of click reaction (Figure 1.7). For instance, thiol groups can undergo both thiol-ene and thiol-yne reactions, alkyne groups can be engaged in the Huisgen 1,3-dipolar cycloaddition and thiol-yne reactions, and maleimide can act as dienophile in the D-A reaction or as vinyl group in thiol-Michael

addition. These groups can be thus of particular interest for the design of new macromolecular architectures.

The following sections are mainly, but not only, focused on the chemical modifications of lignins and tannins and cardanol with the aim to introduce 'clickable' groups.

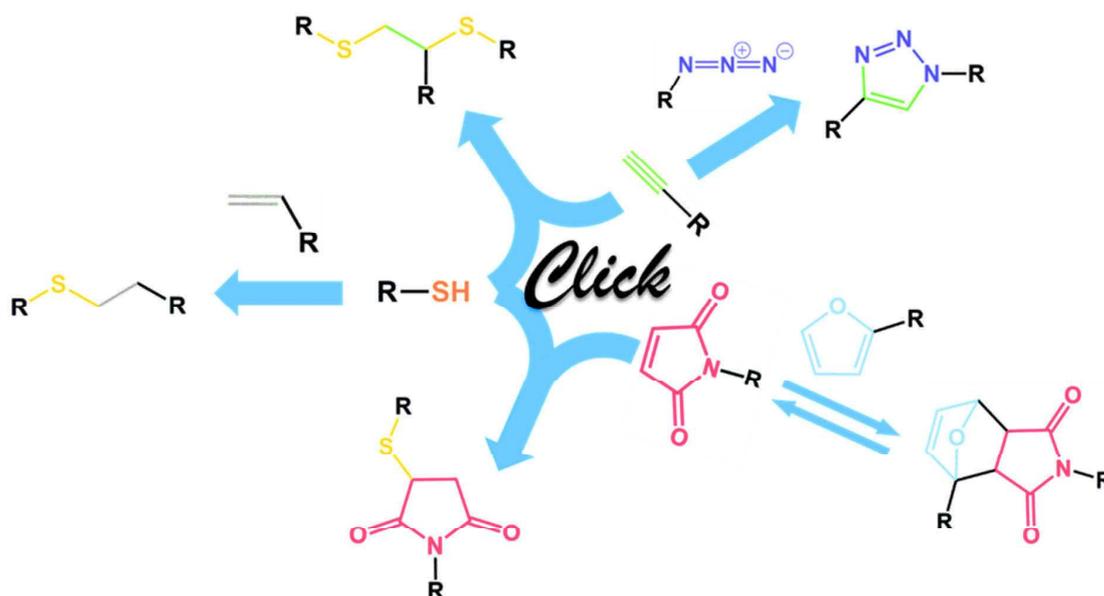
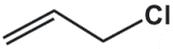
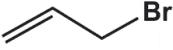
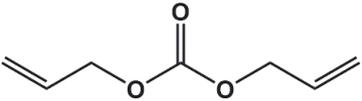
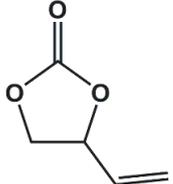
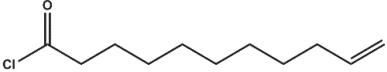
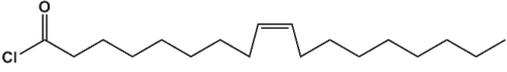
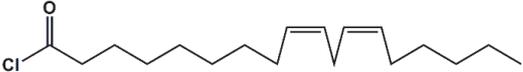


Figure 1.7. Schematic representation of the main “click” reactions.

4.1 Introduction of vinyl and enes groups

Various protocols have been reported in the literature to graft alkene groups mainly on lignins to elaborate aromatic and active compounds. Three different strategies have been applied employing three classes of chemicals such as halogenated vinyl, vinyl carbonates or acyl chlorides derivatives (Table 1.3). These compounds are able to react with polyphenolic OH groups, although by different mechanisms, leading to ethers, carbonates and esters linkage depending on the type of chemicals used and their reactivity toward phenolic and aliphatic OH groups.

Table 1.3. Comparison of the different procedures reporting the grafting of vinyl and internal alkenes groups onto lignin and tannins

Reagent	solvent	catalyst	Byproduct	Ref.
 Allyl chloride	ethanol	NaOH (1.4 eq.)	NaCl, H ₂ O	102
 Allyl bromide	acetone/H ₂ O	NaOH	NaBr, H ₂ O	99
	DMSO	NaOH	NaBr, H ₂ O	100
	DMF	K ₂ CO ₃	KBr, CO ₂ , H ₂ O	101
 Allyl carbonate	-	TBAB	CO ₂ + Allyl alcohol	103
 Vinyl ethylene carbonate	-	K ₂ CO ₃	CO ₂	104
 Undecenoyl Chloride	Methylene Chloride	TEA	TEA-HCl complex	109
 Oleoyl chloride	-	-	HCl	107
 Linoleoyl chloride	acetone	1-methyl imidazole	HCl	110

Allyl bromide was used by Zoia et al.⁹⁹ to obtain an allylated derivatives of soda lignins extracted from softwood. Analogously, with the same reagent, a vinyl group was introduced onto cardanol by reaction with its phenolic group.^{100,101} Allyl chloride was used by Jawerth et al.¹⁰² to convert the phenolic OH groups of coniferyl alcohol, a lignin model compound as well as a starting lignin macromer, into vinyl ethers. For both protocols, in addition to a slight excess of the reagent, a stoichiometric quantity of base is needed to catalyze the reaction and entrap the HCl or HBr, formed as by-products. Base can be inorganic (NaOH, K₂CO₃) or organic (trimethylamine (TEA)), leading to the formation of by-products (NaCl, NaBr, or TEA-HCl salts). In addition, the presence of an organic solvent (acetone/ethanol) is mandatory (20–50 mL/g of lignin). The Williamson like reactions leads to quantitative phenolic and 30-50% aliphatic OH group's derivatization, but the toxicity of vinyl halides, and the poor atom economy and reaction mass efficiency make these allylations not very attractive for a green chemistry. In contrary, carbonates obey to most of the green chemistry requirements. They are harmless compounds, have a good solvent power allowing reactions to be carried out under solvent-free conditions, possess high boiling points allowing the conduction of the reactions under atmospheric pressure, and generally require the use of benign catalysts such as K₂CO₃.

Over and Meier¹⁰³ have exploited diallyl carbonate (DAC) to derivative beech wood organosolv lignin in the presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst at 90-120° C. DAC acts both as reagent and solvent, leading to the allylation of 90% of total OH groups. However, phenolic and aliphatic groups react differently; phenolic groups form an irreversible vinyl ether linkage with the generation of CO₂ and allyl alcohol as by-products, whereas aliphatic OH groups form instead a vinyl carbonate linkage, which is hydrolysable in the presence of a strong base.

Duval and Averous¹⁰⁴ in a recent work used vinyl ethylene carbonate (VEC), a 5 member ring cyclic carbonate instead of DAC, to graft vinyl groups onto different lignins and tannins macromers. Beyond the solvent free conditions, the use of only catalytic amount of K₂CO₃ in this case constitutes

a great advantage compared the case of DAC where stoichiometric amount of TBAB is needed. In addition, only CO₂ is produced as by-products, while allyl alcohol, a very toxic compound, is produced in the case of DAC. Within the reaction, phenolic, aliphatic and carboxylic OH groups of lignin and tannins react through different pathways resulting in derivatives with high double bonds content (up to 7 mmol g⁻¹).

Alkene moieties can also be introduced onto polyphenols macromers by exploiting the possibility to esterify their aliphatic and phenolic OH groups, for instance with fatty acids derivate, in a highly reactive chlorinated form, as reported by Thiebaud et al.^{105,106} The reaction proceeds under catalyst and solvent free conditions, making it a very attractive green treatment which have been applied to graft unsaturated oleic acid onto organosolv Alcell© lignin.¹⁰⁷ The newly introduced alkenes groups provided by oleic acid were then converted into aliphatic OH groups after two synthetic steps in order to produce polyurethanes. It has to be reported that the introduction of double bonds would permit the straightforward polymerization through thiol-ene reaction instead of costly additional synthetic and purification steps. In fact, this approach was recently developed¹⁰⁸ and will be later discussed. Cardanol was also derivatized with the bio-based terminal unsaturated undecylenic acid (prior its chlorination) with triethylamine (TEA) as base in dichloromethane.¹⁰⁹ The product was further functionalized with newly primary OH groups through thiol-ene reaction (more details will be given into paragraph 5).

Polyunsaturated linoleic acid was grafted onto tannins.¹¹⁰ But in this case the acylation was performed in acetone as solvent and 1-methylimidazole as catalyst. Then the tannin linoleate was copolymerized with vegetable oils through metathesis to form thermoset materials.

In a further perspective, others unsaturated fatty acids such as 6-hexenoic and linolenic acids could also be used to derivate polyphenols. Different fatty acid with various chain lengths and alkene's functionality could be used to tune the thermal and mechanical properties of the resultant materials, as already shown recently when different saturated fatty acids were grafted onto lignin. In

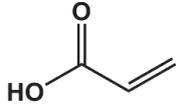
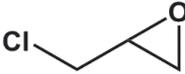
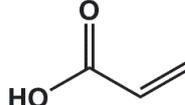
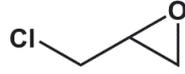
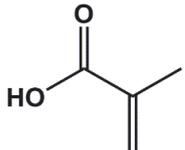
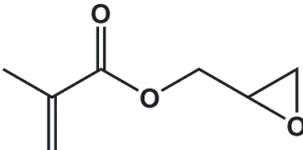
this study, the corresponding modified-lignin were further incorporated into low density polyethylene matrices and act as efficient antioxidants.¹¹¹

4.2 Introduction of acrylate and methacrylate groups

Acrylate and methacrylate moieties are another source of “clickable” double bonds. Acrylation has been performed on lignin, tannins and CNSL through different pathways (Table 1.4).

Table 1.4. Comparison of the different procedures reporting the grafting of acrylic and methacrylic groups onto lignin, tannins and CNSL.

Reagent	Solvent	Catalyst	Byproduct	Ref.
 Methacrylic Anhydride	Dioxane	TEA	TEA- Methacrylate	112
 Methacryloyl Chloride	Dioxane	TEA	TEA-HCl complex	112
	Methylene Chloride	DMAP TEA	TEA-HCl complex	114
 Acryloyl Chloride	Toluene	NaOH(aq.)	H ₂ O, NaCl	119
	-	TEA	TEA-HCl complex	120
	Methylene Chloride	Dibutyl tin dilaurate	-	113

2-Isocyanatoethyl methacrylate				
	Benzene	H ₂ SO ₄	H ₂ O	115
Acrylic Acid				
1. 	1. Propan-2-ol	1. NaOH(aq.)	1. HCl	115
2. 	2. Acrylic acid	2. TBAC	2. -	
1. 	1. Epichlorohydrin	1. TBAC	1. HCl	126
2. 	2. -	2. NaOH(aq.)	2. -	
	Ethyl Acetate	TPP	-	117
	Butyl Acetate			118
Glycidyl methacrylate				

The first lignin acrylate derivatives was reported by Naveau,¹¹² who employed both methacrylic anhydride and methacryloyl chloride to esterify kraft lignin OH groups achieving substitution levels between 17 and 72%.

To improve the acrylate derivatization, Glasser and co-workers used the well-known tin catalyzed quantitative reaction between isocyanate and lignin OH groups to graft isocyanatoethyl methacrylate onto hydroxybutyl organosolv lignin.¹¹³ The introduced double bonds were then used to copolymerize lignin through a free radical polymerization with styrene and methyl methacrylate (MMA). Similarly, Da Cunha et al.¹¹⁴ reported the copolymerization of a methacrylic derivative of

lignin with MMA leading to a high lignin incorporation (up to 44% weight) in the PMMA chains. In this case, the methacrylated lignin was obtained by reacting it with methacryloyl chloride in the presence of dimethylaminopyridine (DMAP) and TEA.

Recently, Podkościelna et al.¹¹⁵ provided an alternative acrylation of lignin by a first reaction with epichlorohydrin. The resulting epoxydated lignin was treated with acrylic acid in the presence of TBAC as catalyst, and hydroquinone as polymerization inhibitor. Alternatively, they proposed also a straightforward acid catalyzed acrylation (H_2SO_4) using acrylic acid and benzene as solvent.

Recently, Pizzi and al. applied exactly the same synthetic route on condensed tannins from Mimosa bark to obtain a homologous acrylated tannin derivatives.¹¹⁶ Tannic acid and also Mimosa bark tannins were instead methacrylated through a slightly different methodology involving glycidyl methacrylate using triphenylphosphine (TPP) and hydroquinone monomethylether as catalyst and inhibitor, respectively.^{117,118}

Acrylated¹¹⁹⁻¹²¹ and methacrylated¹²²⁻¹²⁶ cardanol derivatives were extensively studied mainly to produce UV curable coatings. The introduction of acrylate and methacrylate moieties was achieved either through the straightforward esterification of the cardanol phenolic group with acryloyl chloride,¹¹⁹⁻¹²¹ or by two synthetic steps involving epoxies as intermediates, similarly to what has been reported on lignin and tannins. However, cardanol epoxidation can be realized in two different ways: (i) the reaction of the cardanol phenolic group with epichlorohydrin;¹²⁶ (ii) the epoxidation of the cardanol side chains double bonds.¹²²⁻¹²⁵

Despite these research contributions, which aimed to introduce acrylate moieties onto renewable polyphenols, no investigation has been performed on the exploitation of these derivatives towards potential thiol – ene reactions. In contrary to vinyl and internal alkenes, which can react with thiols only by radical mediated reactions, acrylates and methacrylates can also react through thiol – Michael addition, opening several unexplored “click” opportunities.

4.3 Introduction of alkyne groups

The first functionalization of lignin with alkyne moieties was previously reported by Argyropoulos et al.¹²⁷ In this work, kraft lignin was propargylated in an aqueous solution of NaOH 0.5 M with propargyl bromide at 75 °C for 2h. The product was then induced to self-cross-link through either Claisen rearrangement occurring at 150 °C or an oxidative copper catalyzed coupling. Similarly, propargyl bromide was employed to functionalize cardanol, with K₂CO₃ as basic catalyst and acetone as solvent.¹²⁸

Alkyne's lignin functionalization can also be achieved by grafting alkyne-terminated carboxylic acid such as 5-hexynoic acid *via* carbodiimide mediated esterification (Figure 1.8). The reaction applied to lignin, leads to the esterification of both phenolic and aliphatic OH groups exposing pending alkyne functions.¹²⁹

Han et al.¹³⁰ used the above mentioned 5-hexinoyl chloride to esterify aliphatic OH groups of polycaprolactone (PCL) and PLA chain extended lignin macromers. Chain extended derivatives of lignin^{70,72,131} possess flexible aliphatic chains which counterbalance the rigidity provided by the neat lignin aromatic backbone, thus improving the mechanical properties of the materials prepared with such lignin derivatives.

Up to today, no study has been reported on the thiol – yne polymerization of lignin or other biobased polyphenols, although this reaction was exploited on an alkyne lignin derivatives in order to introduce 1,2,4-triazole groups.¹³² The latter is known to be able to chelate metal ions, in particular Cd (II), providing an example of lignin based adsorbent.

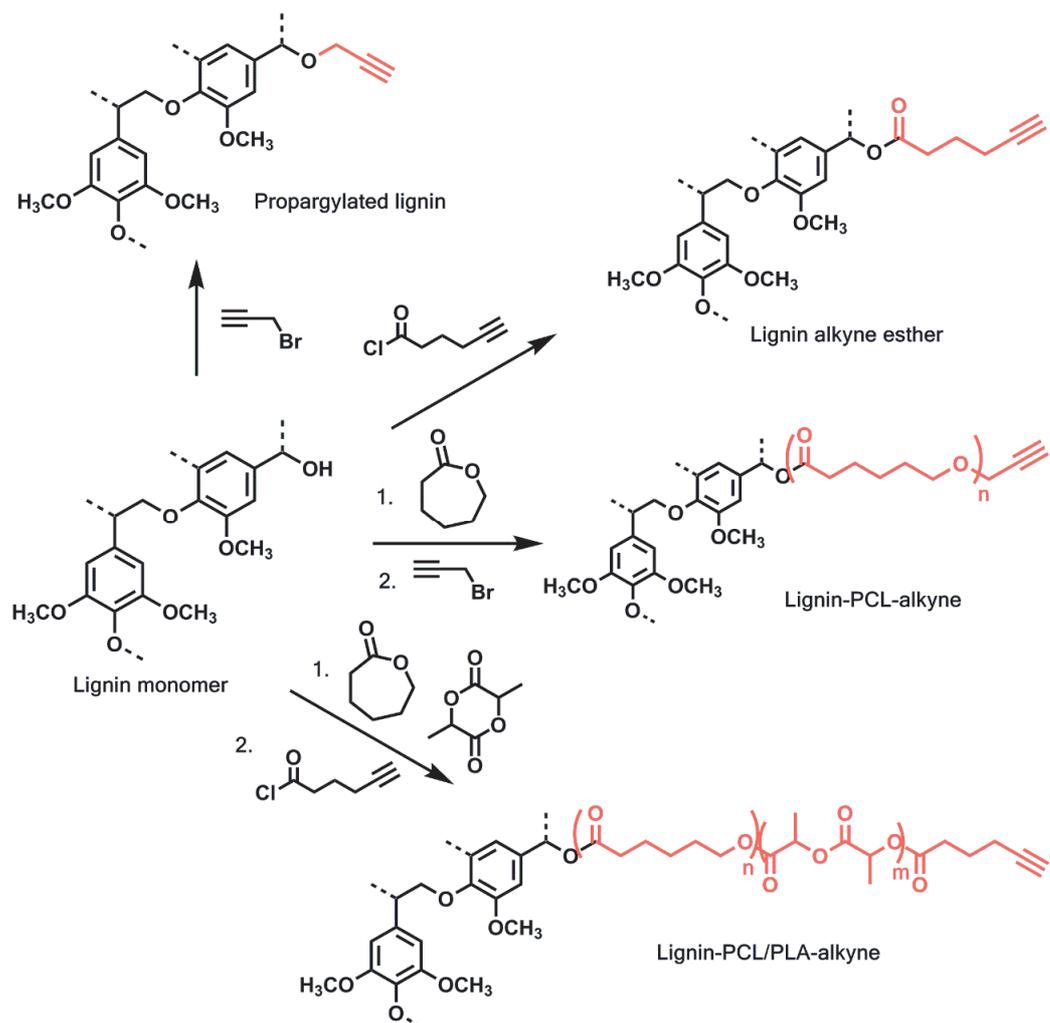
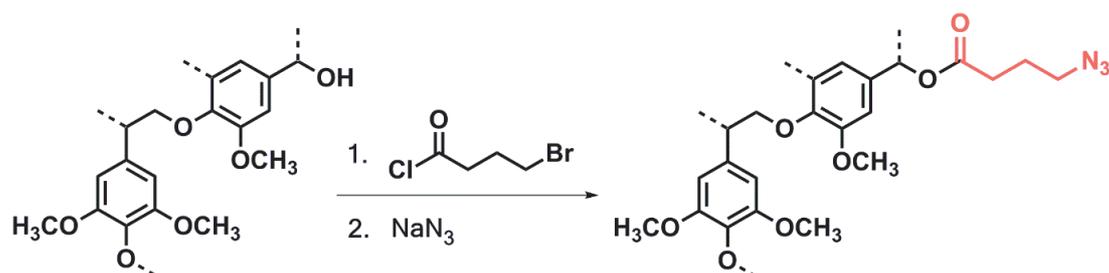


Figure 1.8. Main synthetic strategies to graft alkyne moieties onto lignin macromers.

4.4 Introduction of alkyl azide groups

Han et al. in their work on alkyne's functionalization of lignin reported also the first example of alkyl azide lignin derivatives in a two-step chemical pathway. Lignin was first grafted with 4-bromobutyryl chloride to expose short bromine-terminated aliphatic chains, then the bromine atoms were substituted by S_N2 with azide groups by the reaction with sodium azide in DMF at 50 °C for 12 h (Scheme 1.6).

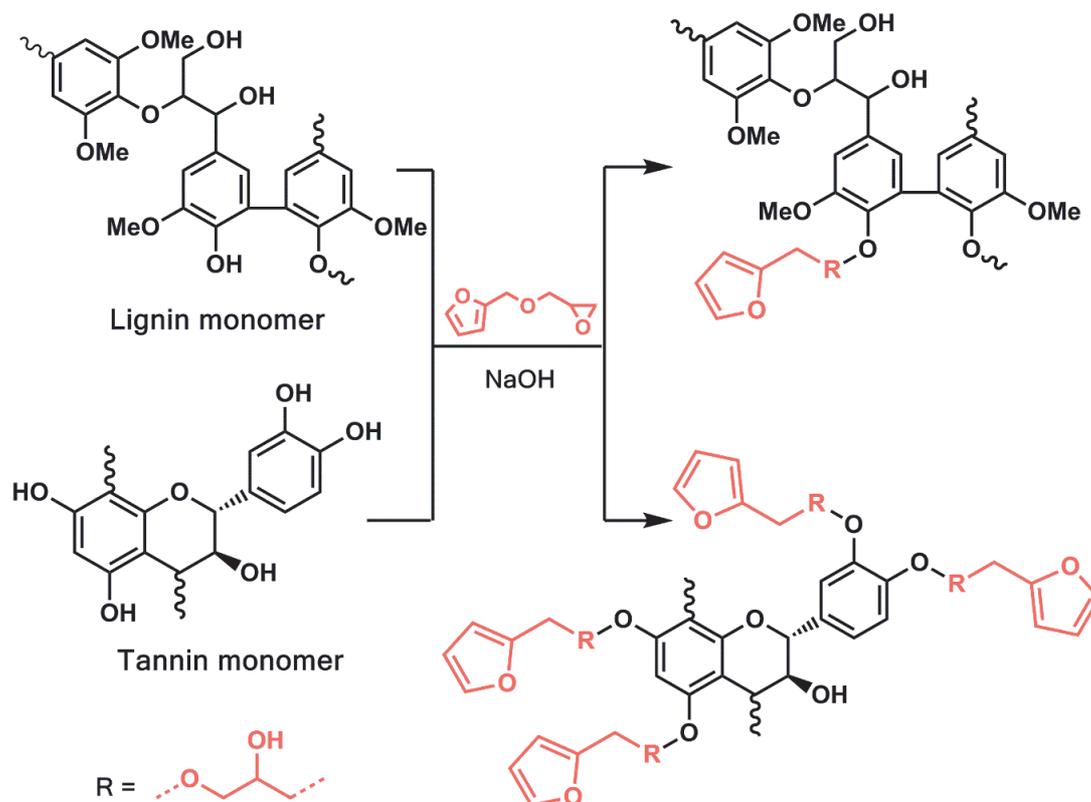


Scheme 1.6. Synthetic pathway used to introduce azide groups onto lignin.

4.5 Introduction of furan groups

Furans as described in previous sections may undergo through a thermally – reversible click reaction with maleimide groups. For this purpose, Duval et al.¹³³ reported in a recent study for the first time the lignin furan functionalization by employing furfuryl glycidyl ether (FGE) as a source of furans (Scheme 7). The reaction was carried out in water containing a stoichiometric amount of NaOH with respect to the total acidic groups in lignin (i.e. both COOH and phenolic OH groups). This way, only carboxylic and phenolic functions are deprotonated, whereas aliphatic OH groups – with a higher pK_a – remain unaffected because of their inability in the protonated form to attack the FGE epoxy ring. By applying the same synthetic protocol, Duval et al.¹³⁴ reported also the furan functionalization of condensed Mimosa tannins (Scheme 1.7).

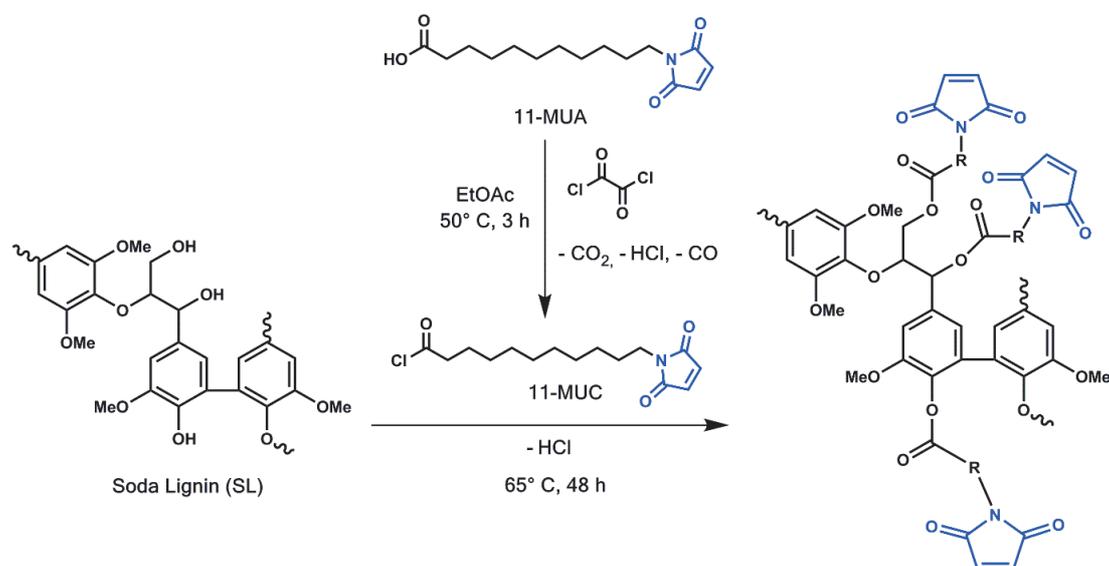
It is worth noting that the first furan tannins derivatives were studied by Foo and Hemingway more than three decades ago,¹³⁵ although in this study the phenolic groups were not involved into the tannins derivatization. Instead, the tannins heterocycle reactivity toward electrophilic aromatic substitution with furfuryl alcohol was employed. The reaction was carried out at 100 °C in presence of acetic acid as solvent and catalyst yielding two products. Catechin is substituted by the furanyl group in the C6 and C8 positions with very poor yield (4 and 1.5%, respectively), due to the self-condensation of furfuryl alcohol under acidic conditions, which leads to poly(furfuryl alcohol).¹³⁶



Scheme 1.7. Furan derivatization of lignin and tannins using furfuryl glycidyl ether.

4.6 Introduction of maleimide groups

Maleimide groups have been introduced on lignin macromers by exploiting the same chemical modification used to graft unsaturated and saturated fatty acid, as previously described. Practically, 6-maleimide hexanoic and 11-maleimide undecanoic acids (11-MUA) were first transformed into their corresponding acyl chlorides and then grafted onto lignin by esterification of both phenolic and aliphatic groups achieving up to 90% total OH groups conversion (Scheme 1.8).^{108,133} Analogously to what observed with fatty acids, the corresponding maleimide derivatives are also able to react with lignin without solvent and catalyst.



Scheme 1.8. Esterification of soda lignin (SL) with 11-MUA to yield maleimido-modified soda¹⁰⁸

4.7 Naturally occurring clickable groups

Among the above described natural polyphenols, CNSL double bonds unsaturation are the groups may be employed straightforwardly through thiol-ene reactions without prior chemical modifications. The monoene, diene, and triene components of CNSL can be quantitatively separated by argentation-thin-layer chromatography, and quantified by UV spectrophotometry¹³⁷ or alternatively by ¹H-NMR.¹³⁸ These polyenes components have been exploited under thiol-ene reactions, more details will be presented below.

In addition to the previously described functional groups grafted onto lignins or tannins, it should be noted that technical lignins already possess some 'clickable' groups in their structure. Indeed, quinone groups, either as *ortho* (1, 2) or *para* (1, 4) forms have been acknowledged to be important chromophores in lignin. Quinone are well-known for their ability to undergo D-A reactions, either as diene or dienophile.¹³⁹

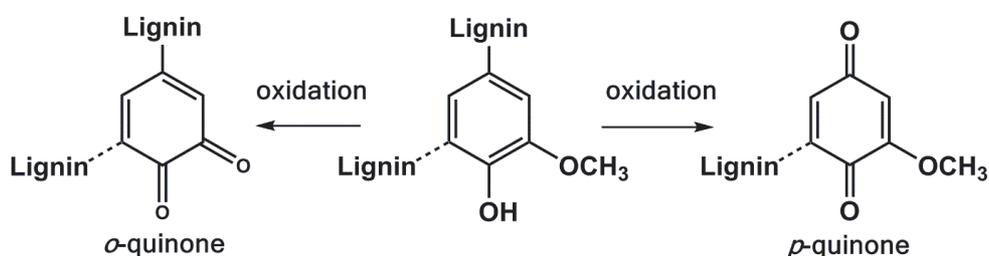
These groups may be formed during the alkaline pulp cooking process from methyl-aryl ether cleavage after subsequent air oxidation of phenolic units.^{140,141} The most reliable technique to quantify lignin's quinone groups, applicable to a wide range of isolated lignins, consists in the

derivatization of the latter with 4-trifluoromethylphenylhydrazin and further ^{19}F NMR analysis with the addition of a fluorinated internal standard.¹⁴² Alternatively, Argyropoulos et al. demonstrated that ^{31}P -NMR can be used as interesting technique for the quinone quantification.¹⁴³

Wozniak et al.¹⁴⁴ reported a number of chemical oxidative techniques have been used to increase the amount of both *o*-quinones and *p*-quinones in lignin and lignin-related compounds. The oxidation occurs on lignin's guaiacyl units either by the degradation of the *para*-alkyl side chain producing the corresponding *p*-quinone, or by demethylation of the guaiacyl methoxyl group resulting in the *o*-quinone (Scheme 1.9).

Wozniak et al.,¹⁴⁵ demonstrated also that some of the synthesized quinone lignin-related compounds may undergo through a DA reaction with various substituted dienes, thus behaving as dienophiles.

The versatility of quinone groups does not limit their reactivity toward DA reaction. In fact, being α,β -unsaturated ketones, they may also undergo Michael addition with thiols, thus opening potential synthetic strategies for the application of the click chemistry on lignin.



Scheme 1.9. Lignin's oxidations pathways generating *o*-quinones and *p*-quinones groups.

5. Synthesis of aromatic polymeric materials through “click” reactions

Although there are several examples of 'clickable' groups that have been introduced on lignins, tannins and cardanol only limited number of studies actually used them in 'click' reactions. However, the very recent years have seen several developments of biobased aromatic polymers obtained through 'click' polymerization.

5.1 Azide – alkyne cycloaddition

The alkyne functionalized lignin's macromers, presented in a previous section, were used by Han et al.¹³⁰ to obtain lignin based polymers through the copper free, thermally induced azide – alkyne click cycloaddition at 130 °C, applying different synthetic strategies (Figure 1.9). One consisted in synthesizing alkyne and azide lignin derivatives, and then co-polymerization, obtaining a polymer with a T_g of 155 °C. Normally, polymers containing a high content of lignin possesses high brittleness and very poor mechanical properties as the condensed rigid phenolic moieties provided by lignin, restricting the mobility of the 3-D polymeric networks. For this reason and to improve the mechanical properties, flexible chains have been included into the 3D structure. These mobile fractions can either be (i) included into the chemical structure with an appropriate linkers used to co-polymerize the lignin's macromers, or (ii) grafted on the lignin's macromers. The first strategy was applied by preparing an azide-terminated PEG (M_w 2000) that was then polymerized with the propargylated lignin. The second one was performed by introducing PCL and PLA linear chains onto the lignin's monomers by ROP with ϵ -caprolactone and L-lactide, respectively. Then, alkyne moieties were added by the derivatization of the terminal OH belonging to the grafted PCL/PLA chains. Finally, the resulting products were co-polymerized with the azide functionalized lignin.

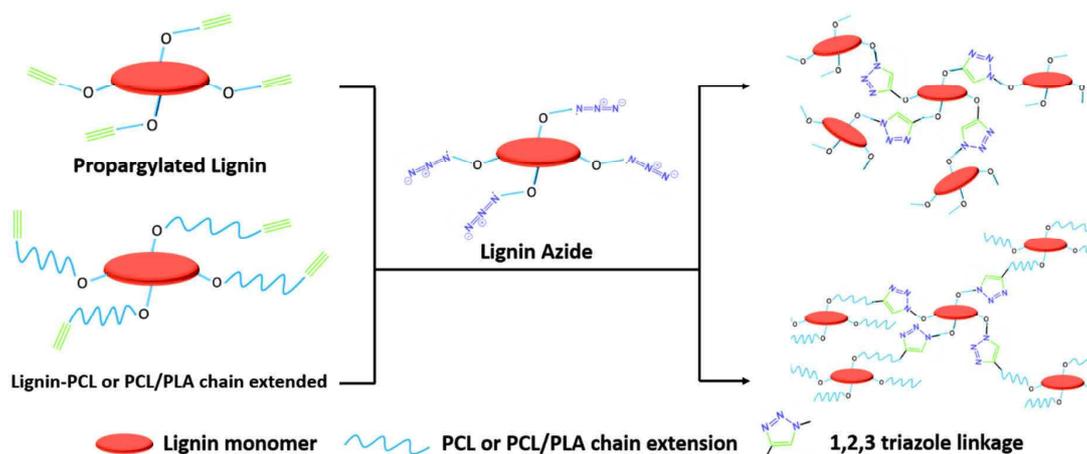
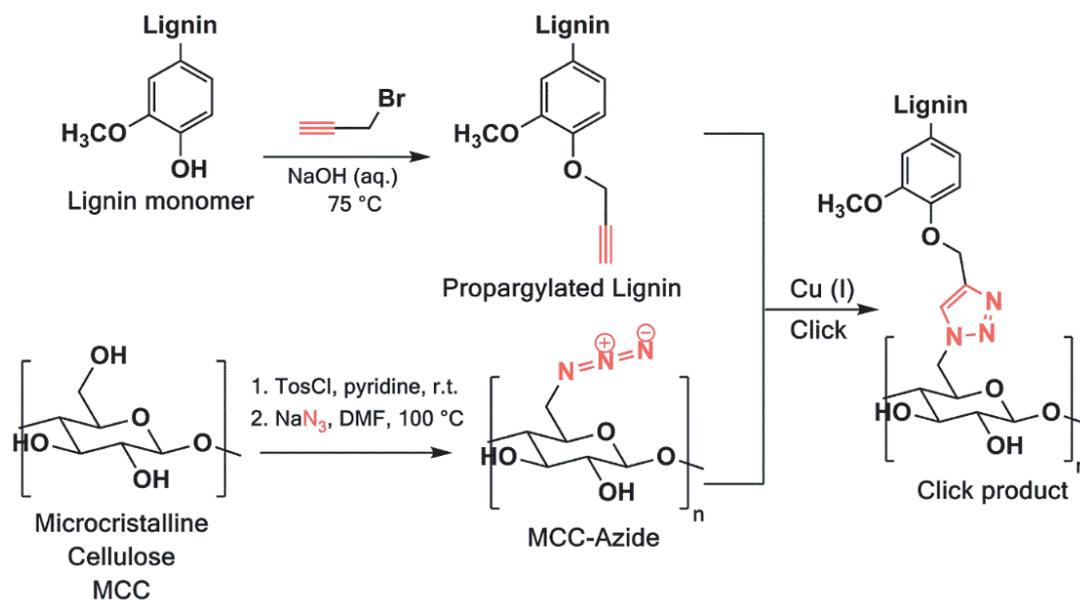


Figure 1.9. 1,3 Huisgen cycloaddition between propargylated lignin, lignin-PCL and lignin PCL/PLA chain extended with azidated lignin.

As expected, the linear PEG and PCL/PLA chains affect the thermal properties of the materials. The flexible spacers exhibit a T_g between -30 and -34 °C and a T_m between 34 and 55 °C, followed by the lignin T_g , occurring above 120 °C. Noting that phase separation was observed in the DSC thermograms.

Liu and Chung¹²⁹ exploited the copper catalyzed azide – alkyne click reaction to graft poly-5-acetylamino pentyl acrylate (PAA) polymeric chains on lignin. The PAA soft domains were synthesized under controlled RAFT polymerization of 5-acetylamino pentyl acrylate monomer, in the presence of a RAFT agent bearing an azide group in its chemical structure. The click reaction was designed to couple a lignin – alkyne derivative with the azido groups present on the synthetic PAA arms. Furthermore, the capacity of the pending acetylamino moieties to form hydrogen bonding provided self-healing properties to the materials, showing the first example of lignin-based self-healing materials.

In a recent study,¹⁴⁶ propargylated kraft lignin was “clicked” with an azide-containing cellulose derivative to produce homogeneous cellulose based transparent films containing 0.2 – 2 % of covalently bonded lignin. The resulting materials exhibit interesting UV absorption properties thanks to the click coupling of 2% lignin with cellulose, opening interesting ways in the design of cellulose-lignin UV light blocker films (Scheme 1.9).



Scheme 1.9. Schematic representation of the click reaction between the propargylated lignin and microcrystalline cellulose derivatized with azide groups.

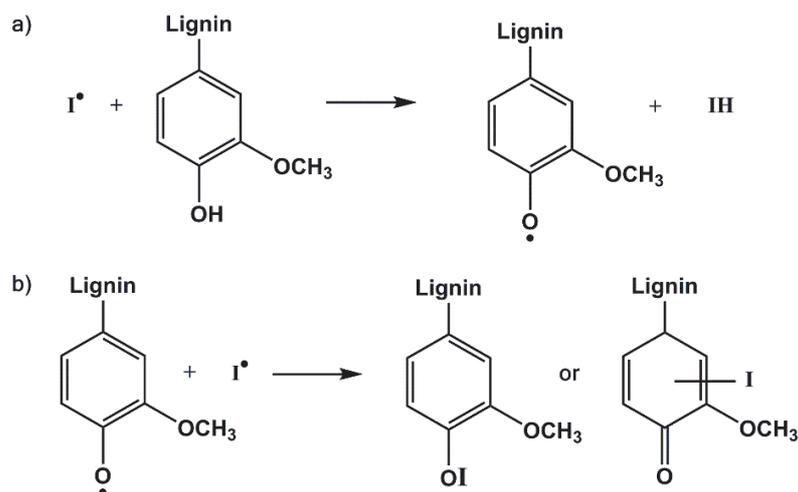
Yang et al.¹²⁸ applied a very similar synthetic strategy to create a cardanol-PVC system in which cardanol acts as a covalently bonded internal plasticizer. Practically, propargylated cardanol was “clicked” with an azide-containing PVC, obtained by the reaction of PVC polymer with sodium azide. The corresponding propargylated cardanol-modified PVC exhibited a decreased T_g and good thermal stability.

5.2 Thiol – ene reactions

Among the different modifications previously described aiming to modify natural resources with alkene moieties, only a couple of examples have been reported in the literature where thiol – ene reactions were used.

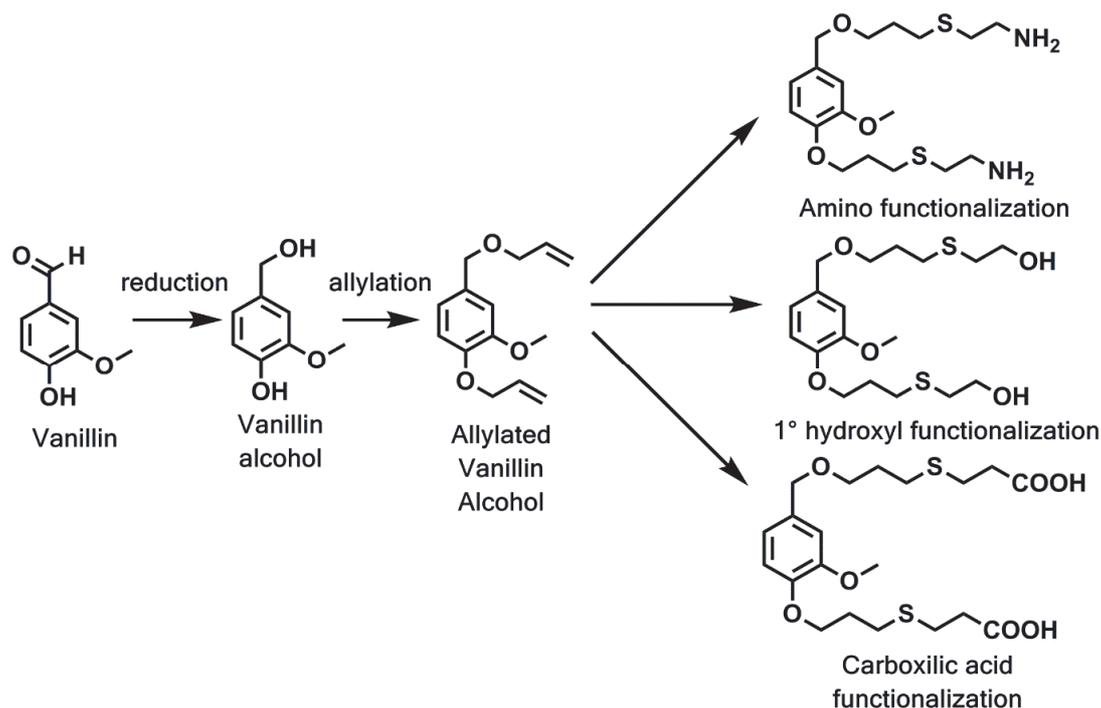
For instance, the allylated coniferyl alcohol (a lignin model compound) was further employed to obtain cross-linked thermoset films *via* radical thiol – ene with a tetra functional thiol.¹⁰² The films thermal properties were then analyzed by DSC, exhibiting a T_g of $17\text{ }^\circ\text{C}$ with absence of crystallinity (given the 3D structure provided by the linker), indicating that small lignin model fractions or

monomers like coniferyl alcohol do not give high T_g thermoset materials. Additionally, lignin may act as a radical scavenger with antioxidant behavior,¹⁴⁷⁻¹⁴⁹ thus potentially inhibiting radical mediated thiol – ene reactions. These antioxidant properties vary with the number of phenolic units present in unmodified lignin. Practically, the study of Da Cunha et al.¹⁵⁰ clarified the effects of the lignin residues when involved in a radical mediated polymerization. The native lignin when mixed with methyl methacrylate and benzyl peroxide (as radical initiator) was found to inhibit the radical methacrylate polymerization unless an excess of initiator was added comparing to the number of phenolic function present on lignin. This can be easily explained by the fact that the initiator abstracts hydrogens from free phenolic OH of lignin generating a stable lignin free radical, which is inactive towards MMA polymerization (Scheme 1.10). However, when lignin was acetylated, the polymerization of MMA proceeded for even very low initiator concentrations and neither inhibition nor retardation period for MMA polymerization was observed, supporting the predominant role of free phenolic functions in the inhibition process. This study suggests that theoretically, the radical thiol-ene may occur on lignins monomers modified with opportune alkene moieties, as long as all the phenolic groups are protected or derivatized.



Scheme 1.10. a) Lignin's phenolic hydrogen abstraction by a radical initiator b) reaction between the radical initiator and the generated lignin free radical.

The utility of thiol – ene reaction can be exploited not only to produce polymeric materials, but also to introduce new chemical reactive sites. In fact, in their recent work Caillol et al.⁶⁴ demonstrated that vanillin (a small phenolic molecule obtainable from lignin), can be functionalized with primary aliphatic OH, primary amine and carboxylic groups after its reduction and allylation with allyl bromide (Scheme 1.11).



Scheme 1.11. Synthetic pathway for vanillin allylation and further functionalization through thiol – ene reaction with amino, primary OH and carboxylic acids groups.

Cardanol can be converted into a polyol or a polyamine, respectively through a straightforward reaction with 2-mercaptoethanol^{109,151} or cysteine hydrochloride.¹⁰¹ The resulting polyol and polyamine based cardanol were further used in the synthesis of polyurethanes.

Recently Buono et al.,¹⁰⁸ developed for the first time lignin based materials through the thiol-ene Michael addition (Figure 1.10). The click polymerization was achieved between a soda lignin maleimide derivatives and commercially available poly-functional thiols, in the presence of TEA as

catalyst in a short time (about 1 minute). The authors showed that the thermo-mechanical properties of the materials can be fine-tuned by controlling the amount of maleimide moieties grafted on lignin, the linker's functionality as well as the linker's chemical backbone. In particular, increasing the thiol linker's functionality from two to four resulted in materials with a higher T_g , T_α and crosslink density as well as enhanced stiffness and strength but reduced elongation at break. Furthermore, an aromatic thiol linker impacts the properties by increasing the values of T_α and T_g as well as the stiffness and strength, due to the limited mobility of the aromatic chains.

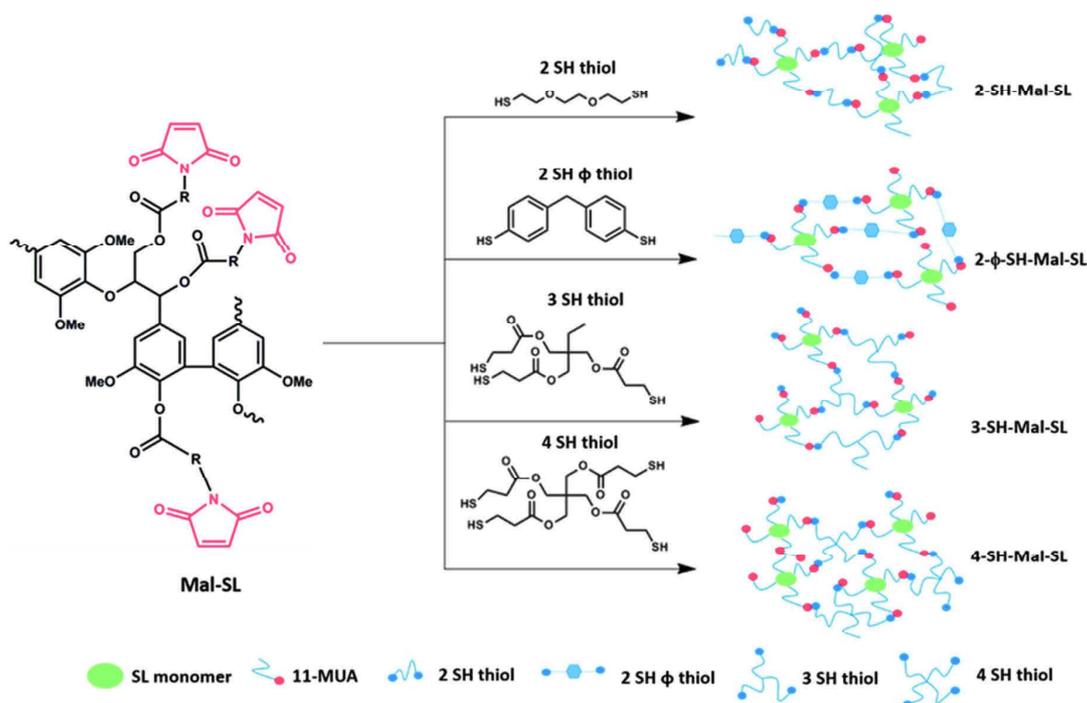


Figure 1.10. Polymerization of maleimide soda lignin with different polyfunctional thiols linkers.¹⁰⁸

5.3 Furan – Maleimide D-A

Recently, Duval et al.¹³³ reported for the first time the elaboration of a thermo-reversible polymeric networks based on Kraft lignin. Two different batches of lignin were synthesized in order to obtain furan and maleimide groups, respectively, linked at the chain ends. The two batches were then co-polymerized in DMSO at 70 °C showing gel formation as result of the cross-linking. Then, the polymeric network quickly returned back into a liquid state after depolymerizing by retro-DA reaction at 120 °C.

In our work, not yet published, a step further has been accomplished to access thermally remendable materials with self-healing properties through clicking furan – maleimide D-A with lignin. Specifically, the same lignin – maleimide derivatives exploited for the synthesis of the thiol – maleimide materials (detailed in the previous sub-paragraph), was bulk polymerized at 60 °C with different polyfunctional furan linkers, accurately designed through the thiol – epoxy reaction between furfuryl glycidyl ether and the corresponding poly-functional thiols (Figure 1.11). The materials showed on demand thermally induced disassembly at 110-130 °C and reassembly when cured again at 60 °C, providing controlled self-healing properties and several efficient reprocessing with a limited impact on the thermo-mechanical properties and the thermal stability of the final materials (Figure 1.12).

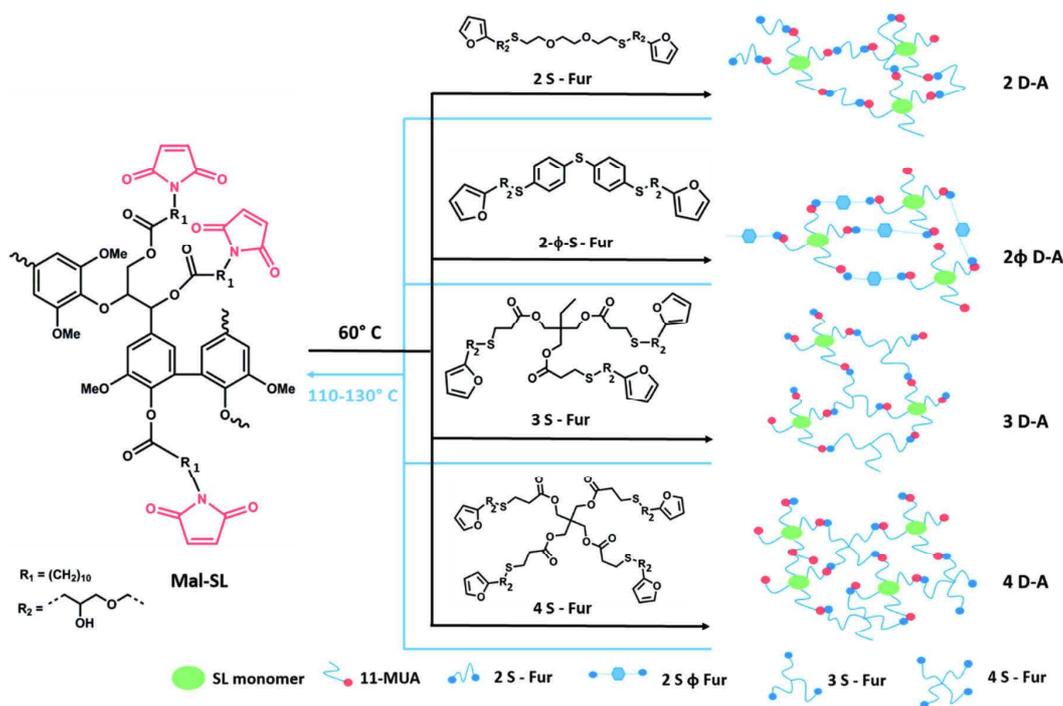


Figure 1.11. Thermo-reversible Diels-Alder polymerization of maleimide functionalized lignin with polyfunctional furan linkers.

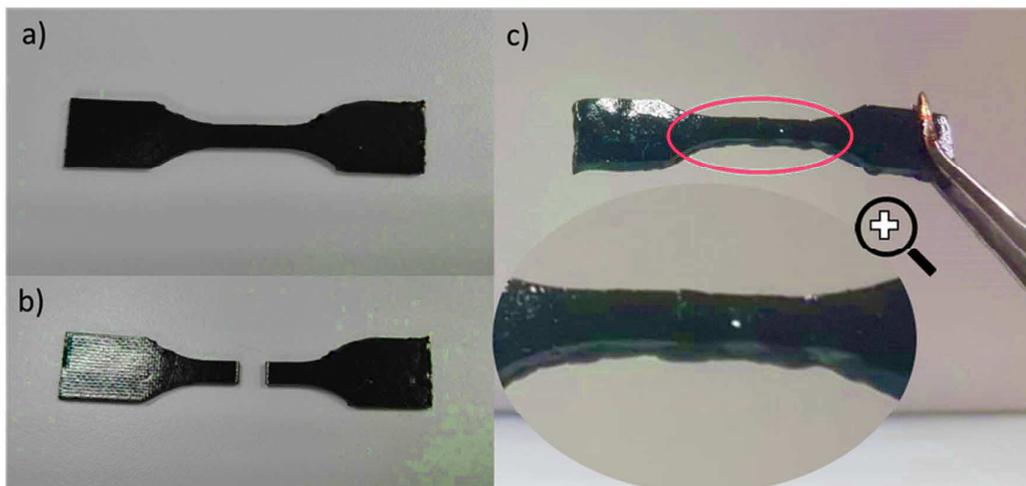


Figure 1.12. Lignin based Diels-Alder material a) initially b) after the cut c) after the self-healing.

In a recent paper, Duval et al.¹³⁴ also described for the first time new tannin-based thermo-reversible materials. Furan-bearing tannins were cross-linked with different telechelic oligomers of polypropylene oxide or polypropylene oxide/polyethylene oxide terminated by maleimide groups. The cross-linking D-A reaction, led to the formation of gels during storage at 70 °C. The gels were able to quickly turn back to the liquid state upon exposure to higher temperatures (120 °C) as effect of the retro D-A. The occurrence of the polymeric network disassembly was also confirmed by DSC and SEC experiments, which however showed that the retro D-A was not complete in short time experiments.

6. Conclusion and perspectives

Despite the worldwide annual production of several million tons of natural polyphenols, only a limited amount is used for commercial high added-value applications including additives, dispersants, binders, adhesives or surfactants. This extremely abundant natural feedstock of aromatic compounds is still underused for valuable application although the recent unprecedented academic and industrial interests as attested by the considerable increase of publications and patents. The main limitation regarding the development of value added chemicals and materials are still predominant, mainly due to the variability of the sources and extraction processes, dispersity and hyperbranched structures of these natural polyphenols.

The “click” chemistry has been acknowledged to be a very powerful tool for polymer and organic chemists to produce, at high yield, controlled macromolecular architectures under benign conditions. Consequently, it could be used to better control the structure variability characteristic of aromatic biobased compounds in order to elegantly overcome these main limitations. In addition, bio-based aromatic macromers could contribute to the development of novel “clickable” substrates for broader implementation of the click chemistry in materials applications.

In this state of the art, we have reported the principal features of the click chemistry applied on the major natural source of aromatic units, and we stressed the unexplored sides that we strongly believe could provide in the future new ways for the development of polymers and materials with controlled and advanced properties.

Definitely, the combination of the click chemistry with the use of natural polyphenols as source of aromatic chemicals represents an economically and environmentally valuable starting point for the chemical industries for the development of renewable aromatic polymers and materials.

Conclusion et perspectives du chapitre 1

La synthèse bibliographique présentée dans ce chapitre montre que La chimie "click" est reconnue comme un outil très puissant pour la chimie organiques et des polymères, pour l'élaboration d'architectures macromoléculaires hautement performantes. Par conséquent, elle pourrait être utilisée pour mieux contrôler la variabilité de la structure caractéristique des composés aromatiques biosourcés afin de surmonter élégamment leurs principales limitations. De plus, plusieurs domaines d'étude inexplorés ont été décrits comme de potentiel axes de recherches académiques et industriels.

Le prochain chapitre (chapitre 2) va être consacré à l'étude de nouveaux polymères à base de lignine obtenus par polymérisation clic du type maléimido-thiol, qui est l'objet principal d'étude de cette thèse. Des films ont pu être préparés et il a été démontré que les propriétés thermiques et mécaniques de ces nouveaux matériaux peuvent être ajustées par l'utilisation de différents thiols multifonctionnels.

References du chapitre 1

- (1) EUBIO_Admin. Market. *European Bioplastics e.V.* <http://www.european-bioplastics.org/market/> date access 17 March 2017
- (2) Noreen, A.; Zia, K. M.; Zuber, M.; Tabasum, S.; Zahoor, A. F. Bio-based polyurethane: An efficient and environment friendly coating systems: A review. *Prog. Org. Coat.* **2016**, *91*, 25–32.
- (3) Zhang, C.; Kessler, M. R. Bio-based Polyurethane Foam Made from Compatible Blends of Vegetable-Oil-based Polyol and Petroleum-based Polyol. *ACS Sustain. Chem. Eng.* **2015**, *3* (4), 743–749.
- (4) Morschbacker, A. Bio-Ethanol Based Ethylene. *Polym. Rev.* **2009**, *49* (2), 79–84.
- (5) Babu, R. P.; O'Connor, K.; Seeram, R. Current progress on bio-based polymers and their future trends. *Prog. Biomater.* **2013**, *2* (1), 8–24.
- (6) Kriegel, R. M.; Huang, X.; Schultheis, M. W. Bio-based polyethylene terephthalate polymer and method of making same. US20090246430 A1, October 1, 2009.
- (7) Kriegel, R.; Huang, X.; Schultheis, M. W.; Bippert, D. A.; Insolia, G. E.; Kolls, B.; Summerville, S. Bio-based polyethylene terephthalate packaging and method of making thereof. US20100028512 A1, February 4, 2010.
- (8) Hermann, B. G.; Blok, K.; Patel, M. K. Producing Bio-Based Bulk Chemicals Using Industrial Biotechnology Saves Energy and Combats Climate Change. *Environ. Sci. Technol.* **2007**, *41* (22), 7915–7921.
- (9) Auras, R. A.; Lim, L.-T.; Selke, S. E. M.; Tsuji, H. *Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications*; New York, John Wiley & Sons, 2011.

- (10) Garlotta, D. A Literature Review of Poly(Lactic Acid). *J. Polym. Environ.* **2001**, *9* (2), 63–84.
- (11) Lunt, J. Large-scale production, properties and commercial applications of polylactic acid polymers. *Polym. Degrad. Stab.* **1998**, *59* (1), 145–152.
- (12) Philip, S.; Keshavarz, T.; Roy, I. Polyhydroxyalkanoates: biodegradable polymers with a range of applications. *J. Chem. Technol. Biotechnol.* **2007**, *82* (3), 233–247.
- (13) Zinn, M.; Witholt, B.; Egli, T. Occurrence, synthesis and medical application of bacterial polyhydroxyalkanoate. *Adv. Drug Deliv. Rev.* **2001**, *53* (1), 5–21.
- (14) Avérous, L. Biodegradable Multiphase Systems Based on Plasticized Starch: A Review. *J. Macromol. Sci. Part C* **2004**, *44* (3), 231–274.
- (15) Averous, L.; Boquillon, N. Biocomposites based on plasticized starch: thermal and mechanical behaviours. *Carbohydr. Polym.* **2004**, *56* (2), 111–122.
- (16) Averous, L.; Fauconnier, N.; Moro, L.; Fringant, C. Blends of thermoplastic starch and polyesteramide: processing and properties. *J. Appl. Polym. Sci.* **2000**, *76* (7), 1117–1128.
- (17) PlasticsEurope - Plastics - the Facts 2016 <http://www.plasticseurope.org/Document/plastics--the-facts-2016-15787.aspx?FolID=2>. date access 17 March 2017
- (18) Suarez, H.; Barlow, J. W.; Paul, D. R. Mechanical properties of ABS/polycarbonate blends. *J. Appl. Polym. Sci.* **1984**, *29* (11), 3253–3259.
- (19) Kulich, D. M.; Gaggar, S. K.; Lowry, V.; Stepien, R. Acrylonitrile–Butadiene–Styrene Polymers. In *Encyclopedia of Polymer Science and Technology*; New York, John Wiley & Sons, Inc., 2002.
- (20) Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J.-M.; Dubois, P. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Mater. Sci. Eng. R Rep.* **2009**, *63* (3), 100–125.
- (21) Arbenz, A.; Avérous, L. Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures. *Green Chem.* **2015**, *17* (5), 2626–2646.
- (22) Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* **2014**, *39* (7), 1266–1290.

- (23) Voirin, C.; Caillol, S.; Sadavarte, N. V.; Tawade, B. V.; Boutevin, B.; Wadgaonkar, P. P. Functionalization of cardanol: towards biobased polymers and additives. *Polym. Chem.* **2014**, *5* (9), 3142–3162.
- (24) Lochab, B.; Shukla, S.; Varma, I. K. Naturally occurring phenolic sources: monomers and polymers. *RSC Adv.* **2014**, *4* (42), 21712–21752.
- (25) Anastas, P.; Warner, J. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, New York, 2000.
- (26) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem. Int. Ed.* **2001**, *40* (11), 2004–2021.
- (27) Moses, J. E.; Moorhouse, A. D. The growing applications of click chemistry. *Chem. Soc. Rev.* **2007**, *36* (8), 1249–1262.
- (28) Qin, A.; Lam, J. W. Y.; Tang, B. Z. Click polymerization. *Chem. Soc. Rev.* **2010**, *39* (7), 2522–2544.
- (29) Kempe, K.; Krieg, A.; Becer, C. R.; Schubert, U. S. “Clicking” on/with polymers: a rapidly expanding field for the straightforward preparation of novel macromolecular architectures. *Chem. Soc. Rev.* **2011**, *41* (1), 176–191.
- (30) Candolle, A. P. de. *Théorie élémentaire de la botanique; ou, Exposition des principes de la classification naturelle et de l’art de décrire et d’étudier les végétaux*; Déterville, Paris, 1813.
- (31) Berstis, L.; Elder, T.; Crowley, M. F.; Beckham, G. T. The radical nature of C-lignin. *ACS Sustain. Chem. Eng.* **2016**, *4* (10), 5327–5335
- (32) Crestini, C.; Melone, F.; Sette, M.; Saladino, R. Milled Wood Lignin: A Linear Oligomer. *Biomacromolecules* **2011**, *12* (11), 3928–3935.
- (33) Ralph, J.; Lundquist, K.; Brunow, G.; Lu, F.; Kim, H.; Schatz, P. F.; Marita, J. M.; Hatfield, R. D.; Ralph, S. A.; Christensen, J. H.; et al. Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl- propanoids. *Phytochem. Rev.* **2004**, *3* (1–2), 29–60.

- (34) Duval, A.; Lawoko, M. A review on lignin-based polymeric, micro- and nano-structured materials. *React. Funct. Polym.* **2014**, *85*, 78–96.
- (35) Aro, T.; Fatehi, P. Production and application of liginosulfonates and sulfonated lignin. *ChemSusChem* **2017**, *10* (9), 1861–1877.
- (36) Lora, J. H. Lignin: A Platform for Renewable Aromatic Polymeric Materials. In *Quality Living Through Chemurgy and Green Chemistry*; Lau, P. C. K., Ed.; Green Chemistry and Sustainable Technology; Springer Berlin Heidelberg, **2016**, 221–261.
- (37) Gartner. Determination of phenolic hydroxyl groups in residual lignin using a modified UV-method. *Nord. Pulp Pap. Res. J.* **1999**, *14* (02), 163–170.
- (38) Tiainen, E.; Drakenberg, T.; Tamminen, T.; Kataja, K.; Hase, A. Determination of Phenolic Hydroxyl Groups in Lignin by Combined Use of ¹H NMR and UV Spectroscopy. *Holzforschung* **2005**, *53* (5), 529–533.
- (39) Lundquist, K.; Sjöholm, R.; Teien, G.; Pakkanen, T.; Servin, R.; Sternerup, H.; Wistrand, L.-G.; Nørskov, L.; Schroll, G. NMR Studies of Lignins. 2. Interpretation of the ¹H NMR Spectrum of Acetylated Birch Lignin. *Acta Chem. Scand.* **1979**, *33b*, 27–30.
- (40) Robert, D. R.; Brunow, G. Quantitative Estimation of Hydroxyl Groups in Milled Wood Lignin from Spruce and in a Dehydrogenation Polymer from Coniferyl Alcohol Using ¹³C NMR Spectroscopy. *Holzforsch. - Int. J. Biol. Chem. Phys. Technol. Wood* **2009**, *38* (2), 85–90.
- (41) Argyropoulos, D. S. Quantitative Phosphorus-31 NMR Analysis of Lignins, a New Tool for the Lignin Chemist. *J. Wood Chem. Technol.* **1994**, *14* (1), 45–63.
- (42) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* **1995**, *43* (6), 1538–1544.
- (43) Trimble, H. *The tannins. A monograph on the history, preparation, properties, methods of estimation, and uses of the vegetable astringents, with an index to the literature of the subject*; Philadelphia, J.B. Lippincott Company, 1892.

- (44) Bate-Smith, E. C. The phenolic constituents of plants and their taxonomic significance. I. Dicotyledons. *J. Linn. Soc. Lond. Bot.* **1962**, *58* (371), 95–173.
- (45) Abascal, K.; Ganora, L.; Yarnell, E. The effect of freeze-drying and its implications for botanical medicine: a review. *Phytother. Res.* **2005**, *19* (8), 655–660.
- (46) C. Ferreira, E.; Rita A. Nogueira, A.; B. Souza, G.; A. R. Batista, L. Effect of drying method and length of storage on tannin and total phenol concentrations in Pigeon pea seeds. *Food Chem.* **2004**, *86* (1), 17–23.
- (47) Asami, D. K.; Hong, Y.-J.; Barrett, D. M.; Mitchell, A. E. Comparison of the Total Phenolic and Ascorbic Acid Content of Freeze-Dried and Air-Dried Marionberry, Strawberry, and Corn Grown Using Conventional, Organic, and Sustainable Agricultural Practices. *J. Agric. Food Chem.* **2003**, *51* (5), 1237–1241.
- (48) Matturro, G.; Danesi, P.; Festuccia, A.; deceased, C. M. Process and plant to extract and concentrate tannins from wood and from other natural products. US7145031 B1, December 5, 2006.
- (49) The Cashew Export Promotion Council Of India|cashew supplier in India|cashew producer <http://www.cashewindia.org/index.php>. Access date 4 April 2017
- (50) Symes, W. F.; Dawson, C. R. Separation and Structural Determination of the Olefinic Components of Poison Ivy Urushiol, Cardanol and Cardol. *Nature* **1953**, *171* (4358), 841–842.
- (51) Calò, E.; Maffezzoli, A.; Mele, G.; Martina, F.; Mazzetto, S. E.; Tarzia, A.; Stifani, C. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. *Green Chem.* **2007**, *9* (7), 754–759.
- (52) Fire-resistant plasticizer for the plastic material industry and method of making thereof. US8349924 B2, January 8, 2010.
- (53) Jaillet, F.; Darroman, E.; Ratsimihety, A.; Auvergne, R.; Boutevin, B.; Caillol, S. New biobased epoxy materials from cardanol. *Eur. J. Lipid Sci. Technol.* **2014**, *116* (1), 63–73.

- (54) Li, S.; Yang, X.; Huang, K.; Li, M.; Xia, J. Design, preparation and properties of novel renewable UV-curable copolymers based on cardanol and dimer fatty acids. *Prog. Org. Coat.* **2014**, *77* (2), 388–394.
- (55) Pizzi, A. Bioadhesives for Wood and Fibres. *Rev. Adhes. Adhes.* **2013**, *1* (1), 88–113.
- (56) Suwanprasop, S.; Nhujak, T.; Roengsumran, S.; Petsom, A. Petroleum Marker Dyes Synthesized from Cardanol and Aniline Derivatives. *Ind. Eng. Chem. Res.* **2004**, *43* (17), 4973–4978.
- (57) Awang, M.; Seng, G. M. Sulfonation of Phenols Extracted from the Pyrolysis Oil of Oil Palm Shells for Enhanced Oil Recovery. *ChemSusChem* **2008**, *1* (3), 210–214.
- (58) Verge, P.; Fouquet, T.; Barrère, C.; Toniazzo, V.; Ruch, D.; Bomfim, J. A. S. Organomodification of sepiolite clay using bio-sourced surfactants: Compatibilization and dispersion into epoxy thermosets for properties enhancement. *Compos. Sci. Technol.* **2013**, *79*, 126–132.
- (59) Lomonaco, D.; Maia, F. J. N.; Mazzetto, S. E. Thermal evaluation of cashew nutshell liquid as new bioadditives for poly(methyl methacrylate). *J. Therm. Anal. Calorim.* **2013**, *111* (1), 619–626.
- (60) Huang, K.; Zhang, Y.; Li, M.; Lian, J.; Yang, X.; Xia, J. Preparation of a light color cardanol-based curing agent and epoxy resin composite: Cure-induced phase separation and its effect on properties. *Prog. Org. Coat.* **2012**, *74* (1), 240–247.
- (61) Besteti, M. D.; Souza, F. G.; Freire, D. M. G.; Pinto, J. C. Production of core-shell polymer particles-containing cardanol by semibatch combined suspension/emulsion polymerization. *Polym. Eng. Sci.* **2014**, *54* (5), 1222–1229.
- (62) Trevisan, M. T. S.; Pfundstein, B.; Haubner, R.; Würtele, G.; Spiegelhalder, B.; Bartsch, H.; Owen, R. W. Characterization of alkyl phenols in cashew (*Anacardium occidentale*) products and assay of their antioxidant capacity. *Food Chem. Toxicol.* **2006**, *44* (2), 188–197.

- (63) Nagabhushana, K. S.; Ravindranath, B. Efficient Medium-Scale Chromatographic Group Separation of Anacardic Acids from Solvent-Extracted Cashew Nut (*Anacardium occidentale*) Shell Liquid. *J. Agric. Food Chem.* **1995**, *43* (9), 2381–2383.
- (64) Fache, M.; Darroman, E.; Besse, V.; Auvergne, R.; Caillol, S.; Boutevin, B. Vanillin, a promising biobased building-block for monomer synthesis. *Green Chem.* **2014**, *16* (4), 1987–1998.
- (65) Fache, M.; Boutevin, B.; Caillol, S. Vanillin Production from Lignin and Its Use as a Renewable Chemical. *ACS Sustain. Chem. Eng.* **2016**, *4* (1), 35–46.
- (66) Pearl, I. A. Vanillin from Lignin Materials. *J. Am. Chem. Soc.* **1942**, *64* (6), 1429–1431.
- (67) Hocking, M. B. Vanillin: Synthetic Flavoring from Spent Sulfite Liquor. *J. Chem. Educ.* **1997**, *74* (9), 1055–1059.
- (68) Ahsan, H.; Ahad, A.; Iqbal, J.; Siddiqui, W. A. Pharmacological potential of tocotrienols: a review. *Nutr. Metab.* **2014**, *11*, 52–74.
- (69) Atkinson, J.; Epanand, R. F.; Epanand, R. M. Tocopherols and tocotrienols in membranes: A critical review. *Free Radic. Biol. Med.* **2008**, *44* (5), 739–764.
- (70) Wu, L. C.-F.; Glasser, W. G. Engineering plastics from lignin. I. Synthesis of hydroxypropyl lignin. *J. Appl. Polym. Sci.* **1984**, *29* (4), 1111–1123.
- (71) Kelley, S. S.; Glasser, W. G.; Ward, T. C. Engineering Plastics from Lignin XIV. Characterization of Chain-Extended Hydroxypropyl Lignins. *J. Wood Chem. Technol.* **1988**, *8* (3), 341–359.
- (72) Laurichesse, S.; Avérous, L. Synthesis, thermal properties, rheological and mechanical behaviors of lignins-grafted-poly(ϵ -caprolactone). *Polymer* **2013**, *54* (15), 3882–3890.
- (73) García, D. E.; Glasser, W. G.; Pizzi, A.; Paczkowski, S. P.; Laborie, M.-P. Modification of condensed tannins: from polyphenol chemistry to materials engineering. *New J. Chem.* **2016**, *40* (1), 36–49.
- (74) Xi, W.; Scott, T. F.; Kloxin, C. J.; Bowman, C. N. Click Chemistry in Materials Science. *Adv. Funct. Mater.* **2014**, *24* (18), 2572–2590.

- (75) Collins, J.; Xiao, Z.; Müllner, M.; Connal, L. A. The emergence of oxime click chemistry and its utility in polymer science. *Polym. Chem.* **2016**, *7*, 3812–3826.
- (76) Kade, M. J.; Burke, D. J.; Hawker, C. J. The power of thiol-ene chemistry. *J. Polym. Sci. Part Polym. Chem.* **2010**, *48* (4), 743–750.
- (77) Nair, D. P.; Podgórski, M.; Chatani, S.; Gong, T.; Xi, W.; Fenoli, C. R.; Bowman, C. N. The Thiol-Michael Addition Click Reaction: A Powerful and Widely Used Tool in Materials Chemistry. *Chem. Mater.* **2014**, *26* (1), 724–744.
- (78) Hoyle, C. E.; Bowman, C. N. Thiol–Ene Click Chemistry. *Angew. Chem. Int. Ed.* **2010**, *49* (9), 1540–1573.
- (79) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis. *Chem. Soc. Rev.* **2010**, *39* (4), 1355–1387.
- (80) Hoogenboom, R. Thiol–Yne Chemistry: A Powerful Tool for Creating Highly Functional Materials. *Angew. Chem. Int. Ed.* **2010**, *49* (20), 3415–3417.
- (81) Gandini, A. The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis. *Prog. Polym. Sci.* **2013**, *38* (1), 1–29.
- (82) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. Organic Azides: An Exploding Diversity of a Unique Class of Compounds. *Angew. Chem. Int. Ed.* **2005**, *44* (33), 5188–5240.
- (83) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective “Ligation” of Azides and Terminal Alkynes. *Angew. Chem.* **2002**, *114* (14), 2708–2711.
- (84) Tornøe, C. W.; Christensen, C.; Meldal, M. Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides. *J. Org. Chem.* **2002**, *67* (9), 3057–3064.
- (85) Diels, O.; Alder, K. Synthesen in der hydroaromatischen Reihe. *Justus Liebigs Ann. Chem.* **1928**, *460* (1), 98–122.

- (86) Liu, Y.-L.; Chuo, T.-W. Self-healing polymers based on thermally reversible Diels–Alder chemistry. *Polym. Chem.* **2013**, *4* (7), 2194–2205.
- (87) Oehlenschlaeger, K. K.; Mueller, J. O.; Brandt, J.; Hilf, S.; Lederer, A.; Wilhelm, M.; Graf, R.; Coote, M. L.; Schmidt, F. G.; Barner-Kowollik, C. Adaptable Hetero Diels–Alder Networks for Fast Self-Healing under Mild Conditions. *Adv. Mater.* **2014**, *26* (21), 3561–3566.
- (88) Syrett, J. A.; Becer, C. R.; Haddleton, D. M. Self-healing and self-mendable polymers. *Polym. Chem.* **2010**, *1* (7), 978–987.
- (89) Inoue, K.; Yamashiro, M.; Iji, M. Recyclable shape-memory polymer: Poly(lactic acid) crosslinked by a thermoreversible Diels–Alder reaction. *J. Appl. Polym. Sci.* **2009**, *112* (2), 876–885.
- (90) Canary, S. A.; Stevens, M. P. Thermally reversible crosslinking of polystyrene via the furan–maleimide Diels–Alder reaction. *J. Polym. Sci. Part Polym. Chem.* **1992**, *30* (8), 1755–1760.
- (91) Du, P.; Wu, M.; Liu, X.; Zheng, Z.; Wang, X.; Sun, P.; Joncheray, T.; Zhang, Y. Synthesis of linear polyurethane bearing pendant furan and cross-linked healable polyurethane containing Diels–Alder bonds. *New J. Chem.* **2014**, *38* (2), 770–776.
- (92) Bicu, I.; Mustata, F. Polymers from a levopimaric acid–acrylic acid Diels–Alder adduct: Synthesis and characterization. *J. Polym. Sci. Part Polym. Chem.* **2007**, *45* (24), 5979–5990.
- (93) Posner, T. Beiträge zur Kenntniss der ungesättigten Verbindungen. II. Ueber die Addition von Mercaptanen an ungesättigte Kohlenwasserstoffe. *Berichte Dtsch. Chem. Ges.* **1905**, *38* (1), 646–657.
- (94) Roper, T. M.; Kwee, T.; Lee, T. Y.; Guymon, C. A.; Hoyle, C. E. Photopolymerization of pigmented thiol–ene systems. *Polymer* **2004**, *45* (9), 2921–2929.
- (95) Gou, L.; Opheim, B.; Coretsopoulos, C. N.; Scranton, A. B. Consumption of the Molecular Oxygen in Polymerization Systems Using Photosensitized Oxidation of Dimethylantracene. *Chem. Eng. Commun.* **2006**, *193* (5), 620–627.

- (96) Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N. Thiol–Yne Photopolymerizations: Novel Mechanism, Kinetics, and Step-Growth Formation of Highly Cross-Linked Networks. *Macromolecules* **2009**, *42* (1), 211–217.
- (97) Hensarling, R. M.; Doughty, V. A.; Chan, J. W.; Patton, D. L. “Clicking” Polymer Brushes with Thiol-yne Chemistry: Indoors and Out. *J. Am. Chem. Soc.* **2009**, *131* (41), 14673–14675.
- (98) Konkolewicz, D.; Gray-Weale, A.; Perrier, S. Hyperbranched Polymers by Thiol–Yne Chemistry: From Small Molecules to Functional Polymers. *J. Am. Chem. Soc.* **2009**, *131* (50), 18075–18077.
- (99) Zoia, L.; Salanti, A.; Frigerio, P.; Orlandi, M. Exploring Allylation and Claisen Rearrangement as a Novel Chemical Modification of Lignin. *BioResources* **2014**, *9* (4), 6540–6561.
- (100) Hannoda, Y.; Akasaka, Y.; Shibata, M. Bio-based thermosetting bismaleimide resins using cardanyl linolenate and allyl cardanyl ether. *React. Funct. Polym.* **2015**, *97*, 96–104.
- (101) Darroman, E.; Bonnot, L.; Auvergne, R.; Boutevin, B.; Caillol, S. New aromatic amine based on cardanol giving new biobased epoxy networks with cardanol. *Eur. J. Lipid Sci. Technol.* **2015**, *117* (2), 178–189.
- (102) Jawerth, M.; Lawoko, M.; Lundmark, S.; Perez-Berumen, C.; Johansson, M. Allylation of a lignin model phenol: a highly selective reaction under benign conditions towards a new thermoset resin platform. *RSC Adv.* **2016**, *6* (98), 96281–96288.
- (103) Over, L. C.; Meier, M. A. R. Sustainable allylation of organosolv lignin with diallyl carbonate and detailed structural characterization of modified lignin. *Green Chem.* **2015**, *18* (1), 197–207.
- (104) Duval, A.; Averous, L. Solvent and halogen-free modification of biobased polyphenols to introduce vinyl groups: versatile aromatic building blocks for polymer synthesis. *ChemSusChem* **2017**, *10* (8), 1813–1822.
- (105) Thiebaud, S.; Borredon, M. E. Solvent-free wood esterification with fatty acid chlorides. *Bioresour. Technol.* **1995**, *52* (2), 169–173.

- (106) Thiebaud, S.; Borredon, M. E.; Baziard, G.; Senocq, F. Properties of wood esterified by fatty-acid chlorides. *Bioresour. Technol.* **1997**, *59* (2), 103–107.
- (107) Laurichesse, S.; Huillet, C.; Avérous, L. Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethane synthesis. *Green Chem.* **2014**, *16* (8), 3958–3970.
- (108) Buono, P.; Duval, A.; Averous, L.; Habibi, Y. Lignin-Based Materials Through Thiol–Maleimide “Click” Polymerization. *ChemSusChem* **2017**, *10* (5), 984–992.
- (109) Fu, C.; Liu, J.; Xia, H.; Shen, L. Effect of structure on the properties of polyurethanes based on aromatic cardanol-based polyols prepared by thiol-ene coupling. *Prog. Org. Coat.* **2015**, *83*, 19–25.
- (110) Luo, C.; Grigsby, W. J.; Edmonds, N. R.; Al-Hakkak, J. Vegetable oil thermosets reinforced by tannin–lipid formulations. *Acta Biomater.* **2013**, *9* (2), 5226–5233.
- (111) Koivu, K. A. Y.; Sadeghifar, H.; Nousiainen, P.; Argyropoulos, D. S.; Sipila, J. The Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin. *ACS Sustain. Chem. Eng.* **2016**, *4* (10), 5238–5247.
- (112) Naveau, H. P. Methacrylic derivatives of lignin. *Cellul. Chem. Technol.* **1975**, *9*, 71–75
- (113) Glasser, W. G.; Wang, H.-X. Derivatives of Lignin and Ligninlike Models with Acrylate Functionality. In *Lignin*; ACS Symposium Series; American Chemical Society, **1989**, *397*, 515–522.
- (114) Da Cunha, C.; Deffieux, A.; Fontanille, M. Synthesis and polymerization of lignin-based macromonomers. III. Radical copolymerization of lignin-based macromonomers with methyl methacrylate. *J. Appl. Polym. Sci.* **1993**, *48* (5), 819–831.
- (115) Podkościelna, B.; Sobiesiak, M.; Zhao, Y.; Gawdzik, B.; Sevastyanova, O. Preparation of lignin-containing porous microspheres through the copolymerization of lignin acrylate derivatives with styrene and divinylbenzene. *Holzforschung* **2015**, *69* (6), 769–776.

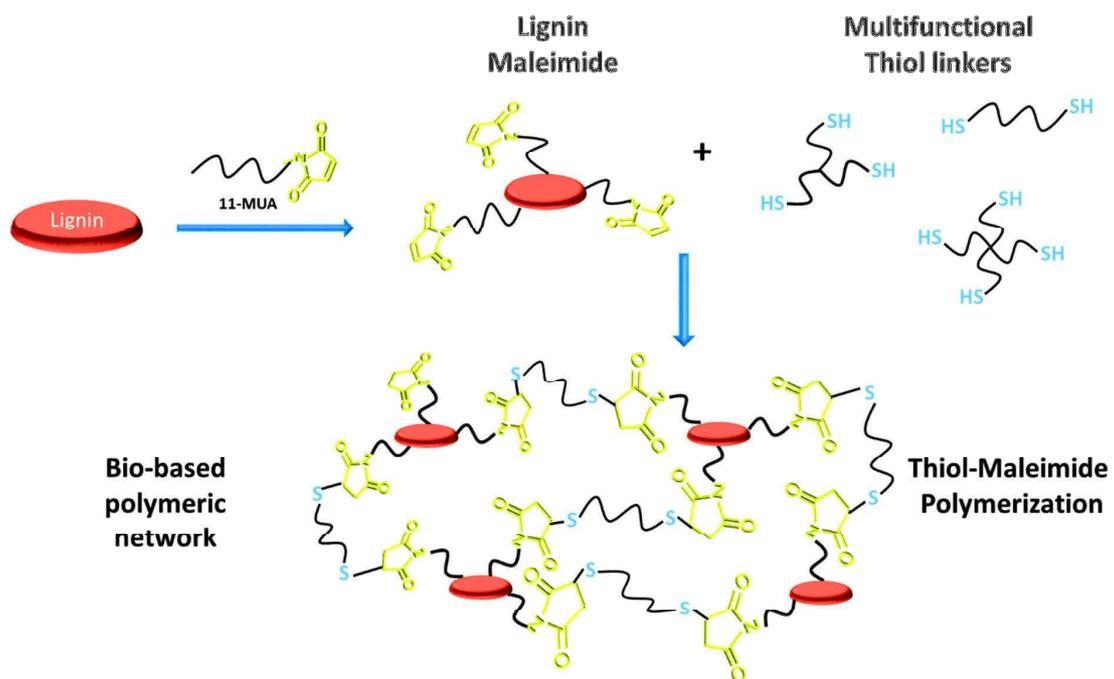
- (116) Jahanshahi, S.; Pizzi, A.; Abdulkhani, A.; Shakeri, A. Analysis and Testing of Bisphenol A—Free Bio-Based Tannin Epoxy-Acrylic Adhesives. *Polymers* **2016**, *8* (4), 143–157.
- (117) Liu, R.; Zheng, J.; Guo, R.; Luo, J.; Yuan, Y.; Liu, X. Synthesis of New Biobased Antibacterial Methacrylates Derived from Tannic Acid and Their Application in UV-Cured Coatings. *Ind. Eng. Chem. Res.* **2014**, *53* (27), 10835–10840.
- (118) Liu, R.; Zhu, J.; Luo, J.; Liu, X. Synthesis and application of novel UV-curable hyperbranched methacrylates from renewable natural tannic acid. *Prog. Org. Coat.* **2014**, *77* (1), 30–37.
- (119) John, G.; Pillai, C. K. S. Self-crosslinkable monomer from cardanol: crosslinked beads of poly(cardanyl acrylate) by suspension polymerization. *Makromol. Chem. Rapid Commun.* **1992**, *13* (5), 255–259.
- (120) John, G.; Pillai, C. K. S. Synthesis and characterization of a self-crosslinkable polymer from cardanol: Autooxidation of poly(cardanyl acrylate) to crosslinked film. *J. Polym. Sci. Part Polym. Chem.* **1993**, *31* (4), 1069–1073.
- (121) I, S. K.; Foerst, G.; Schubert, R.; Bartsch, E. Synthesis and Micellization Properties of New Anionic Reactive Surfactants Based on Hydrogenated Cardanol. *J. Surfactants Deterg.* **2012**, *15* (2), 207–215.
- (122) Liu, R.; Zhang, X.; Zhu, J.; Liu, X.; Wang, Z.; Yan, J. UV-Curable Coatings from Multiarmed Cardanol-Based Acrylate Oligomers. *ACS Sustain. Chem. Eng.* **2015**, *3* (7), 1313–1320.
- (123) Liu, J.; Liu, R.; Zhang, X.; Li, Z.; Tang, H.; Liu, X. Preparation and properties of UV-curable multi-arms cardanol-based acrylates. *Prog. Org. Coat.* **2016**, *90*, 126–131.
- (124) Liu, R.; Zhu, G.; Li, Z.; Liu, X.; Chen, Z.; Ariyasivam, S. Cardanol-based oligomers with “hard core, flexible shell” structures: from synthesis to UV curing applications. *Green Chem.* **2015**, *17* (6), 3319–3325.
- (125) Sultania, M.; Rai, J. S. P.; Srivastava, D. Studies on the synthesis and curing of epoxidized novolac vinyl ester resin from renewable resource material. *Eur. Polym. J.* **2010**, *46* (10), 2019–2032.

- (126) Ladmiral, V.; Jeannin, R.; Fernandes Lizarazu, K.; Lai-Kee-Him, J.; Bron, P.; Lacroix-Desmazes, P.; Caillol, S. Aromatic biobased polymer latex from cardanol. *Eur. Polym. J.* **2017**, *in press*.
- (127) Sen, S.; Sadeghifar, H.; Argyropoulos, D. S. Kraft Lignin Chain Extension Chemistry via Propargylation, Oxidative Coupling, and Claisen Rearrangement. *Biomacromolecules* **2013**, *14* (10), 3399–3408.
- (128) Yang, P.; Yan, J.; Sun, H.; Fan, H.; Chen, Y.; Wang, F.; Shi, B. Novel environmentally sustainable cardanol-based plasticizer covalently bound to PVC via click chemistry: synthesis and properties. *RSC Adv.* **2015**, *5* (22), 16980–16985.
- (129) Liu, H.; Chung, H. Self-Healing Properties of Lignin-Containing Nanocomposite: Synthesis of Lignin-graft-poly(5-acetylaminopentyl acrylate) via RAFT and Click Chemistry. *Macromolecules* **2016**, *49* (19), 7246–7256.
- (130) Han, Y.; Yuan, L.; Li, G.; Huang, L.; Qin, T.; Chu, F.; Tang, C. Renewable polymers from lignin via copper-free thermal click chemistry. *Polymer* **2016**, *83*, 92–100.
- (131) Sadeghifar, H.; Cui, C.; Argyropoulos, D. S. Toward Thermoplastic Lignin Polymers. Part 1. Selective Masking of Phenolic Hydroxyl Groups in Kraft Lignins via Methylation and Oxypropylation Chemistries. *Ind. Eng. Chem. Res.* **2012**, *51* (51), 16713–16720.
- (132) Jin, C.; Zhang, X.; Xin, J.; Liu, G.; Wu, G.; Kong, Z.; Zhang, J. Clickable Synthesis of 1,2,4-Triazole Modified Lignin-Based Adsorbent for the Selective Removal of Cd(II). *ACS Sustain. Chem. Eng.* **2017**, *5* (5), 4086–4093.
- (133) Duval, A.; Lange, H.; Lawoko, M.; Crestini, C. Reversible crosslinking of lignin via the furan–maleimide Diels–Alder reaction. *Green Chem.* **2015**, *17* (11), 4991–5000.
- (134) Duval, A.; Couture, G.; Caillol, S.; Avérous, L. Biobased and Aromatic Reversible Thermoset Networks from Condensed Tannins via the Diels–Alder Reaction. *ACS Sustain. Chem. Eng.* **2017**, *5* (1), 1199–1207.
- (135) Foo, L. Y.; Hemingway, R. W. Condensed Tannins: Reactions of Model Compounds with Furfuryl Alcohol and Furfuraldehyde. *J. Wood Chem. Technol.* **1985**, *5* (1), 135–158.

- (136) Gandini, A.; Belgacem, M. N. Furans in polymer chemistry. *Prog. Polym. Sci.* **1997**, *22* (6), 1203–1379.
- (137) Tyman, J. H. P. Long-chain phenols. *J. Chromatogr. A* **1975**, *111* (2), 277–284.
- (138) Tyman, J. H. P.; Jacobs, N. The composition of the unsaturated phenolic components of anacardic acid. *J. Chromatogr. A* **1971**, *54*, 83–90.
- (139) Nawrat, C. C.; Moody, C. J. Quinones as Dienophiles in the Diels–Alder Reaction: History and Applications in Total Synthesis. *Angew. Chem. Int. Ed.* **2014**, *53* (8), 2056–2077.
- (140) Hayashi, A.; Kinoshita, K.; Taniguchi, A. (Ritsumeikan U. Demethylation of lignin during pulping, 2: Correlation between demethylation and coloring with soda cooking. *J. Jpn. Wood Res. Soc. Jpn.* **1975**, *21* (8), 480–484.
- (141) Hayashi, A.; Kinoshita, K.; Taniguchi, A.; Nakamura, T. Demethylation of lignin during pulping, 3: Correlation between oxidation product of quinones and lignin chromophore. *J. Jpn. Wood Res. Soc.* **1975**, *21* (8), 472–473.
- (142) Ahvazi, B. C.; Crestini, C.; Argyropoulos, D. S. ¹⁹F Nuclear Magnetic Resonance Spectroscopy for the Quantitative Detection and Classification of Carbonyl Groups in Lignins. *J. Agric. Food Chem.* **1999**, *47* (1), 190–201.
- (143) Argyropoulos, D. S.; Zhang, L. Semiquantitative Determination of Quinonoid Structures in Isolated Lignins by ³¹P Nuclear Magnetic Resonance. *J. Agric. Food Chem.* **1998**, *46* (11), 4628–4634.
- (144) Wozniak, J. C.; Dimmel, D. R.; Malcolm, E. W. The Generation of Quinones from Lignin and Lignin-Related Compounds. *J. Wood Chem. Technol.* **1989**, *9* (4), 491–511.
- (145) Wozniak, J. C.; Dimmel, D. R.; Malcolm, E. W. Diels–Alder Reactions of Lignin-Derived Quinones. *J. Wood Chem. Technol.* **1989**, *9* (4), 513–534.
- (146) Sadeghifar, H.; Venditti, R.; Jur, J.; Gorga, R. E.; Pawlak, J. J. Cellulose-Lignin Biodegradable and Flexible UV Protection Film. *ACS Sustain. Chem. Eng.* **2016**, *5* (1), 625–631.

- (147) Pan, X.; Kadla, J. F.; Ehara, K.; Gilkes, N.; Saddler, J. N. Organosolv Ethanol Lignin from Hybrid Poplar as a Radical Scavenger: Relationship between Lignin Structure, Extraction Conditions, and Antioxidant Activity. *J. Agric. Food Chem.* **2006**, *54* (16), 5806–5813.
- (148) Dizhbite, T.; Telysheva, G.; Jurkjane, V.; Viesturs, U. Characterization of the radical scavenging activity of lignins—natural antioxidants. *Bioresour. Technol.* **2004**, *95* (3), 309–317.
- (149) Lu, F.-J.; Chu, L.-H.; Gau, R.-J. Free radical-scavenging properties of lignin. *Nutr. Cancer* **1998**, *30* (1), 31–38.
- (150) Da Cunha, C.; Deffieux, A.; Fontanille, M. Synthesis and polymerization of lignin macromonomers. II. Effects of lignin fragments on methyl methacrylate radical polymerization. *J. Appl. Polym. Sci.* **1992**, *44* (7), 1205–1212.
- (151) Yao, L.; Chen, Q.; Xu, W.; Ye, Z.; Shen, Z.; Chen, M. Preparation of cardanol based epoxy plasticizer by click chemistry and its action on poly(vinyl chloride). *J. Appl. Polym. Sci.* **2017**, *134* (23), 44890-44897.

Chapitre 2 : Matériaux à base de lignines obtenues par polymérisation « clic » thiol- maléimide



Introduction du chapitre 2

L'état de l'art réalisé dans le chapitre 1 a montré que la combinaison de la chimie clic avec l'utilisation de polyphénols naturels comme source de produits chimiques aromatiques représente un point de départ valable pour le développement de polymères et matériaux aromatiques renouvelables. Nous avons également souligné que la chimie clic a été peu exploitée pour ce qui concerne les polyphénols naturels.

Dans ce contexte, nous avons montré l'intérêt de l'utilisation de la réaction clic thiol-ene pour obtenir des polymères renouvelables à base de lignine avec la publication de l'article scientifique « matériaux à base de lignine obtenus par polymérisation clic de type maléimide-thiol » qui est présenté par la suite. Dans cette étude, des macromères de lignine ont été greffés par une réaction d'estérification avec l'acide 11-maleimide-undecénoïque (obtenu à partir de l'huile de ricin), sans solvants ni catalyseurs. Les dérivés de lignine à base de fonctions maléimides ont été ensuite polymérisés par une réaction thiol-ene avec différents thiols polyfonctionnels aliphatique et aromatiques.

Lignin-based materials through thiol - maleimide “click” polymerization

Pietro Buono,^[a] Antoine Duval,^[b] Luc Averous^[b] and Youssef Habibi*^[a]

^a Department of Materials Research and Technology (MRT), Luxembourg Institute of Science and Technology (LIST), 5 avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

^b BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, Strasbourg Cedex 2 67087, France

*e-mail: youssef.habibi@list.lu

Abstract

In the present work we propose an environmentally friendly approach to transform renewable feedstocks into value-added materials. This transformation pathway is conducted under green conditions, without the use of solvents and catalyst. First, controlled modification of lignin, a major biopolymer present in wood and plants, was achieved through the esterification with 11-maleimidoundecylenic acid (11-MUA), a derivative from ocastor oil that contains maleimide groups. Different degrees of substitution were achieved by using various amounts of the 11-MU acyl chloride leading to an efficient conversion of lignin hydroxyl groups as demonstrated by ¹H and ³¹P NMR analyses. These fully biobased maleimide-lignin derivatives were reacted through an extremely fast (about one minute) thiol-ene “click” polymerization with thiol-containing linkers. Aliphatic and aromatic thiol-linkers bearing from 2 to 4 thiol groups were used in order to tune the reactivity and crosslinking density. The properties of the resulting materials were evaluated by swelling tests, thermal and mechanical analyses showing that varying the linker functionality and structure allows to accurately tailor the thermal and mechanical properties of the final materials, thus providing interesting perspectives for lignin towards functional aromatic polymers.

1. Introduction

Lignocellulosic biomass is considered to be one of the most promising renewable resources to replace fossil counterpart for the elaboration of biobased polymer materials.¹ Lignins are one of the main components of this biomass. They present an aromatic backbone, making it the most important renewable source of aromatic structures, explaining the intensive research activities worldwide. Lignin is formed by a dehydrogenative enzymatic radical polymerization process, involving three phenylpropanoid monomers: coumaryl, coniferyl and sinapyl alcohols.² The proportions of these monomers varies with the botanical origin, thus creating a wide diversity of lignins.³

In their native forms, lignins present complex, apparently unordered structures, where the different units are connected by ethers or condensed C-C bonds.⁴ Their isolation from botanical sources may occur through different industrial extraction processes, leading to different types of lignin commonly divided into sulfur or sulfur-free lignin. The majority of lignin is fractionated through sulfur processes (Kraft or sulfite) that are mainly used in pulping industry. Kraft lignin is the most important one in terms of quantity, but is mostly burnt in plant to generate energy.

Lignosulfonates obtained by the sulfite process are thus the principal source of available lignin, with already well-established applications as dispersants or binders.⁵ Soda and *organosolv* lignins are obtained by sulfur-free processes, and constitute a rather recent source of available technical lignin with and then with promising applications in polymeric materials.^{6,7}

Recent years have seen the development of high performance lignin-based functional materials,⁸⁻¹¹ possessing properties such as antibacterial, antioxidant or UV-absorbance.¹²⁻¹⁶ A key strategy to further implement lignin into the polymer chemistry seems to be its chemical modification.¹⁷ In particular, aliphatic and phenolic hydroxyl (OH) groups can be easily modified through esterification or alkylation, either to chain extend¹⁸⁻²⁰ or introduce new chemically active sites, *e.g.* allyls,²¹ alkynes,²² benzyls,²³ phenols,²⁴ epoxy²⁵, cyclic carbonates groups²⁶ and silyl groups.²⁷

Introduced by Sharpless and co-workers,²⁸ the “click chemistry” involves reactions characterized by quick and quantitative yields under mild conditions. These reactions should also produce inoffensive by-products easily removable by non-chromatographic methods. Click reactions represent an extremely powerful tool in chemistry, leading to a wide range of applications.²⁹ In polymer chemistry, they paved the way to great developments in the preparation of controlled macromolecular architectures.^{30,31}

Thiol-ene “click” reaction for instance, is widely employed in the field of bioconjugation,³² but also shows great potential in polymer and material chemistry.^{33–35} The presence of two electron-withdrawing carbonyl groups in *cis*-conformation together with the ring strain, make the C=C double bond of maleimides extremely reactive toward thiol-ene reactions,³⁴ and should allow the formation of the thioether adduct within very short reaction times. Recently, “click” reactions were employed to produce lignin-based polymers, either by the thermally reversible furan – maleimide Diels-Alder [4 + 2] cycloaddition³⁶ or by Huisgen 1,3-dipolar cycloaddition between azide and alkyne groups.³⁷

The synergetic combination between click chemistry and a green approach using biopolymers as chemical feedstock could lead not only to the prevention from environmental issues but constitute a holistic approach for sustainable development. The aim of this study was focused on the well-known reaction between thiols and maleimides to obtain novel and biobased aromatic macromolecular architectures establishing the first example of lignin-based thiol-maleimide polymeric materials. In this study, soda lignin (SL) was first modified to introduce maleimide groups, through an esterification with 11-maleimido-undecenoyl chloride (11-MUC) prepared from the corresponding 11-maleimido-undecylenic acid (11-MUA), a derivative from the biobased castor oil. The maleimido-soda lignin (Mal-SL) was then polymerized with different polyfunctional thiols. The properties of the ensuing materials were evaluated by thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), swelling and mechanical tests.

2. Experimental Section

2.1 Reagents and Materials

Soda lignin (SL, Protobind 1000) was obtained from Green Value SA (Switzerland). It is a sulfur-free lignin obtained after extraction and fractionation from a mixture of wheat straw (*Triticum sp.*) and Sarkanda grass (*Saccharum officinarum*), according to a patented process.³⁸ SL is a low molar mass lignin (M_n below 1000 g mol^{-1}), with a high degree of condensation and low content in residual ether bonds.⁴ The lignin was used as received without further purification.

11-maleimidoundecanoic acid (11-MUA) (95%), 4,4'-thiobisbenzenethiol (98%), trimethylolpropane tris(3-mercaptopropionate) (>95%), pentaerythritol tetrakis(3-mercaptopropionate) (>95%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), chromium(III) acetylacetonate (99.99%), cholesterol (>99%), triethylamine (TEA) (>99%), chloroform-*d* (100%, 99.96 atom% D) and dimethyl sulfoxide-*d*₆ (100%, 99.96 atom% D) were purchased from Sigma-Aldrich; oxalyl chloride (>98%), 3,6-dioxa-1,8-octanedithiol from TCI Europe; ethyl acetate (99.6%, ACS reagent) and methanol (>98%, ACS reagent) from Fisher Scientific; pyridine (99.5%, extra dry over molecular sieve) and dichloromethane (DCM) (>99%, extra pure, stabilized with ethanol) from Acros Organics.

2.2 Synthesis and materials processing

Chlorination of 11-Maleimidoundecanoic acid

(11-MUA) 11-Maleimidoundecanoic (11-MUA) (25 g, 88.9 mmol) was placed in a two necked 250 mL flame dried round bottom flask flushed with argon and charged with a stirring bar. Ethyl acetate (35 mL) was then added and the solution cooled down to 0 °C under a nitrogen flow. An excess of oxalyl chloride (11.5 mL, 133.3 mmol) was then added dropwise at 0 °C (15 min) and finally heated at 50 °C for 3 h. The excess of oxalyl chloride and solvent were evaporated under vacuum. The product, 11-maleimidoundecenoyl chloride (11-MUC) was obtained as a low melting yellow solid and used

without any further purification. ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 6.70 (2H, s, CH ring), 3.56 (2H, t, $\text{CH}_2\text{-N}$), 2.89 (2H, t, CH_2COCl), 1.71 (2H, m, $\text{CH}_2\text{CH}_2\text{-N}$), 1.60 (2H, m, $\text{CH}_2\text{CH}_2\text{COCl}$), 1.39 – 1.20 (10H, aliphatic chain's protons); ^{13}C NMR (400 MHz, CDCl_3 , δ (ppm)): 173.06 (COCl), 170.94 (CO ring), 134.05 (CH ring), 47.10 (CH_2N), 39.27 (CH_2COCl), 33.94 ($\text{CH}_2\text{CH}_2\text{N}$), 29.29 – 25.03 (aliphatic chain's carbons); IR (cm^{-1}): 3101 (C-H stretch maleimide ring), 2927 and 2855 (C-H aliphatic stretching), 1797 (C=OCl stretch), 1702 (C=O maleimide ring stretch), 826 and 695 (C-H bend maleimide).

Maleimido functionalization of soda lignin (SL)

SL was esterified with respectively 0.7, 1.1 or 1.3 equivalents of 11-MUC compared to the amount of total lignin hydroxyl groups. The resultant lignin derivatives will be named Mal-SL_0.7, Mal-SL_1.1 or Mal-SL_1.3, respectively. In agreement with some green chemistry principles, the reaction was carried out in solvent-free and catalyst-free conditions at 65 °C, as recently reported by Thiebaud et al.,^{39,40} with slight modifications depending on the reactions. When 1.1 eq 11-MUC were used, the temperature was increased to 90 °C after 24h to overcome the high viscosity of the system, while when only 0.7 eq were employed, 25 mL CHCl_3 were added to homogenize the reaction mixture. At the end of the reaction, a dark viscous product was obtained. 100 mL of methanol were added to quench the unreacted 11-MUC, and the mixture was left under stirring for additional 30 min. Solvents were then evaporated under vacuum and the resultant products maleimido-soda lignin (Mal-SL) finally dried under high vacuum for 24 h.

Thiol-ene polymerization of Mal-SL

10 g of Mal-SL were dissolved in 20 mL DCM in a two necked 100 mL flask. A solution of thiol linker was prepared by dissolving the corresponding thiol (3,6-dioxa-1,8-octanedithiol, trimethylolpropane tris(3-mercaptopropionate) or pentaerythritol tetrakis(3-mercaptopropionate)) in a mixture of TEA (TEA/SH molar ratio 1:1) and DCM (5 mL). 4,4'-thiobisbenzenethiol was instead dissolved in a mixture of methanol (MeOH) (5 mL) and TEA (TEA/SH molar ratio 1:1). The thiol linker solution was

then added to the Mal-SL solution at room temperature. The maleimido /SH molar ratio was set to 1:1.2. After 1 minute of reaction a viscous gel formed, impeding the reaction stirring. The reaction was stopped, TEA and DCM were evaporated under vacuum, and the polymer was washed with 4 x 50 mL of MeOH to eliminate the unreacted thiol linker. It was finally dried for 24 h under high vacuum.

Materials processing

The materials prepared by thiol-ene polymerization were compression molded for 20 min at 120 °C on a Carver manual press (Wabash, IN, USA) equipped with heating plates. Polymers were placed in a tile mold Carver (Wabash, IN, USA) enabling to produce plates of 5 cm x 5 cm x 0.2 cm. For the first 10 min, the polymers were left to soften applying a load of 1 ton-force. After several degassing steps, the materials were pressed with a constant applied load of 7 metric tons for the remaining 10 min. The plates were then cooled down to room temperature under pressure during 10 min by a water circulation within the plates.

2.3 Characterizations

NMR spectroscopies

All NMR spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer. ³¹P NMR analysis was performed on lignin samples phosphitylated with 2-Chloro-4,4,5,5-tetramethyl-1,3,2 dioxaphospholane, using cholesterol as internal standard, according to standard protocols.⁴¹ 128 scans were recorded with a 15 s delay and a spectral width of 80 ppm (180-100 ppm). For quantitative ¹H-NMR analysis, about 20 mg of lignin were dissolved in 0.5 mL of DMSO-*d*₆ before the addition of 100 μL of a standard solution of pentafluorobenzaldehyde (PFB) in DMSO-*d*₆. 32 scans were collected with a 10 s delay

Fourier transform infrared spectroscopy (FTIR)

The FTIR analyses were conducted on a Bruker Tensor 27 (Ettlingen, Germany) in attenuated total reflection (ATR) mode. 40 scans were collected between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1} .

Size Exclusion Chromatography (SEC)

SEC analysis were performed on a Shimadzu chromatograph equipped with a 5 μ PL-gel pre- column, two PL-gel 5 μ MIXED-C and a 5 μ 100 Å 300 mm columns. Detection was performed with refractive index (RI, Shimadzu RID-10A) and ultra-violet (UV, Shimadzu SPD-M10A diode array) detectors. Chloroform (CHCl_3) was used as the eluent at a flow rate of 0.8 mL min^{-1} . Neat SL was characterized after acetylation,²⁷ to ensure its full dissolution in the eluent, whereas the Mal-SL were analyzed as such. All determinations of molar mass were performed relative to linear polystyrene standards from 580 to 1 650 000 g mol^{-1} .

Thermal Gravimetric Analysis (TGA)

TGA were performed on a STA 409PC Luxx apparatus from NETZSCH at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ up to 800 $^{\circ}\text{C}$ under an argon atmosphere (flow rate = 90 mL min^{-1}). About 30 mg sample were analyzed.

Differential Scanning Calorimetry (DSC)

DSC thermograms were recorded on a TA DSC Q200 calorimeter (TA Instruments). The samples were first heated to 105 $^{\circ}\text{C}$ and maintained at this temperature for 15 min to erase thermal history. They were then cooled to 0 $^{\circ}\text{C}$ and heated to 200 $^{\circ}\text{C}$. Glass transition temperatures (T_g) were recorded on the second heating run.

Uniaxial tensile tests

Dumbbell-shaped samples (5 cm length and 2.2 mm width) were cut from the compression molded plates, and analyzed on a universal testing machine Instron 5967 (Norwood, MA, USA) equipped

with a 100 N load cell operating at 5 mm min⁻¹ crosshead speed. They were dried in a vacuum oven for 24 h at 40 °C and successively preconditioned overnight under the environmental conditions of measurement. 3 to 4 measurements were performed for each lignin-based material at room temperature and 50% relative humidity.

Dynamic Mechanical Analysis (DMA)

DMA was measured on a Netzsch DMA 42 C equipment (Selb, Germany). Samples were cut from the compression molded plates. DMA was conducted in tensile mode from -80 °C to 150 °C at a 2 °C min⁻¹ heating rate and a frequency of 5 Hz with free lengths of 7 mm. Storage modulus E' , loss modulus E'' , and loss factor $\tan \delta = E''/E'$ were continuously recorded as a function of the temperature. The cross linking density (ν_e) was calculated by Equation 2.1, from the storage modulus measured at the material's rubbery plateau, E'_{rub} , according to the theory of elasticity.^{42,43}

$$\nu_e \text{ (mol L}^{-1}\text{)} = \frac{E'_{rub}}{RT} \quad (2.1)$$

Swelling tests

The thiol-maleimide polymers were swollen in H₂O and methanol. Each experiment was run in triplicate on ca. 0.330 g of film immersed in 25 mL of solvent. The films of initial mass m_i were let to swell at room temperature until constant weight, and weighed to measure the swollen mass (m_{sw}), and then dried to a constant weight (m_{dry}). The degree of swelling (SW) and the soluble fraction were determined by Equation 2.2 and 2.3, respectively.

$$SW \text{ (\%)} = 100 \times \frac{m_{sw} - m_{dry}}{m_{dry}} \quad (2.2)$$

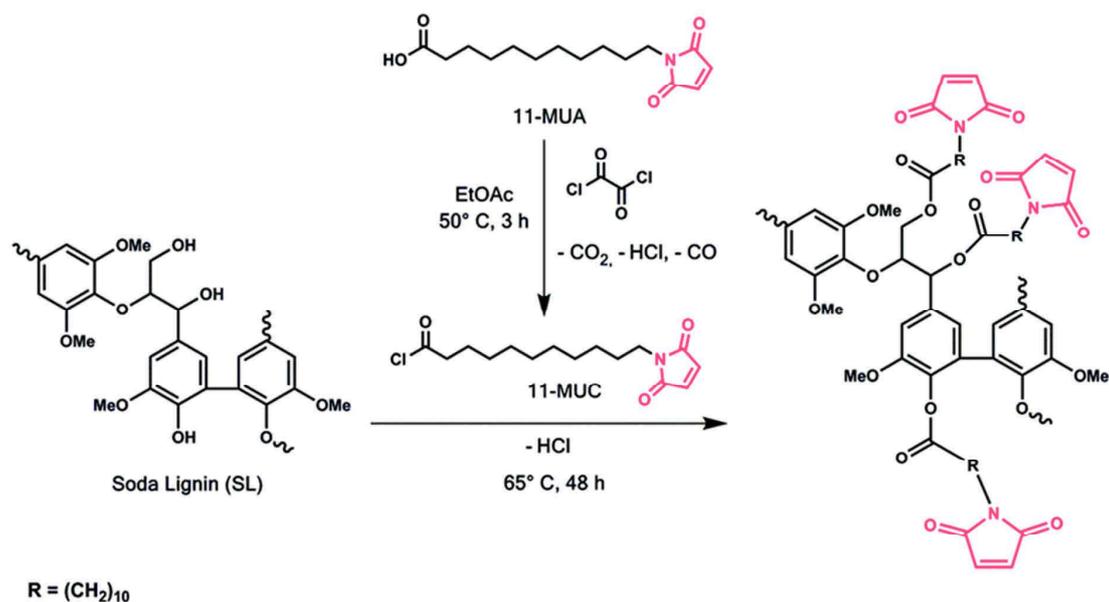
$$\text{Sol. fraction (\%)} = \frac{m_i - m_{dry}}{m_i} \times 100 \quad (2.3)$$

The methanol soluble fraction was then recovered after solvent evaporation and analyzed by SEC.

3. Results and Discussions

3.1 Synthesis of maleimide soda lignin (Mal-SL)

The OH groups in SL were esterified with 11-MUA, to expose pendant maleimide groups. Similarly to previously reported results,³⁶ 11-MUA was first converted into an acyl chloride derivative (11-MUC) to increase the reactivity (Scheme 2.1). The derivatization of SL was then conducted with 0.7, 1.1 and 1.3 eq. of 11-MUC under solvent- and catalyst-free conditions. The success of the functionalization was evidenced by FTIR, ³¹P and ¹H NMR (Figures S2.1 and S2.2 Annexe I).



Scheme 2.1. Esterification of soda lignin (SL) with 11-MUA to yield maleimido-modified soda lignin (Mal-SL).

³¹P NMR spectra reveal the disappearance of both phenolic and aliphatic OH groups during the reaction. Figure 2.1 reports the conversion depending on the amount of 11-MUC introduced for the reaction. Aliphatic OH groups are converted to a higher extent than their phenolic counterpart, as already reported during the esterification of lignin with various fatty acids.^[38] With a slight excess of 11-MUC, the total conversion of OH groups reaches 83% (1.1 eq) and 89% (1.3 eq).

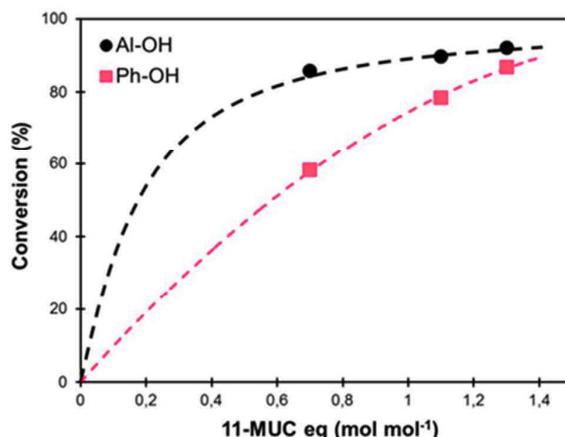


Figure 2.1. Conversion of aliphatic and phenolic OH groups of SL during the reaction with 11-MUC.

Considering the initial content of SL in OH groups (5.2 mmol g^{-1}) and the mass increase caused by the grafting, the content of the final material in maleimide groups can be calculated from the conversion by the equation 2.4:

$$x_{\text{maleimide}} (\text{mol g}^{-1}) = \frac{\chi_{\text{OH}} \times [\text{OH}]_{\text{tot}}}{1 + \chi_{\text{OH}} \times [\text{OH}]_{\text{tot}} \times 263.4} \quad (2.4)$$

where χ_{OH} stands for the conversion of OH groups, $[\text{OH}]_{\text{tot}}$ is the total content of SL in OH groups (5.2 mmol g^{-1}) and 263.4 g mol^{-1} corresponds to the molar mass of the grafted chain (= M11-MUA – 18). The resulting results are gathered in Table 2.1.

Table 2.1. Content in maleimide groups of the derivatized lignins.

Samples	11-MUC eq	Maleimide content (mmol g^{-1})	
		by ^{31}P NMR	by ^1H NMR
Mal-SL_0.7	0.7	1.77	1.92
Mal-SL_1.1	1.1	1.95	2.10
Mal-SL_1.3	1.3	2.02	2.11

The derivatized lignins were also analyzed by ^1H NMR (Figure 2.2a), which evidences a strong signal at 7.00 ppm belonging to the maleimide ring double bond protons (2 H, signal a). The saturated side chain of 11-MUA produces signals in the 0.75 – 1.75 ppm region (16 H, signal d), whereas the protons close to the maleimide ring appear at 3.38 ppm (2H, signal b). The protons in α position to

the ester linkage appear at 2.18 ppm (2H, signal c). These last ones are free from overlap with other lignin-related signals and were thus used to quantify the amount of grafted 11-MUA. The values reported in Table 1 correlate well with those obtained by ^{31}P NMR (Equation 2.4).

FTIR spectra also give an evidence of the successful derivatization (Figure 2.2b). The broad OH vibrations between 3500 and 3300 cm^{-1} in SL is largely reduced after the grafting, whereas the C-H stretch is strongly increased. Strong carbonyl vibration of maleimide was detected at 1701 cm^{-1} , together with the esters stretching around 1750 cm^{-1} . The C-H bending in maleimide groups is visible at 827 and 695 cm^{-1} .

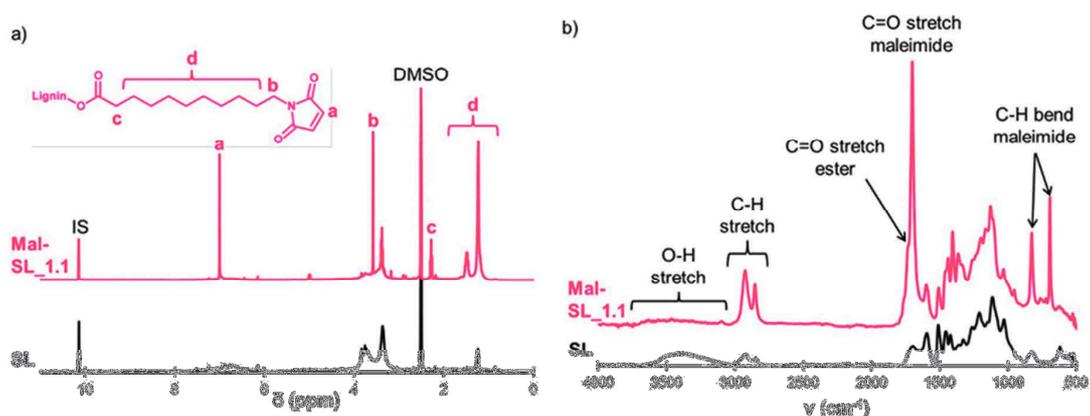


Figure 2.2. ^1H NMR (a) and FTIR (b) spectra of SL and Mal-SL_{1.1}.

SEC of the derivatized lignins are presented on Figure 2.3a. The molar mass distributions are progressively shifted toward higher molar masses as a result of the grafting. The absence of signal in the high molar mass region suggests the absence of crosslinking side reactions. A sharp peak is also detected at $M \approx 400\text{ g}\cdot\text{mol}^{-1}$. Thanks to the diode array detector, it is possible to visualize the full UV spectrum at this specific elution time, and to compare it to the UV spectrum of the main elution peak (Figure 2.3b). The UV spectrum of the main elution peak displays a peak at 280 nm , which corresponds to the absorption of the aromatic rings from the lignin. The shoulder around 300 nm attests for the presence of maleimide groups attached to the lignin. The UV spectrum of the low molar mass elution peak has a single peak centered at 300 nm , corresponding to the absorbance of

the maleimide groups, but reveals the absence of lignin. This elution peak can thus be assigned to methyl 11-maleimidoundecanoate (MMU), formed by the reaction between the remaining 11-MUC and the methanol added to quench the reaction.

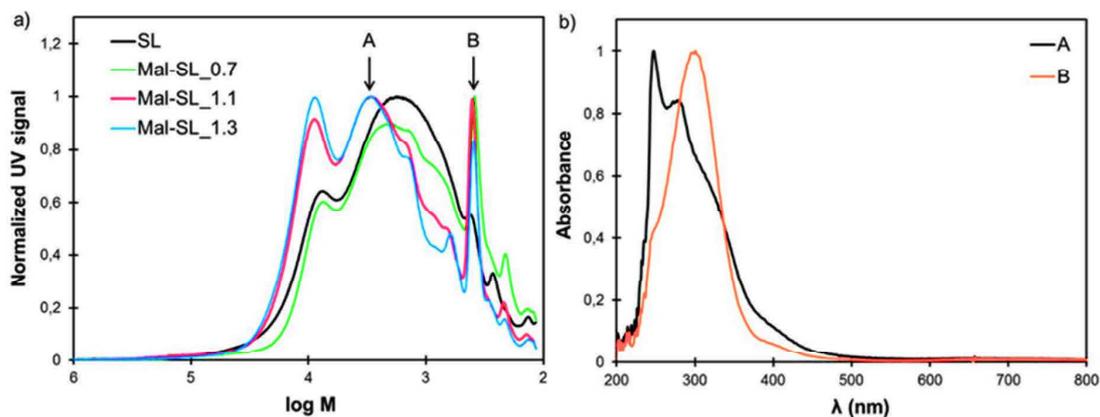
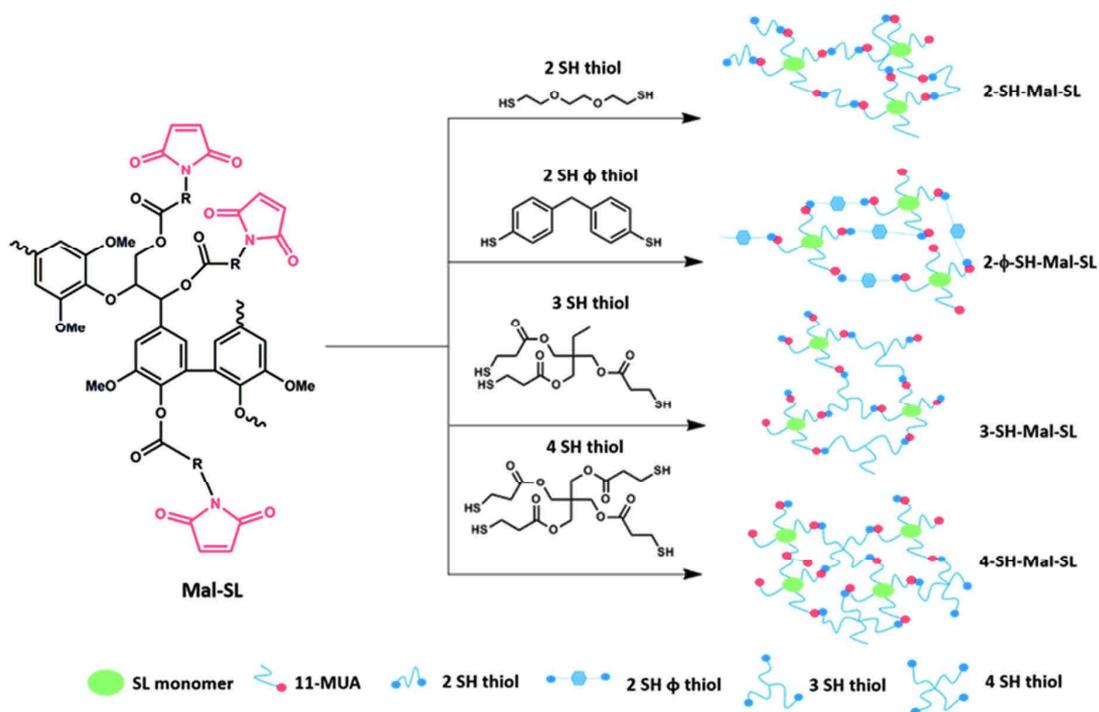


Figure 2.3. (a) SEC chromatogram (CHCl_3 , PS calibration) of SL and Mal-SL. (b) Full UV-vis spectra of Mal-SL_1.1 at two elution times indicated by the arrows on Figure (a).

3.1 Synthesis of thiol-maleimide lignin-based polymeric materials

Mal-SL_0.7, Mal-SL_1.1 and Mal-SL_1.3 were then reacted with thiols, in a Michael addition “click” reaction in the presence of TEA. Using polyfunctional thiols linkers, polymer networks were produced within an extremely short reaction time: a viscous gel formed in about 1 minute after mixing the Mal-SL and the thiol linker solutions. Four different linkers were selected, as exemplified on Scheme 2.2: bi-, tri- and tetra-functional aliphatic thiols and bifunctional aromatic thiol.

They are later referred to as 2-SH, 3-SH, 4-SH and 2- ϕ -SH, respectively. The resulting materials will be named 2-SH-Mal-SL, 3-SH-Mal-SL, 4-SH-Mal-SL and 2- ϕ -SH-Mal-SL, and related to 0.7, 1.1 and 1.3 Mal-SL used for the synthesis.



Scheme 2.2. Illustration of Mal-SL polymerization with the corresponding poly-functional thiols linkers.

All the reactions led to insoluble polymer networks, except 2-SH-Mal-SL_1.3, 3-SH-Mal-SL_1.3 and 2-SH-Mal-SL_0.7, which disintegrated during the methanol wash, probably because of a too low crosslink density. The materials were analyzed in the solid state by FTIR, and the collected data are presented in Figure S2.3a, S2.3b and S2.3c from Annexe 1. The disappearance of the peculiar C-H vibrations in maleimide groups at 827 and 695 cm^{-1} indicates that all the chemically active sites have reacted through the thiol-ene reaction. For 2-φ-SH-Mal-SL materials, aromatic C-H bending of the thiophenol group appears at 812 cm^{-1} , whereas the materials prepared with the linkers containing ester bonds (3-SH-Mal-SL and 4-SH-Mal-SL) exhibit an additional aliphatic ester stretch band at 1733 cm^{-1} . FTIR spectra of unwashed materials also exhibit S-H vibrations between 2550-2600 cm^{-1} (Figure S2.3), whereas it is absent after the methanol wash, showing that it was an effective work-up to remove the unreacted thiols.

3.2 Evaluation of the structure of the thiol-maleimide networks

The structure of the thiol-maleimide networks was evaluated by swelling tests in water and methanol and dynamic mechanical analysis. Table 2.2 gathers all the results.

The structure of the thiol-maleimide networks was evaluated by swelling tests in water and methanol and dynamic mechanical analysis. Table 2 gathers all the results.

For a given Mal-SL, increasing the linker functionality leads to a decrease in swelling, as a result of a higher crosslink density (Figures S2.4 and S2.6). The materials prepared with the aromatic linker swell much less in water than those prepared with aliphatic ones (Figure S2.6). This is probably due to the lower affinity of the aromatic chain toward the corresponding polar solvents.

For a given linker, the swelling is generally minimal for the materials prepared with Mal-SL_{1.1}. With Mal-SL_{1.3}, as a consequence of the excess 11-MUC used for the lignin derivatization, the presence of MMU molecules inside the network may consume part of the SH groups, leading to a material less efficiently crosslinked. With Mal-SL_{0.7}, the incomplete functionalization of the lignin with maleimide groups leads to a reduced crosslinking density, and thus a higher swelling.

Part of the materials is solubilized during the swelling tests. It accounts for 3 – 16% or 2 – 27 % of the initial mass in water and methanol, respectively. For a given linker, the mass loss is slight for materials prepared with Mal-SL_{1.1}. In materials prepared with Mal-SL_{1.3}, part of the linker reacts with the free MMU present in the lignin. The formed molecules are not covalently integrated into the network, and can thus be extracted during the swelling tests, as confirmed by SEC measurements on the soluble fractions in methanol. For materials prepared with Mal-SL_{0.7} some low molar mass lignin fragments can also be extracted from the materials, because of the lower crosslink density.

Dynamic mechanical analyses (DMA) were then conducted on the materials to evaluate the viscoelastic properties. The materials were analyzed in tensile mode (Table 2.2). The curves showing

the evolution of the storage modulus E' and the loss factor $\tan \delta$ with the temperature are available in Annexe I (Figures S2.8, S2.9 and S2.10). The main relaxation temperature, T_α , which can be associated to the glass temperature of the material, was determined at the maximum of the peak of $\tan \delta$. The storage modulus on the rubbery plateau was used to calculate the crosslink density ν_e using Equation 1.

Increasing the linker functionality from 2 to 4 leads to an increase in ν_e (Table 2.2) and T_α (Figure 2.5a) subsequently. The T_α is much higher for the materials bas 2ed on- ϕ -SH linker, because of the rigidity and lack of rotational freedom of the aromatic chains.

Increasing the amount of 11-MUC used to derivatize the lignin also enhances the crosslink density (Table 2.2), because it increases the conversion of the OH groups, and consequently the number of maleimide groups available to react with the thiol linker. However, an excess of 11-MUC also leads to the presence of small molecules of MUM entrapped into the network, which can act as plasticizer, thus strongly reducing the T_α (Figure 2.5b).

Table 2.2. Swelling tests in water and methanol and main DMA results.

Samples	Swelling in H ₂ O		Swelling in MeOH		DMA	
	SW (%)	Sol fraction (%)	SW (%)	Sol fraction (%)	T_α (° C)	ν_e (mol L ⁻¹)
2-SH-Mal-SL_1.3 ^a	-	-	-	-	-	-
3-SH-Mal-SL_1.3 ^a	-	-	-	-	-	-
4-SH-Mal-SL_1.3	68.1 ± 0.7	11.8 ± 0.2	23.0 ± 0.1	16.6 ± 0.6	19.9 ± 0.3	1.95
2- ϕ -SH-Mal-SL_1.3	34.3 ± 2.3	8.3 ± 0.9	21.9 ± 0.4	8.2 ± 0.3	46.0 ± 8.8	0.85
2-SH-Mal-SL_1.1	73.6 ± 3.0	5.2 ± 0.1	31.5 ± 1.5	26.5 ± 0.8	20.2 ± 1.4	0.37
3-SH-Mal-SL_1.1	62.2 ± 1.0	7.8 ± 0.3	22.8 ± 0.5	17.7 ± 0.4	19.2 ± 1.6	1.18
4-SH-Mal-SL_1.1	37.6 ± 3.0	5.9 ± 0.4	21.8 ± 0.7	10.6 ± 0.7	31.1 ± 0.6	1.54
2- ϕ -SH-Mal-SL_1.1	15.2 ± 0.5	3.2 ± 0.1	24.7 ± 0.4	2.4 ± 1.9	44.0 ± 3.3	0.51
2-SH-Mal-SL_0.7 ^a	-	-	-	-	-	-
3-SH-Mal-SL_0.7	40.4 ± 1.3	3.3 ± 0.3	33.6 ± 1.9	11.7 ± 2.3	58.8 ± 0.1	0.52
4-SH-Mal-SL_0.7	66.3 ± 3.1	16.0 ± 0.7	28.2 ± 0.2	23.6 ± 0.6	44.6 ± 11.1	0.81
2- ϕ -SH-Mal-SL_0.7 ^b	39.0 ± 1.2	5.1 ± 1.1	25.5 ± 0.4	3.9 ± 0.2	-	-

^a Could not be processed in 2 mm film. ^b Successfully processed in 2 mm film, but not analyzable by DMA due to high brittleness.

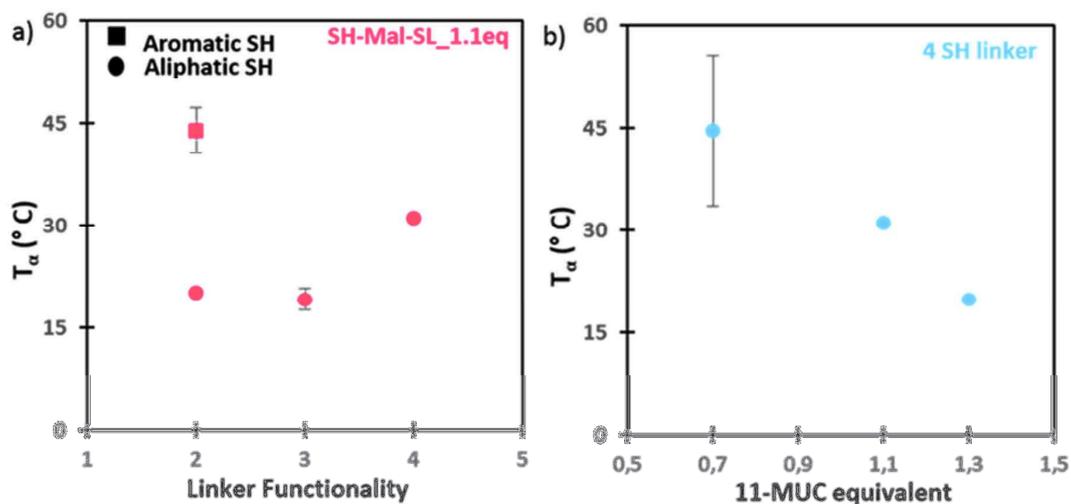


Figure 2.5. (a) T_α of the materials prepared with Mal-SL_1.1 depending on the linker functionality. (b) T_α of the materials prepared with 4-SH linker depending on the amount of 11-MUC employed for the synthesis of Mal-SL.

3.3 Thermal and mechanical properties of the thiol-maleimide lignin-based materials

The thermal stability of the prepared polymeric materials was evaluated with TGA, and all results are gathered Table S1 in SI. The materials obtained from Mal-SL_1.1 have a significantly higher thermal stability, with 2-SH-Mal-SL_1.1 and 2- ϕ -SH-Mal-SL_1.1 the most thermally stable ($T_{95\%}$ of 250 °C). The materials prepared from Mal-SL_0.7 and Mal-SL_1.3 exhibit a lower thermal stability, with a $T_{95\%}$ included in a range of temperature between 185 and 227 °C.

Glass transition temperatures T_g were measured by DSC and the results are summarized in Table S2.1 in Annexe I. The trend is the same as the T_α determined by DMA. Three distinct effects must be taken into account: the influence of the linker's functionality, the amount of MUM byproduct entrapped into the polymer network, and the linker's chemical backbone (aromatic or aliphatic). The T_g increases linearly with the aliphatic linker functionality, with the only exception of 4-SH-Mal-SL_0.7, which exhibits an unexpectedly low T_g , probably because of some network defects.

(Figure 2.6a). The phenomenon can easily be explained by the higher cross-linking density provided by multi-multifunctional linkers, which contribute to shift the T_g towards higher values. The T_g decreases with the amount of 11-MUC used to derivatize the lignins, because the excess of 11-MUC leads to the presence of small MUM molecules entrapped into the polymer networks, which act as plasticizer (Figure 2.6b). Finally, using an aromatic linker instead of an aliphatic one increases the T_g by almost 30 °C, because of the rigidity of the aromatic chain. This leads to the materials having the highest T_g of the whole materials set.

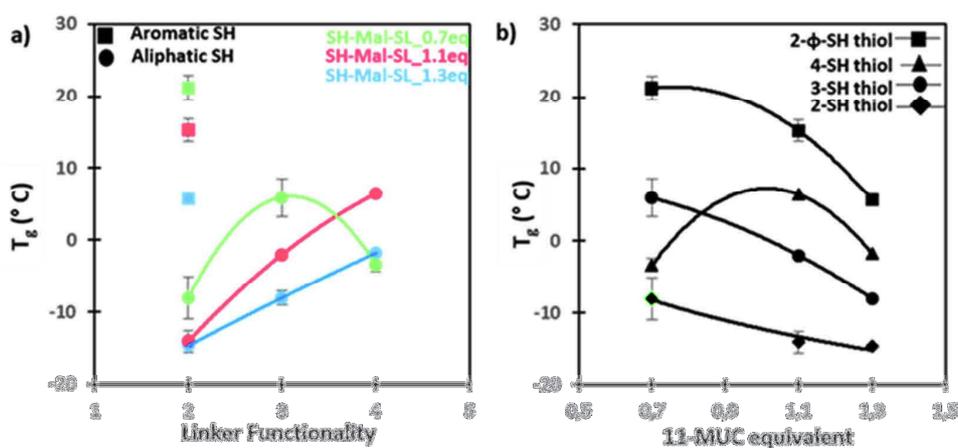


Figure 2.6. T_g of the thiol-maleimide lignin-based materials depending on the linker functionality (a) or the amount of 11-MUC employed for the synthesis of Mal-SL (b).

Tensile properties of the materials were then measured at room temperature. The results are presented on Figure 2.7, and summarized in Table S2.2 in Annexe I. The mechanical properties are directly related to the crosslink density of the materials: increasing the linker functionality results in materials of higher Young's modulus and tensile strength, while reducing the elongation at break (Figure 2.7a to c). The obtained materials are stretchable (up to 100% elongation for 2-SH-Mal-SL_1.1), with satisfying stiffness and strength. The aromatic thiol linker provides additional stiffness and strength (E around 20 MPa and σ around 3.5 MPa), because of the rigidity of the aromatic chain, while maintaining good elongation properties (up to 77%). The stiffest material was 3-SH-Mal-SI_0.7 (E = 67.0 MPa, σ = 5.7 MPa).

The functionalization of the lignin with an excess of 11-MUC was shown to be detrimental for all uniaxial tensile properties (Figures 2.7d to f). It arises from the presence of MUM small molecules inside the networks, which act as plasticizer but also introduce defects in the network, resulting in reduced mechanical properties

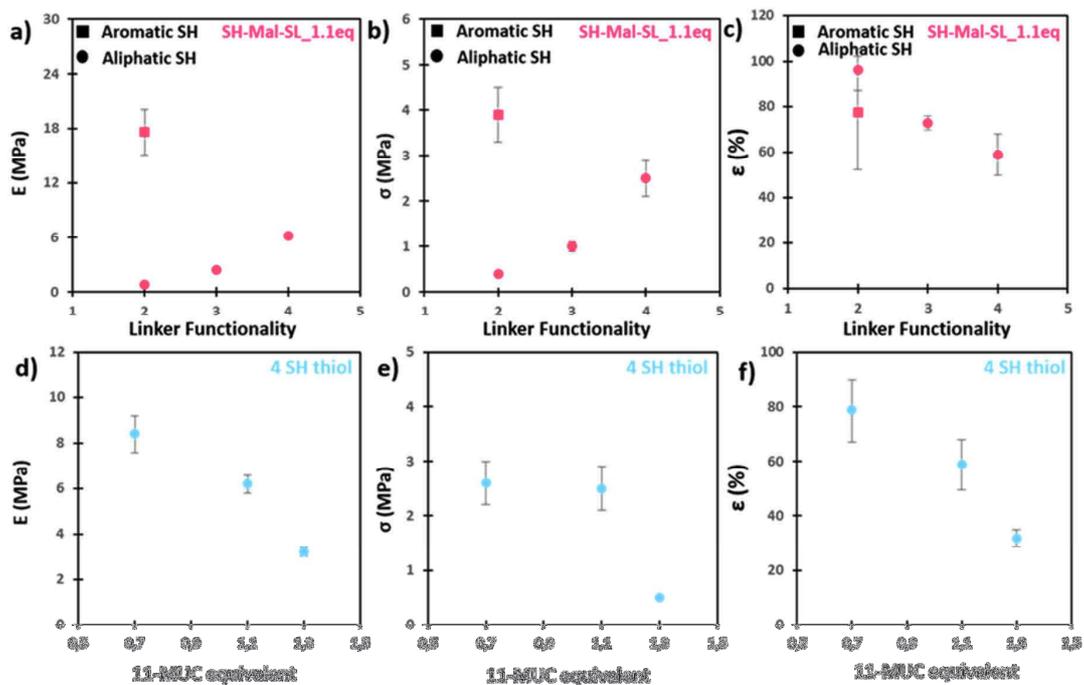


Figure 2.7. Mechanical properties of the materials prepared with Mal-SL_1.1: Young's Modulus E (a), tensile strength σ (b) and elongation at break ϵ (c). Mechanical properties of the materials based on 4-SH linker: Young's Modulus E (d), tensile strength σ (e) and elongation at break ϵ (f).

4. Conclusion

Fully biobased maleimide-lignin derivatives with controlled content of maleimide groups were obtained by the coupling of soda lignin (SL) and 11-maleimidoundecylenic acid (11-MUA) under solvent- and catalyst-free conditions. The resulting maleimide-containing lignin derivatives were then successfully polymerized through thiol-ene "click" reaction with different polyfunctional thiol linkers. Increasing the thiol linker functionality from 2 to 4 results in materials with a higher crosslink density.

It leads to higher T_{α} and T_g , as well as enhanced stiffness and strength, but reduced elongation at break. Furthermore aromatic thiols impact the material's properties by increasing T_{β} , T_g , stiffness and strength. When used in excess, 11-MUC is transformed into methyl 11-maleimidoundecanoate and was able to react with the thiol linkers forming small molecules that remained entrapped in the polymer network, where they can act as plasticizer, thus reducing the T_{α} , T_g , and mechanical properties.

Overall, new lignin based polymeric materials, having a final lignin content between 30 to 40%, were developed through a green and fast polymerization technique leading to materials with noticeable thermal and mechanical properties. Varying the linker functionality and structure, thermal and mechanical properties could be widely tuned, opening wide perspectives for the future utilization of lignin as a building blocks to produce novel aromatic and biobased materials with tailored properties. A screening of potential applications of these new lignin-based polymers is under way.

Conclusion et perspectives du chapitre 2

Dans ce chapitre nous avons décrit les nouveaux matériaux entièrement biosourcés à base de lignine préparés par maleimide-thiol polymérisation.

Une teneur contrôlée en groupes maléimides a été obtenue par couplage de lignine de soda (SL) et d'acide 11-maléimidoundécylénique (11-MUA) dans des conditions exemptes de solvants et de catalyseurs. Les dérivés résultants de lignine contenant des maléimides ont ensuite été polymérisés avec succès par une réaction clic thiol-ene avec différents lieux thiol polyfonctionnels.

L'augmentation de la fonctionnalité de liaisons thiol de 2 à 4 résulte en matériaux avec une densité de réticulation plus élevée et une T_{α} et T_g supérieurs, ainsi qu'à une rigidité et à une résistance accrues, mais à un allongement réduit. En outre, les thiols aromatiques ont un impact sur les propriétés du matériau en augmentant le T_{α} , le T_g , la rigidité et la résistance. Lorsqu'il est utilisé en excès, le 11-MUC est transformé en 11-maléimidoundécanoate de méthyle et a réussi à réagir avec les liaisons thiol formant de petites molécules qui restent piégées dans le réseau polymère, où elles peuvent agir comme plastifiant, réduisant ainsi le T_{α} , le T_g et propriétés mécaniques.

Dans le prochain chapitre, nous décrirons l'autre réaction clic que le groupe maléimide peut effectuer: la réaction thermoréversible avec les furannes. Ce dernier ouvre la possibilité de concevoir des matériaux auto-réparant, illustrés dans notre article scientifique suivant « Thermally Healable and Remendable Lignin-Based Materials Through Diels – Alder Click Polymerisation ».

Références du chapitre 2

- (1) Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Davison, B. H.; Dixon, R. A.; Gilna, P.; Keller, M.; et al. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* **2014**, *344* (6185), 1246843.
- (2) Ralph, J.; Lundquist, K.; Brunow, G.; Lu, F.; Kim, H.; Schatz, P. F.; Marita, J. M.; Hatfield, R. D.; Ralph, S. A.; Christensen, J. H.; et al. Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl- propanoids. *Phytochem. Rev.* **2004**, *3* (1–2), 29–60.
- (3) Gellerstedt, G.; Henriksson, G. Lignins: Major Sources, Structure and Properties. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Amsterdam, 2008; pp 201–224.
- (4) Constant, S.; Wienk, H. L. J.; Frissen, A. E.; Peinder, P. de; Boelens, R.; Es, D. S. van; Grisel, R. J. H.; Weckhuysen, B. M.; Huijgen, W. J. J.; Gosselink, R. J. A.; et al. New insights into the structure and composition of technical lignins: a comparative characterisation study. *Green Chem.* **2016**, *18* (9), 2651-2665.
- (5) Lora, J. Industrial Commercial Lignins: Sources, Properties and Applications. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Amsterdam, 2008; pp 225–241.
- (6) Laurichesse, S.; Avérous, L. Synthesis, thermal properties, rheological and mechanical behaviors of lignins-grafted-poly(ϵ -caprolactone). *Polymer* **2013**, *54* (15), 3882–3890.
- (7) Laurichesse, S.; Huillet, C.; Avérous, L. Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethane synthesis. *Green Chem.* **2014**, *16* (8), 3958–3970.
- (8) Duval, A.; Lawoko, M. A review on lignin-based polymeric, micro- and nano-structured materials. *React. Funct. Polym.* **2014**, *85*, 78–96.
- (9) Chung, H.; Washburn, N. R. Chemistry of lignin-based materials. *Green Mater.* **2013**, *1* (3), 137–160.

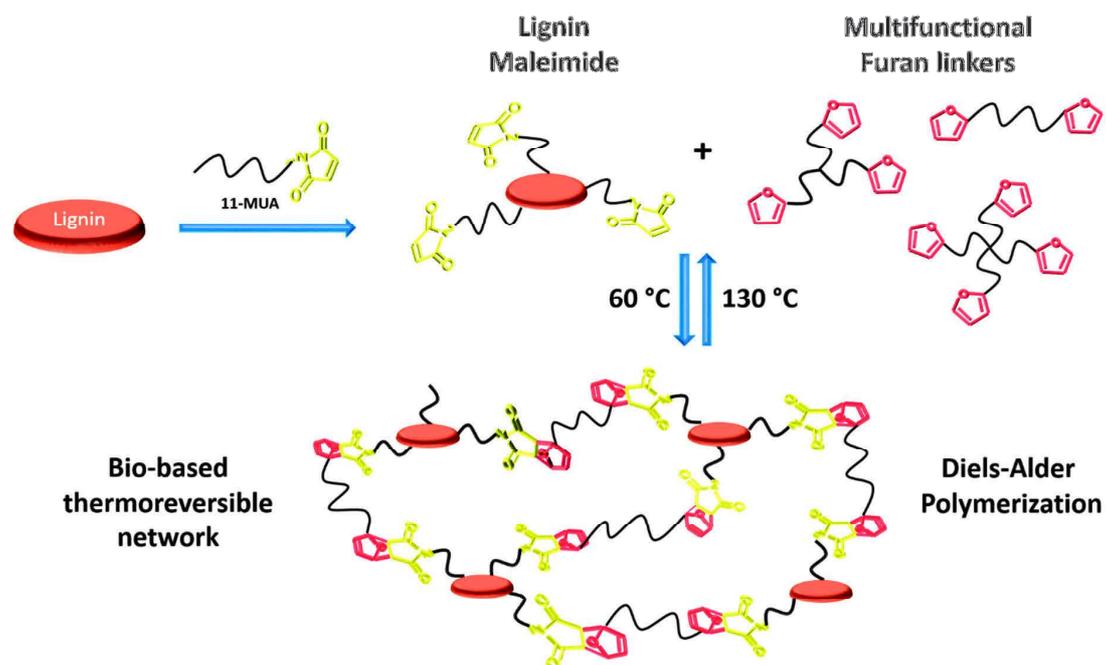
- (10) Hilburg, S. L.; Elder, A. N.; Chung, H.; Ferebee, R. L.; Bockstaller, M. R.; Washburn, N. R. A universal route towards thermoplastic lignin composites with improved mechanical properties. *Polymer* **2014**, *55* (4), 995–1003.
- (11) Holmberg, A. L.; Nguyen, N. A.; Karavolias, M. G.; Reno, K. H.; Wool, R. P.; Epps, T. H. Softwood Lignin-Based Methacrylate Polymers with Tunable Thermal and Viscoelastic Properties. *Macromolecules* **2016**, *49* (4), 1286–1295.
- (12) Dehne, L.; Vila Babarro, C.; Saake, B.; Schwarz, K. U. Influence of lignin source and esterification on properties of lignin-polyethylene blends. *Ind. Crops Prod.* **2016**, *86*, 320–328.
- (13) Domenek, S.; Louaifi, A.; Guinault, A.; Baumberger, S. Potential of Lignins as Antioxidant Additive in Active Biodegradable Packaging Materials. *J. Polym. Environ.* **2013**, *21* (3), 692–701.
- (14) Hambardzumyan, A.; Foulon, L.; Chabbert, B.; Aguié-Béghin, V. Natural Organic UV-Absorbent Coatings Based on Cellulose and Lignin: Designed Effects on Spectroscopic Properties. *Biomacromolecules* **2012**, *13* (12), 4081–4088.
- (15) Yu, J.; Wang, J.; Wang, C.; Liu, Y.; Xu, Y.; Tang, C.; Chu, F. UV-Absorbent Lignin-Based Multi-Arm Star Thermoplastic Elastomers. *Macromol. Rapid Commun.* **2015**, *36* (4), 398–404.
- (16) Park, S.; Kim, S. H.; Won, K.; Choi, J. W.; Kim, Y. H.; Kim, H. J.; Yang, Y.-H.; Lee, S. H. Wood mimetic hydrogel beads for enzyme immobilization. *Carbohydr. Polym.* **2015**, *115*, 223–229.
- (17) Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* **2014**, *39* (7), 1266–1290.
- (18) Glasser, W. G.; Barnett, C. A.; Rials, T. G.; Saraf, V. P. Engineering plastics from lignin .2. Characterization of hydroxyalkyl lignin derivatives. *J. Appl. Polym. Sci.* **1984**, *29* (5), 1815–1830.
- (19) Kelley, S. S.; Glasser, W. G.; Ward, T. C. Engineering plastics from lignin .14. Characterization of chain-extended hydroxypropyl lignins. *J. Wood Chem. Technol.* **1988**, *8* (3), 341–359.

- (20) De Oliveira, W.; Glasser, W. G. Engineering plastics from lignin .16. Starlike macromers with propylene-oxide. *J. Appl. Polym. Sci.* **1989**, *37* (11), 3119–3135.
- (21) Over, L. C.; Meier, M. A. R. Sustainable allylation of organosolv lignin with diallyl carbonate and detailed structural characterization of modified lignin. *Green Chem.* **2015**, *18* (1), 197–207.
- (22) Sen, S.; Sadeghifar, H.; Argyropoulost, D. S. Kraft Lignin Chain Extension Chemistry via Propargylation, Oxidative Coupling, and Claisen Rearrangement. *Biomacromolecules* **2013**, *14* (10), 3399–3408.
- (23) Duval, A.; Lange, H.; Lawoko, M.; Crestini, C. Modification of Kraft Lignin to Expose Diazobenzene Groups: Toward pH- and Light-Responsive Biobased Polymers. *Biomacromolecules* **2015**, *16* (9), 2979–2989.
- (24) Podschun, J.; Stücker, A.; Saake, B.; Lehnen, R. Structure–Function Relationships in the Phenolation of Lignins from Different Sources. *ACS Sustain. Chem. Eng.* **2015**, *3* (10), 2526–2532.
- (25) Hofmann, K.; Glasser, W. G. Engineering plastics from lignin .21. Synthesis and properties of epoxidized lignin-poly(propylene oxide) copolymers. *J. Wood Chem. Technol.* **1993**, *13* (1), 73–95.
- (26) Salanti, A.; Zoia, L.; Orlandi, M. Chemical modifications of lignin for the preparation of macromers containing cyclic carbonates. *Green Chem.* **2016**, *18* (14), 4063–4072.
- (27) Buono, P.; Duval, A.; Verge, P.; Averous, L.; Habibi, Y. New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation. *ACS Sustain. Chem. Eng.* **2016**, *4* (10), 5212–5222.
- (28) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem. Int. Ed.* **2001**, *40* (11), 2004–2021.
- (29) Moses, J. E.; Moorhouse, A. D. The growing applications of click chemistry. *Chem. Soc. Rev.* **2007**, *36* (8), 1249–1262.

- (30) Kempe, K.; Krieg, A.; Becer, C. R.; Schubert, U. S. "Clicking" on/with polymers: a rapidly expanding field for the straightforward preparation of novel macromolecular architectures. *Chem. Soc. Rev.* **2011**, *41* (1), 176–191.
- (31) Qin, A.; Lam, J. W. Y.; Tang, B. Z. Click polymerization. *Chem. Soc. Rev.* **2010**, *39* (7), 2522–2544.
- (32) Roberts, M. J.; Bentley, M. D.; Harris, J. M. Chemistry for peptide and protein PEGylation. *Adv. Drug Deliv. Rev.* **2002**, *54* (4), 459–476.
- (33) Pounder, R. J.; Stanford, M. J.; Brooks, P.; Richards, S. P.; Dove, A. P. Metal free thiol–maleimide "Click" reaction as a mild functionalisation strategy for degradable polymers. *Chem. Commun.* **2008**, *41*, 5158–5160.
- (34) Lowe, A. B. Thiol-ene "click" reactions and recent applications in polymer and materials synthesis. *Polym. Chem.* **2010**, *1* (1), 17–36.
- (35) Nair, D. P.; Podgórski, M.; Chatani, S.; Gong, T.; Xi, W.; Fenoli, C. R.; Bowman, C. N. The Thiol–Michael Addition Click Reaction: A Powerful and Widely Used Tool in Materials Chemistry. *Chem. Mater.* **2014**, *26* (1), 724–744.
- (36) Duval, A.; Lange, H.; Lawoko, M.; Crestini, C. Reversible crosslinking of lignin via the furan–maleimide Diels–Alder reaction. *Green Chem.* **2015**, *17* (11), 4991–5000.
- (37) Han, Y.; Yuan, L.; Li, G.; Huang, L.; Qin, T.; Chu, F.; Tang, C. Renewable polymers from lignin via copper-free thermal click chemistry. *Polymer* **2016**, *83*, 92–100.
- (38) Abächerli, A.; Doppenberg, F. Method for preparing alkaline solutions containing aromatic polymers. US6239198 B1, May 29, 2001.
- (39) Thiebaud, S.; Borredon, M. E.; Baziard, G.; Senocq, F. Properties of wood esterified by fatty-acid chlorides. *Bioresour. Technol.* **1997**, *59* (2), 103–107.
- (40) Vaca-Garcia, C.; Borredon, M. E. Solvent-free fatty acylation of cellulose and lignocellulosic wastes. Part 2: reactions with fatty acids¹. *Bioresour. Technol.* **1999**, *70* (2), 135–142.

- (41) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* **1995**, *43* (6), 1538–1544.
- (42) Crawford, R. J. *Plastics Engineering*; Butterworth-Heinemann, 1998.
- (43) McCrum, N. G.; Buckley, C. P.; Bucknall, C. B. *Principles of Polymer Engineering*; Oxford University Press, 1997.
- (44) Koivu, K. A. Y.; Sadeghifar, H.; Nousiainen, P.; Argyropoulos, D. S.; Sipila, J. The Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin. *ACS Sustain. Chem. Eng.* **2016**, *4* (10), 5238–5247.

Chapitre 3 : Matériaux thermoréversibles et auto-réparants à base de lignines obtenues par polymérisation à base de réactions Diels-Alder



Introduction du chapitre 3

La versatilité des groupes maleimide permet d'effectuer une autre réaction clic : une réaction thermoréversible à base de furannes. Les réactions de Diles-Alder (DA) entre les furannes et les maleimides ont été démontrées comme étant un outil très utile pour l'élaboration de réseaux de polymères recyclables et de matériaux auto-réparants. La formation directe du produit de réaction DA a lieu à 50-70 ° C, et son désassemblage à 110 -150 ° C (réaction rétro DA). Ceci permet la dépolymérisation/repolymérisation à la demande. Cela ouvre une voie chimique vers l'élaboration de matériaux thermoréversibles et auto-réparants.

Sur la base de l'expérience acquise avec le travail de recherche sur les matériaux thiol-ene (présenté dans le précédent chapitre), nous avons élaboré des polymères à base de lignine à travers de la polymérisation furane-maleimide.

Des liens à base de furane ont été préparés à partir des thiols polyfonctionnels issus des travaux présentés précédemment et ensuite polymérisés avec le dérivé de lignine contenant des fonctions maléimides, fournissant ainsi le premier exemple connu de matériaux à base de lignine thermo réversibles et auto-réparant.

Thermally Healable and Remendable Lignin-Based Materials through Diels – Alder Click Polymerization

Pietro Buono,^[a] Antoine Duval,^[b] Luc Averous^[b] and Youssef Habibi*^[a]

^a Department of Materials Research and Technology (MRT), Luxembourg Institute of Science and Technology (LIST), 5 avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

^b BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, Strasbourg
Cedex 2 67087, France

*e-mail: youssef.habibi@list.lu

Abstract

We report in this work the preparation and in depth characterization of thermo-reversible healable materials based on lignin, a major naturally occurring aromatic biopolymer. Following an environmentally friendly chemical pathway, a derivative of soda lignin (SL) bearing maleimide groups and poly-functional furan linkers were clicked through the furan – maleimide Diels – Alder (D-A) polymerization in a solvent free media and without the use of catalyst. The furan linkers were obtained by the thiol – epoxy reaction between furfuryl glycidyl ether and thiols of functionalities from 2 to 4. The different degree of substitution of maleimide lignin derivatives and linker functionalities allowed the tuning of the thermo-mechanical properties of the resultant materials. The latter exhibit on demand thermally induced disassembly and reassembly of the polymeric networks when heated at 110 – 130 °C and then cured at 60 °C, providing controlled self-healing properties and an efficient reprocessing with a limited impact on the thermo-mechanical properties and the thermal stability of the final materials. This study provides interesting perspectives for the production of renewable lignin-based aromatic polymers, demonstrating that an effective chemical

modification together with tailored molecular architectures could pave the way for the development of high value added materials from this underused aromatic feedstock.

1. Introduction

Since the mid-sixties, the plastics production increased exponentially, to reach 322 million tons in 2015. Even with the global economic crisis, in the next years the production is expected to more than double by 2050.¹ Plastics are increasingly used across the economy, serving as a key material for an increasing number of industrial sectors, to replace more and more some conventional materials and finding new usages. However, the increased limitation of the availability of some specific fossil fractions, such as the BTX (Benzene-Toluene-Xylene) hydrocarbons, could affect in a close future the production of e.g., aromatic polymers, which possess irreplaceable advantages. The rigid backbone provided by aromatic rings included in the polymeric chains gives unique properties in terms of impact resistance, heat resistance, fire resistance, low shrinkage and chemical resistance.²⁻⁴ Then, researchers are urged to find long-lasting and sustainable alternatives for these aromatic resources.

Lignin is the most abundant biopolymer that could be used to replace aromatic fossil-based resources.⁵⁻⁹ Among the 50 Mt lignin generated from biomass processing per year, only about 100 Kt is commercially available, while the majority is still burnt in pulping plants for energy production.^{10,11} Despite significant achievements, the wide diversity and the structural complexity of lignin still constitutes major drawback for its use in high value applications. Chemical modification have been acknowledged to be an important tool to circumvent these limitations, mainly by improving the chemical reactivity, reducing the brittleness of polymers, increasing the solubility in organic solvents and facilitating the ease of processing of lignin.¹²

“Click” reactions are characterized by quick and quantitative yields under mild conditions.^{13,14} In addition they produce inoffensive by-products easily removable by non-chromatographic methods.

Recently, these reactions were employed to produce lignin-based polymers by Huisgen 1,3-dipolar cycloaddition between azide and alkyne groups¹⁵ and by thiol – maleimide Michael addition.¹⁶ Duval et al. developed through furan – maleimide Diels-Alder (D-A) [4 + 2] cycloaddition thermally reversible lignin¹⁷ and tannin¹⁸ based polymers. D-A reactions have been shown to be a very useful tool for the design of recyclable polymer networks and self-healing materials.¹⁹⁻²³ The straightforward formation of the D-A adduct, occurring at 50-70 °C, and its disassembly upon heating at 110-150 °C (retro D-A reaction) allows the on-demand depolymerisation – repolymerisation, which opens the path toward the preparation of thermo-reversible and self-healing materials. It has been demonstrated that the use of small molecules bearing multiple reactive sites as linker provides thermally-reversible polymer networks having enough mobility to heal the cracks of the sample through network reconnection.²⁴⁻²⁶ Lignin has yet been poorly explored towards the production of remendable materials. Liu et al. were able to develop this class of polymers based on lignin macromonomers as scaffold (10 to 20 wt % of lignin) through RAFT polymerization involving poly 5-acetylaminopentyl acrylate as synthetic linkers.²⁷

In the present work, we investigated the thermally reversible furan – maleimide D-A [4 + 2] cycloaddition to produce the first example of lignin-based reprocessible and self-healing materials having a lignin content of about 30 %wt. Following our previous work on thiol-ene,¹⁶ we designed through thiol-epoxy reactions various poly-functional furan linkers of functionalities ranging from 2 to 4. Subsequently, we polymerized them with a modified soda lignin (SL) carrying maleimide groups. The polymerization was performed following the principles of green chemistry, in bulk, without solvent nor catalyst. The resultant polymers were processed in films and were analyzed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA) and mechanical tests. To test the stability of these materials, they were re-processed and the thermo-mechanical properties reanalyzed. Self-healing properties were further demonstrated on the microscopic (crack healing), macroscopic levels and through tensile test of healed materials.

2. Experimental Section

2.1 Reagents and Materials

Soda lignin (SL, Protobind 1000) was obtained from Green Value SA (Switzerland). It is a technical and sulfur-free lignin obtained after extraction and fractionation from a mixture of wheat straw (*Triticum sp.*) and Sarkanda grass (*Saccharum officinarum*), according to a patented process.²⁸ SL contains 1.9 mmol g⁻¹ of aliphatic hydroxyl groups and 3.3 mmol g⁻¹ of phenolic hydroxyl groups as calculated by ³¹P NMR and an average molecular weight (M_n) of 1120, with a polydispersity index of 3.9.²⁹ The lignin was used as received without further purification. 11-maleimidoundecanoic acid (11-MUA) (95%), 4,4'-thiobisbenzenethiol (98%), trimethylolpropane tris(3-mercaptopropionate) (>95%), pentaerythritol tetrakis(3-mercaptopropionate) (>95%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), chromium(III) acetylacetonate (99.99%), cholesterol (>99%), tetrabutylammonium fluoride solution 1.0 M in THF, chloroform-*d* (100%, 99.96 atom% D) and dimethyl sulfoxide-*d*₆ (100%, 99.96 atom% D) were purchased from Sigma-Aldrich; oxalyl chloride (>98%), 3,6-dioxa-1,8-octanedithiol from TCI Europe; tetrahydrofuran (THF) (99.6%, ACS reagent, stabilized with BHT), pyridine (99.5%, extra dry over molecular sieve), dichloromethane (DCM) (>99%, extra pure, stabilized with ethanol) and furfuryl glycidyl ether, (97%) from Acros Organics.

2.2 Syntheses and materials processing

Chlorination of 11-MUA and Maleimido functionalization of soda lignin (SL)

11-maleimidoundecanoic acid was first converted into the corresponding 11-maleimidoundecanoyl chloride (11-MUC) as previously reported.¹⁶ Then SL was esterified with 11-MUC without solvent and catalyst at 90° C for 48 h. At the end of the reaction, a dark viscous product was obtained. Methanol (100 mL) was added to quench the unreacted 11-MUC, and the mixture was left stirring for an additional 30 min. The solvent was then evaporated under vacuum and the resultant maleimido-soda lignin (Mal-SL) products finally dried under high vacuum for 24 h. A master batch of about 40 g of Mal-SL was prepared by using 1.0 equivalent of 11-MUC compared to the amount of total lignin hydroxyl groups.

Syntheses of poly-functional furan linkers

A 100 mL round bottomed flask equipped with a stirring bar was charged with 27 mmol of the corresponding thiol (3,6-dioxa-1,8-octanedithiol, 4,4'-thiobisbenzenethiol, trimethylolpropane tris(3-mercaptopropionate) or pentaerythritol tetrakis(3-mercaptopropionate)) and FGE at a SH:epoxy ratio of 1:1. The flask was placed in an ice bath until the mixture reached the temperature of 0-5° C, then a TBAF 1.0 M THF solution was added at a molar ratio TBAF:SH 0.2:1, according to the protocol of Gadwal et al.³⁰ A very exothermic and instant reaction was observed. The reaction mixtures were left to stir for 1 hour. THF was then evaporated under vacuum, the crude mixture was diluted with DCM and washed twice with deionized water and once with brine to remove the TBAF. The organic phase was finally dried over MgSO₄ and concentrated under vacuum to yield the corresponding poly-functional furan linker (90 to 95% yield).

Model reaction between Mal-SL and FGE

100 mg Mal-SL was dissolved into 2 mL of DMSO-*d*₆. FGE was then added to obtain a furan/maleimide ratio of 1:1 (mol/mol). The reaction mixture was placed in an oil bath regulated at 60 °C, and aliquots of 200 µL were taken at regular intervals. They were diluted up to 650 µL with DMSO-*d*₆ and analyzed by ¹H NMR to determine the conversion and *endo/exo* ratio.

D-A polymerization of Mal-SL

A 100 mL round bottomed flask was charged with 8 g of Mal-SL (16 mmol maleimide groups) and the corresponding furan linker (16 mmol furan content). 15 mL of DCM were then added in order to dissolve and homogenize the monomers. Successively, DCM was evaporated and collected for further reuse and the polymerization performed in bulk in an oven at 60° C for 48 h. The progress of the reaction was monitored by FTIR.

Materials processing

The materials prepared by D-A polymerization were compression molded for 30 min at 130 °C on a Carver manual press (Wabash, IN, USA) equipped with heating plates. Polymers were placed in a tile mold Carver (Wabash, IN, USA) enabling to produce plates of 5 cm x 5 cm x 0.2 cm. For the first 5 min, the polymers were left to soften applying a load of 1 metric ton-force. After several degassing steps, the materials were pressed with a constant applied load of 7 metric tons for the remaining 25 min. The plates were then cooled down to room temperature under pressure during 5 min, by a water circulation within the plates.

The square materials were then cured in the oven for 48 h at 60 °C and post cured for additional 24 hours at room temperature, prior to be analyzed. To test the reprocessing ability of the materials, they were cut in small pieces and reprocessed according to the same procedure, before to be analyzed.

Study of the self-healing behavior

The surface of the materials was scratched with a surgical blade, and the materials placed in an oven at 60 °C. Optical pictures were recorded with a stereomicroscope Leica MZ 125 (Heerbrugg, Switzerland) in order to evaluate the evolution of the crack. The pictures were taken after 1, 2 and 24 h at 60° C; after additional 20 min at 110° C and finally after additional 30 min at 130° C.

The macroscopic self-healing ability of 2 D-A was then evaluated by cutting a Dumbbell-shaped (5 cm length and 2.2 mm width) specimen used for the tensile test in 2 pieces, placing them in contact, and heating them up for 20 min at 120° C. Finally, the film was cured overnight at 60° C and post cured for additional 24 hours under the tensile test experimental conditions (room temperature and 50% relative humidity). All the samples were heated up in an oven.

2.3 Characterization Techniques

NMR spectroscopies

All NMR spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer. ³¹P NMR analysis was performed on lignin samples phosphorylated with 2-Chloro-4,4,5,5-tetramethyl-1,3,2

dioxaphospholane, using cholesterol as internal standard, according to standard protocols.³¹ 128 scans were recorded with a 15 s delay and a spectral width of 80 ppm (180-100 ppm).

For quantitative ¹H-NMR analysis, about 20 mg of lignin were dissolved in 0.5 mL of DMSO-*d*₆ before the addition of 100 μL of a standard solution of pentafluorobenzaldehyde (PFB) in DMSO-*d*₆. 32 scans were collected.

Fourier transform infrared spectroscopy (FTIR)

The FTIR analyses were conducted on a Bruker Tensor 27 (Ettlingen, Germany) in attenuated total reflection (ATR) mode. 40 scans were collected between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹.

High resolution mass spectroscopy (HRMS)

Mass characterization was also performed by high-resolution mass spectrometry (HRMS), using a LTQ/Orbitrap Elite (Thermo Scientific) equipped with an atmospheric pressure matrix-assisted laser desorption/ionization source (AP-MALDI PDF+, Masstech). This analytical setup allows for the investigation of MALDI-produced ions using accurate mass measurement (sub-ppm relative error) and structural confirmation by multistage mass spectrometry (MSn).

Size Exclusion Chromatography (SEC)

SEC analyses were performed on a Shimadzu chromatograph equipped with a 5μ PL-gel pre-column, two PL-gel 5μ MIXED-C and a 5μ 100 Å 300 mm columns. Detection was performed with refractive index (RI, Shimadzu RID-10A) and ultra-violet (UV, Shimadzu SPD-M10A diode array) detectors. Chloroform (CHCl₃) was used as the eluent at a flow rate of 0.8 mL min⁻¹. Neat SL was characterized after acetylation,²⁹ to ensure its full dissolution in the eluent, whereas the Mal-SL were analyzed as such. All determinations of molar mass were performed relative to linear polystyrene standards from 580 to 1 650 000 g mol⁻¹.

Thermal Gravimetric Analysis (TGA)

TGA were performed on a STA 409PC Luxx apparatus from NETZSCH at a heating rate of 10 °C min⁻¹ up to 800 °C under an argon atmosphere (flow rate = 90 mL min⁻¹). About 30 mg sample were analyzed twice.

Differential Scanning Calorimetry (DSC)

DSC thermograms were recorded on a TA DSC Q200 calorimeter (TA Instruments). Different heating runs were performed depending on the information to be acquired. For the qualitative studies on the D-A polymerization, the monomers mixtures were heated up from -30 °C to 130 °C. The retro D-A was investigated by heating the materials for 40 minutes under isothermal run at 110 and 130 °C. The glass transition temperature (T_g) of the materials were recorded by cooling down the materials to -60 °C, followed by a heating run up to 130 °C (3 measurements for each material).

Uniaxial Tensile Tests

Dumbbell-shaped samples (5 cm length and 2.2 mm width) were cut from the compression molded plates, and analyzed on a universal testing machine Instron 5967 (Norwood, MA, USA) equipped with a 100 N load cell operating at 5 mm min⁻¹ crosshead speed. The specimens, after the thermal curing at 60 °C for two days, were successively preconditioned for 24h additional hours under the environmental conditions of measurement. 3 to 4 measurements were performed for each lignin-based material at room temperature and 50% relative humidity.

Dynamic Mechanical Analysis (DMA)

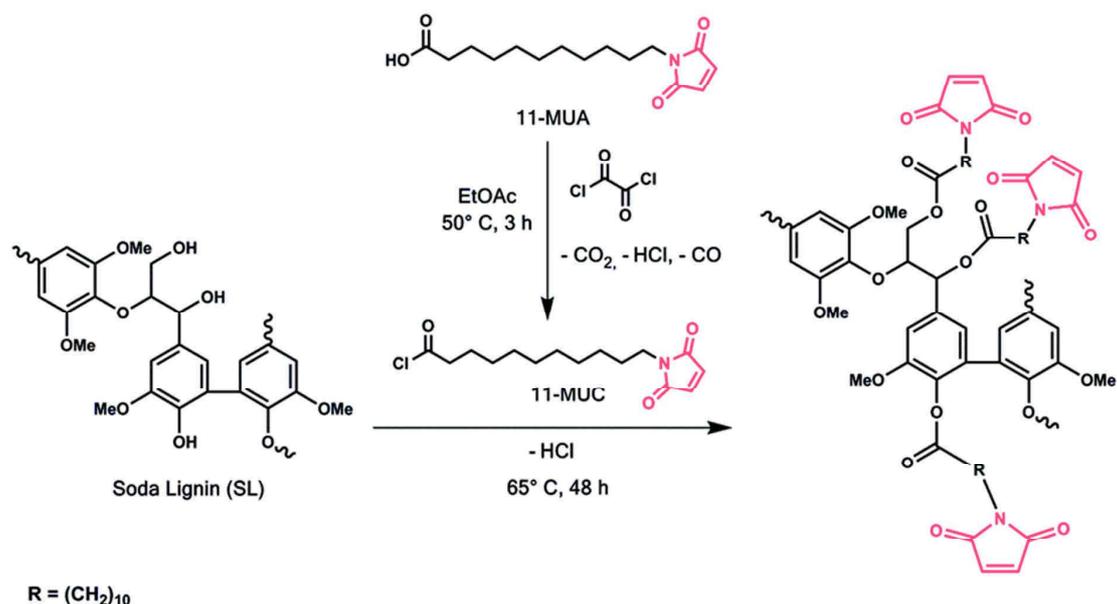
DMA was measured on a Netzsch DMA 42 C equipment (Selb, Germany). 3 Samples were cut from the compression molded plates and analyzed. DMA was conducted in tensile mode from -50 °C to 110 °C at a 2 °C min⁻¹ heating rate and a frequency of 1 Hz with free lengths of 7 mm. Storage modulus E' , loss modulus E'' , and loss factor $\tan \delta = E''/E'$ were continuously recorded, as a function of the temperature. The crosslink density was calculated according to Equation (3.1) from the storage modulus measured at the material's rubbery plateau E'_{rub} (R is the gas constant), according to the theory of elasticity.^{32,33}

$$v_e \text{ (mol L}^{-1}\text{)} = \frac{E'_{rub}}{RT} \quad (3.1)$$

3. Results and Discussion

3.1 Synthesis of maleimide-functionalized SL (Mal-SL) and furan linkers

The OH groups in SL were esterified with 11-MUA to obtain a lignin exposing pendant maleimide groups, similarly as previously reported.¹⁶ 11-MUA was first converted into 11-MUC, and the esterification was then performed in bulk and without any catalyst (Scheme 3.1). 1.0 equivalent of 11-MUC was used to obtain the maleimide-containing SL derivative, denoted Mal-SL.

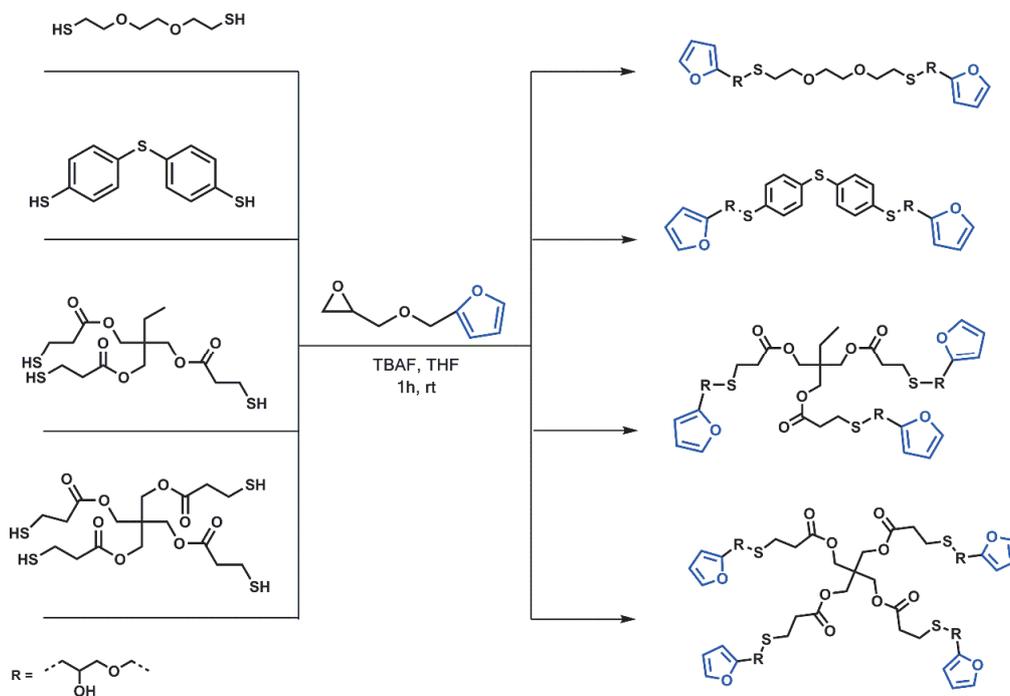


Scheme 3.1. Esterification of soda lignin (SL) with 11-MUA to yield maleimido-modified soda lignin (Mal-SL).

Mal-SL was fully characterized by FTIR, ³¹P and ¹H NMR spectroscopy, as well as SEC. The corresponding data, which clearly confirm the successful grafting, are available in Annexe II (Figure S3.1). The maleimide content of Mal-SL was calculated as 1.99 mmol g⁻¹, as the average of the quantitative ³¹P and ¹H NMR, in good accordance with our previous study.¹⁶

Starting from commercially available thiols, chain extended poly-functional furan linkers were designed with different degree of functionality and chemical features. Bi-, tri-, and tetrafunctional aliphatic furans and a bi-functional aromatic furan were obtained through the reaction between the

corresponding thiols and furfuryl glycidyl ether (FGE), as exemplified in Scheme 3.2. They were denoted as 2 S-Fur, 3 S-Fur, 4 S-Fur and 2ϕ S-Fur, respectively.



Scheme 3.2. Synthesis of polyfunctional furan linkers from the corresponding thiols.

The reaction is catalyzed by TBAF. On the first stage, the epoxy ring of FGE is opened by the fluoride anion F^- of TBAF (the detailed reaction scheme is available in Annexe II, Scheme S3.1). The resultant alkoxide then deprotonates the thiol, given the difference of 6-7 pK_a scale between the two species. Finally, the generated thiolate anion, a powerful nucleophile, replaces the fluorine atom by a S_N2 reaction, creating an irreversible thio-ether linkage.^{34,35} The linkers were fully characterized by FTIR, 1H NMR, ^{13}C NMR and HRMS, which confirm the structures reported on Scheme 3.2. All the characterizations are reported in the Annexe II.

3.2 Model reaction between Mal-SL and FGE

Mal-SL was reacted with FGE, the furan monomer used in the synthesis of the furan linker. In this case, the formation of the D-A adduct can easily be followed by 1H NMR, since the gelation of the

mixture doesn't occur. ^1H NMR spectra clearly attest for the formation of the D-A adduct (Figure 3.1a). The assignment of the relevant peaks is based on the ^1H NMR study of the initial compounds and results reported by Froidevaux et al.³⁶

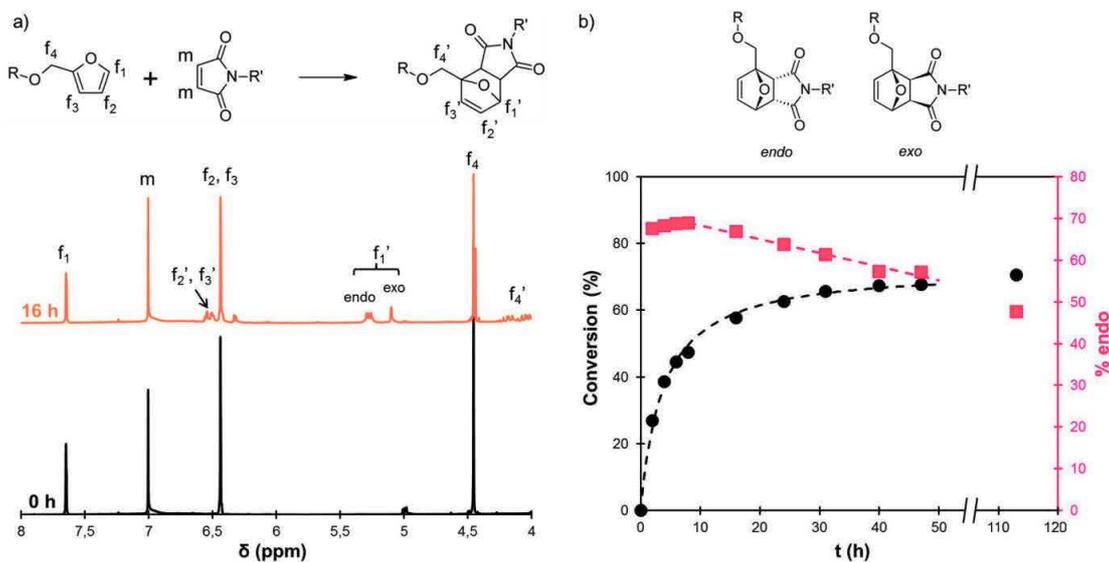


Figure 3.1. (a) ^1H NMR spectra of the mixture of Mal-SL and FGE after 0 and 24 h at 60 °C, (b) evolution of the conversion and percentage of *endo* structures with the reaction time at 60 °C.

To quantify the conversion, the signals from the H atoms f_1 (in the furan) and f_1' (in the D-A adduct) were used, because they are free from overlap with other signals (Figure 3.1a). On the contrary, signals from the DA adduct f_2' and f_3' overlap with the corresponding signals in the furan (f_2 and f_3 , Figure 3.1a). The signals from the maleimide in the DA adduct (m') are in the 3 – 4 ppm region, and overlap with other lignin-related signals.

The conversion was calculated by equation (3.2), where I_{f_1} and $I_{f_1'}$ are the integrals of the signals of H atoms f_1 and f_1' , respectively:

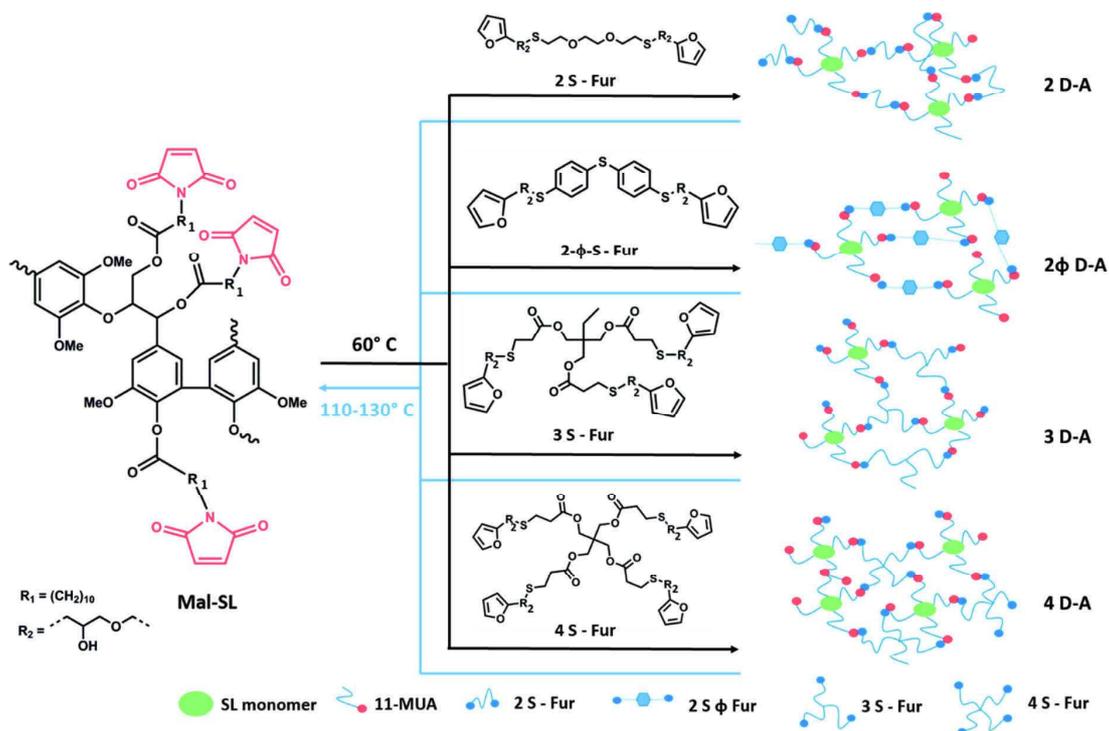
$$X (\%) = 100 \times \frac{I_{f_1'}}{I_{f_1} + I_{f_1'}} \quad (3.2)$$

The evolution of the conversion with the reaction time at 60 °C is reported on Figure 3.1b. The conversion at the equilibrium is 71%, which is close to previously reported values for this kind of reaction.³⁷⁻³⁹ Since the D-A reaction is an equilibrium between the forward and retro reactions, limited conversions are reached. The final conversion can be increased by reducing the reaction temperature, but only to the detriment of a very slow kinetic.³⁷⁻³⁹

The signal of f_1' also allows the quantification of the *endo* and *exo* structures of the D-A adduct, since the chemical shift differs for each diastereomer (Figure 3.1a). Figure 3.1b shows the evolution of the percentage of *endo* structures with the reaction time. The *endo* adduct, which is kinetically favored, is first formed to about 70%. When the reaction time increases, the content in the thermodynamically more stable *exo* adduct increases. The *exo* adduct becomes predominant after more than 4 days of reaction. Since it is well known that the *endo* adduct undergoes retro D-A reactions at lower temperature than the *exo* adduct,³⁶ it is then possible to tailor the thermal reversibility of the corresponding networks.

3.3 D-A polymerization and retro D-A of Mal-SL

Mal-SL was then polymerized in bulk with the poly-functional furan linkers, as depicted on Scheme 3.3.



Scheme 3.3. Thermo-reversible D-A polymerization of Mal-SL with the polyfunctional furan linkers.

DSC was used to monitor the polymerization. The monomer mixture was introduced into the DSC, cooled down to -30 °C and further heated up to 130 °C. The thermograms reported in Figure 3.2 show an exothermic peak starting around 50 – 60 °C indicating the beginning of the D-A polymerization, followed by an endothermic peak at 110 °C corresponding to the retro D-A.

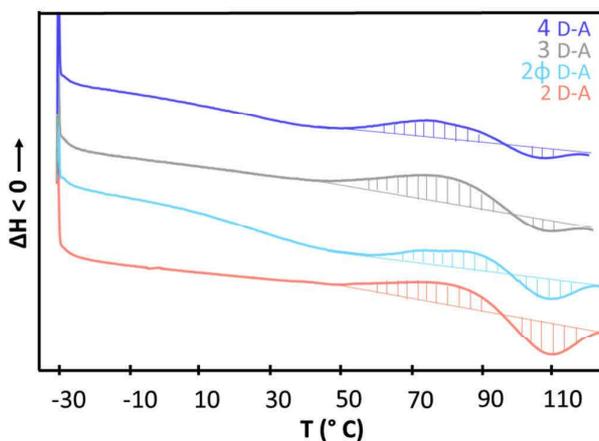


Figure 2. Thermograms of the four monomers mixtures from -30 to 130° C

The D-A polymerization and the retro D-A in bulk were evidenced by FTIR. Figure 3.3 shows the results obtained with the linker 2 S-Fur, whereas similar data measured with the other linkers are available in the Annexe II (Figures S3.20 and S3.21). After 24 h at 60 °C, the C-H bending of the maleimide groups, visible at 827 and 695 cm^{-1} , completely disappeared for the whole set of polymerizations, attesting to the occurrence of the D-A cycloaddition. After 48 hours of reaction, the cross-linked networks formed homogeneous solid materials, which were named as 2 D-A, 3 D-A, 4 D-A and 2 ϕ D-A (Scheme 3). They were recovered from the flasks and then compression molded into films. The obtained materials were heated in the DSC in isothermal mode at 110 and 130° C for 30 minutes, before to be analyzed by FTIR. Figure 3.3 shows that the peaks of the maleimide groups reappear after the thermal treatment, confirming the chemical reversibility of the D-A adduct.

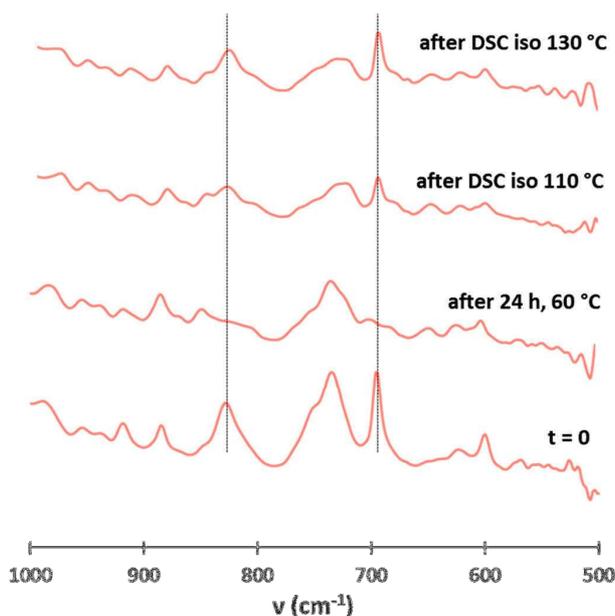


Figure 3.3. FTIR spectrum for 2 D-A after its monomers homogenization, 24h at 60 °C, and after DSC analysis carried out in isothermal at 110 and 130 °C.

3.4 Characterization of the lignin based D-A materials

The thermal stability of the lignin based D-A materials was evaluated by TGA, The results are detailed in the Annexe II (Figure S3.22 and Table S3.2). The materials obtained from the tri and tetra functional linker have the highest thermal stability, with $T_{95\%} = 227$ or 229°C , respectively (Table 3.1). TGA curves almost completely overlapped. The material prepared with the bi functional aliphatic linker exhibits the lowest thermal stability with a $T_{95\%} = 208^\circ\text{C}$. For all the materials, the thermal degradation starts at temperatures much higher than the temperature of the retro D-A reaction. Consequently, the depolymerization can be performed without any concern of thermal degradation.

Table 3.1. $T_{95\%}$ of the lignin based D-A materials measured by TGA.

	TGA
	$T_{95\%}$ ($^\circ\text{C}$)
2 D-A	208 ± 2.0
2ϕ D-A	224 ± 2.5
3 D-A	227 ± 1.0
4 D-A	229 ± 1.0

The glass transition temperatures (T_g) were measured by DSC and the results summarized in Table S3.2. Figure 2.4a shows the influence of the linker functionality and chemical structure (aromatic aliphatic). T_g increases with the aliphatic linker functionality. This phenomenon can be explained by the higher crosslinking density provided by the multifunctional linkers. The aromaticity increases the T_g by more than 20°C , because of the higher rigidity provided by the aromatic rings. Then, the material based on the aromatic linker has the highest T_g of the whole set.

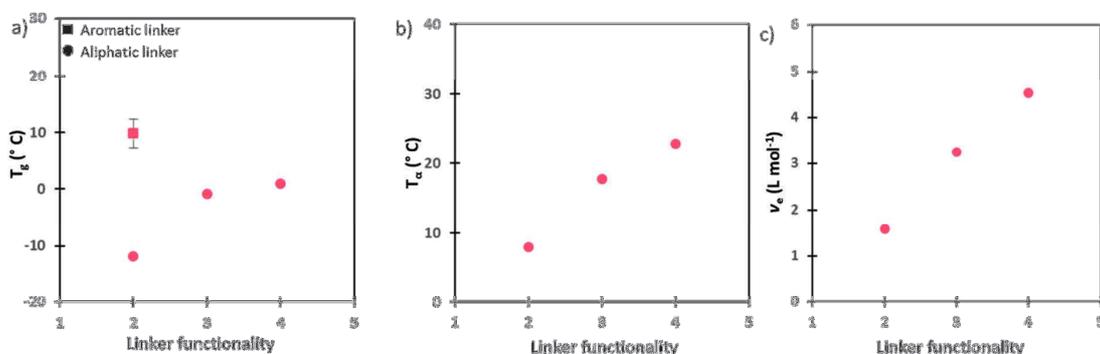


Figure 2.4. T_g (a), T_α (b) and cross linking density ν_e (c) of the lignin based D-A materials depending on the linker's functionality.

DMA was then conducted to evaluate the viscoelastic properties. The materials were analyzed in tensile mode from -60°C to 110°C . Unfortunately, due to a high brittleness at low temperature, the materials based on aromatic linker could not be analyzed. Figure S3.23 shows the evolution of the storage modulus E' and the loss factor $\tan \delta$. The main relaxation temperature, T_α , taken as the peak of $\tan \delta$ curve, follows the same evolution as the T_g measured by DSC, *i.e.* increases with the linker functionality (Figure 2.4b). This effect can be attributed to the higher cross linking density provided by the multifunctional linkers (figure 2.4c), which was calculated from the values of the storage modulus E' on the rubbery plateau (Equation 3.1).

The uniaxial tensile properties were then measured. The results are illustrated in Figure 2.5a – c and summarized in Table S3.2. The static mechanical properties confirm the observations of DSC and DMA. An increase in the linker functionality results in stiffer materials, with higher Young's modulus and tensile strength, and leads to a decrease in the elongation at break. All the materials exhibit interesting elongation properties, with 2 D-A being the most stretchable one (up to 140%). Despite its aromatic backbone and high rigidity, 2 ϕ D-A surprisingly shows a high elongation at break (115 %). These results are in good accordance with the mechanical properties of the materials prepared through the thiol-ene polymerization in our previous study¹⁶ in which it was also observed a linear increase of the Young's modulus and tensile strength in function of the linker's functionality. However, in this study, higher elongation at break ϵ can be obtained due to the thiols chain extension which provides a higher stretch ability.

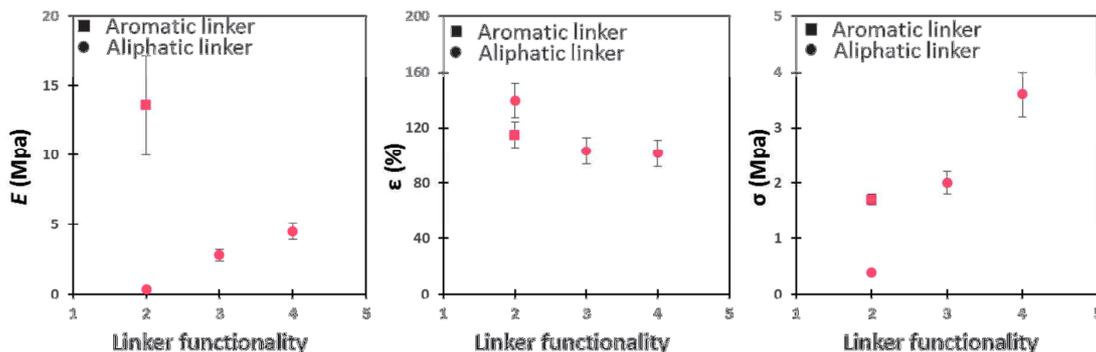


Figure 2.5. Mechanical properties of the lignin based D-A materials related to the linker's functionality a) Young's modulus E , b) elongation at break ϵ , and c) tensile strengths σ .

3.5 Reprocessing of the lignin based D-A materials

As shown before, the effective thermoreversibility of the D-A adduct gives the possibility to depolymerize the lignin-based networks. This feature was exploited to reprocess the materials, which gives the opportunity to easily reuse the materials. The lignin based D-A materials were finely cut and reprocessed several times, as detailed in the experimental section (Figure 3.6 a – c). Their properties were evaluated after each cycle by DSC, DMA and tensile tests.

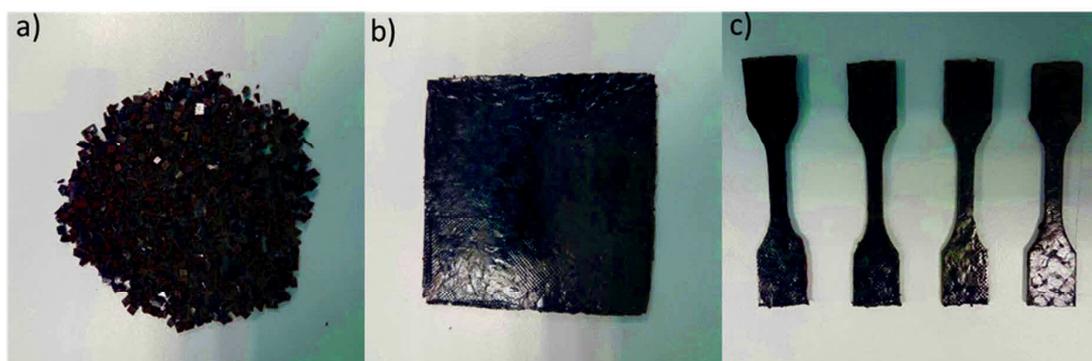


Figure 3.6. Lignin based D-A materials a) recovered after the first processing b) after the reprocessing and c) cut in bone shape for tensile measurements.

The results of the TGA of the reprocessed materials are detailed in the SI (Figure S3.24a – d and Table S3.2). No significant changes are observed after reprocessing the materials, confirming that

the thermal stability of the materials is high enough to allow the reprocessing after the retro D-A reaction.

The thermal and thermo-mechanical properties of the reprocessed materials were measured by DSC and DMA. The results are summarized in Table S3.2. T_g increases after each processing cycle (Figure 3.7a), even though this increment is less pronounced between the 2nd and the 3rd processing cycle. The same trend is observed for T_α (Figure 3.7b). DMA curves are available in the Annexe II (Figure S3.25).

The mechanical properties of the materials are reported in Figure 3.7 c – e. The repeated processing cycles generally lead to more fragile materials, with an increased Young’s modulus and tensile strength and a reduced elongation at break. This trend is particularly marked for the material prepared with the aromatic linker, which shows very high Young’s modulus (141.8 MPa) and poor elongation (10%) after 3 processing cycles. On the other hand, the material obtained with the bi functional aliphatic linker is the least affected by the reprocessing. It keeps a stretch ability of 130% and a stable Young’s modulus and tensile strength after 3 processing steps.

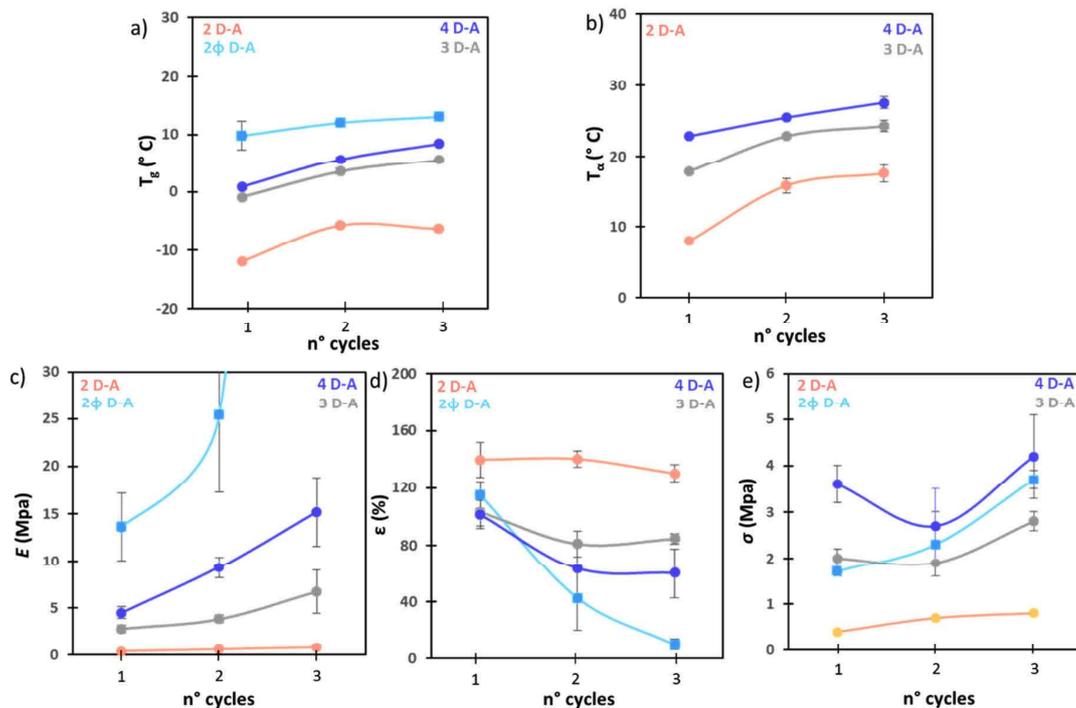


Figure 3.7. Thermo-mechanical properties of the lignin based D-A materials related to the number of reprocessing a) T_g b) T_α c) Young's modulus E d) elongation at break ϵ and e) tensile strengths σ

3.6 Self-healing properties

The self-healing behavior of the D-A materials under thermal treatment was first investigated by following the evolution of a crack under polarized optical microscopy. Photographs were taken at different intervals during the healing process. Figure 3.8 shows the evolution of the crack for the materials prepared with the bi- and tetra-functional aliphatic linkers. The materials prepared with the tri-functional linker and with the aromatic linker behave similarly, and the results are shown in the Annexe II (Figure S3.26).

A material prepared by the irreversible thiol-maleimide reactions was taken as reference,¹⁶ and is shown for comparison on Figure 3.8 g – i.

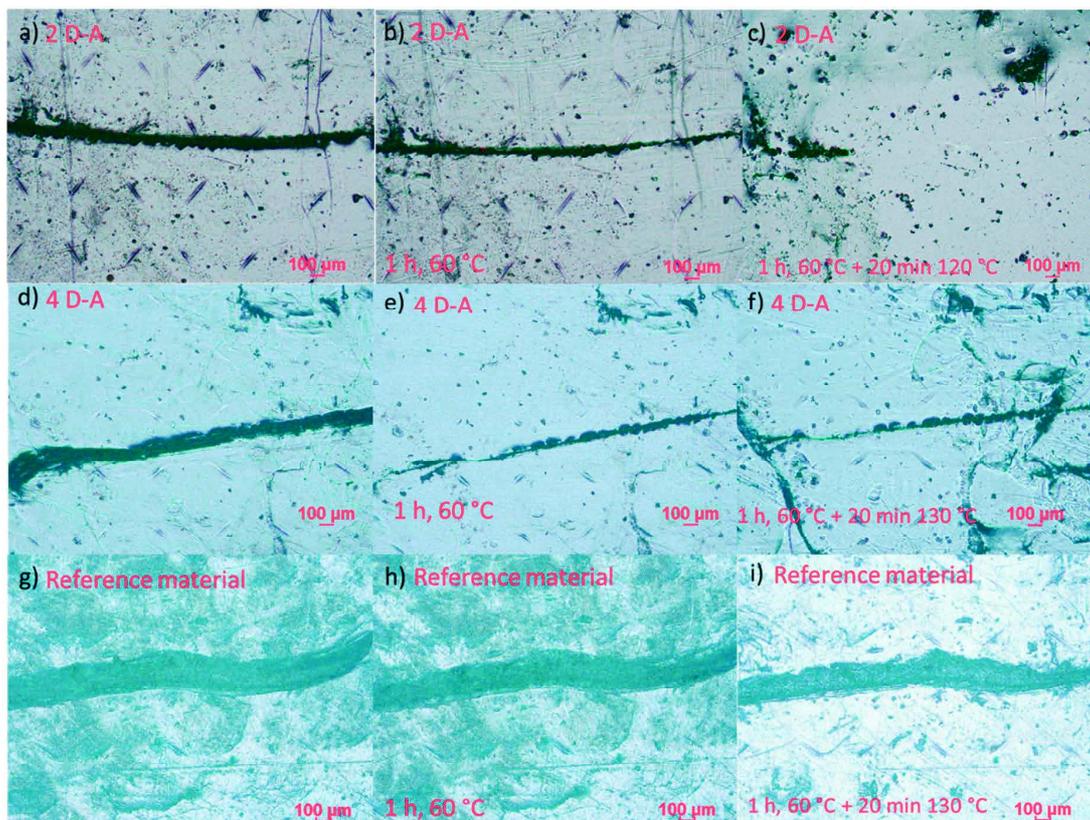


Figure 3.8. Optical microscope picture of a) 2 D-A after scratch b) 2 D-A after curing at 60 °C for 1h c) 2 D-A after curing at 60 °C for 1h with additional 20 min at 110 °C d) 4 D-A after scratch e) 4 D-A after curing at 60 °C for 1h f) D-A after curing at 60 °C for 1h with additional 20 min at 130 °C g) reference material after scratch h) reference material after curing at 60 °C for 1h i) reference material after curing at 60 °C for 1h with additional 20 min at 130 °C.

The self-healing process is evident for the D-A materials after only 1 h at 60° C (Fig 3.8b and e). The crack is reduced, whereas it remains for the material irreversibly cross-linked. After 24 hours at 60° C, no further improvements were observed in the healing process. However, increasing the temperature allows further self-healing. The partial depolymerization of the polymeric network due to the retro D-A favors the chain mobility, allowing the free active groups to react again and the crack to heal. Almost full recovery was observed for 2 S-Fur-Mal-SL (Fig. 3.8c) after 20 min at 110° C, and for 4 S-Fur-Mal-SL after additional 20 min at 130° C. The higher cross-linking density provided by the tetra-functional linker requires a higher temperature to achieve the healing process. These results are in good accordance with previous publications, which show that the healing process requires a curing at the temperature in which the retro D-A occurs.^{19,24,40}

The healing ability was then macroscopically confirmed for 2 D-A. A dumbbell-shaped specimen was cut in two pieces, which were then placed in contact, healed at 120 °C for 20 min, and cured overnight at 60 °C. The two pieces recombined together, as shown in Figure 3.9, allowing to be held horizontally by the pliers. Similar results were obtained with 4 D-A (Figure S3.27). The same test was performed also on a material prepared by the irreversible thiol-maleimide reaction and taken as reference. The reference material does not recombine together under the above mentioned conditions, confirming that the thermoreversible linkage is responsible of the self – healing properties, thus excluding the possibility of adhesion due to non-covalent interactions.

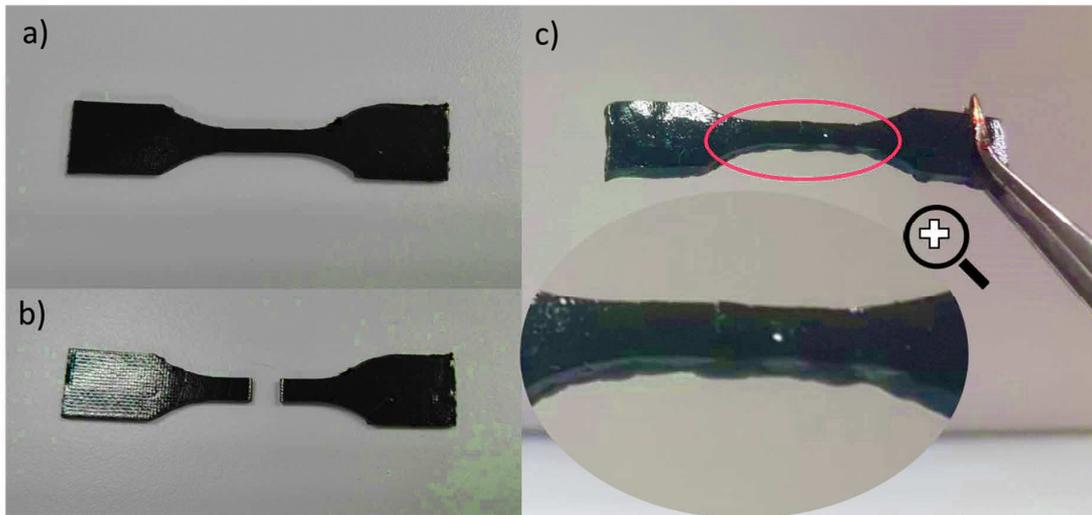


Figure 3.9. 2 S-Fur-Mal-SL a) before the cut b) after the cut c) after the self-healing.

The mechanical properties of the healed material were compared with those of the neat material.

Figure 3.10 shows the corresponding stress-strain curves, which reveal that the healing process preserved the mechanical properties.

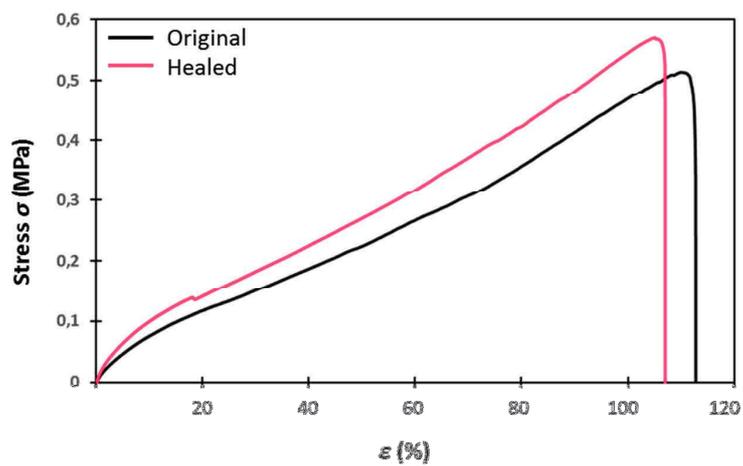


Figure 3.10. Stress - elongation curves of 2 D-A before and after the healing process.

4. Conclusions

Thermo-reversible and self-healing lignin based materials were successfully elaborated for the first time through the design of Diels – Alder (D-A) macromolecular architectures. A technical lignin obtained by a soda process was esterified with 11-maleimidoundecylenic acid. The resulting maleimide-containing lignin derivatives were then polymerized through the D-A click polymerization with different polyfunctional furan linkers. Increasing the linker functionality from two to four resulted in materials with a higher T_g , T_{α} crosslink density as well as enhanced stiffness and strength, but reduced elongation at break. Different reprocessing cycles were successfully performed for each material. The properties of the materials with aliphatic linkers are kept stable after several reprocessing cycles, whereas with aromatic linker the material become fragile. The molecular mobility of the linker seems to be the key point to tailor the reprocessing ability. The polymeric networks show self-healing properties when scratched and further cured at 110/130 °C indicating the reversibility of the D-A linkages. The materials when cut, re-joined and cured at 130 °C, are able to mend and recombine back together.

Overall, these new lignin-based polymeric materials were developed through a sustainable pathway, on agreement with a green chemistry, without the use of solvents and catalyst except for the linkers synthesis, leading to an aromatic material with noticeable thermal and mechanical properties (stretch ability: 100-140%). In a close future, UV absorption with corresponding material's stability after UV irradiation can be investigated, thus providing interesting perspectives for the production of lignin based self-healing UV-protecting films with tailored thermo-mechanical properties.

Conclusion et perspectives du chapitre 3

Des matériaux à base de lignine thermo réversibles et auto-réparants ont été élaborés avec succès pour la première fois grâce à la synthèse d'architectures macromoléculaires en utilisant les réaction du type Diels-Alder.

Conformément à l'étude précédente, l'augmentation de la fonctionnalité des liens, de deux à quatre, a donné lieu à des matériaux avec une température de transition vitreuse, une température de relaxation, une densité de liaison plus élevée ainsi qu'une rigidité et une résistance mécanique accrue, avec un allongement réduit. Cette étude montre que sur la base d'un système de polymérisation différent, nous pouvons obtenir des matériaux avec des propriétés thermo-mécaniques reproductibles. En outre, les propriétés des matériaux avec des liens aliphatiques sont maintenues stables après plusieurs cycles. Tandis qu'avec un lien sur une base aromatique, le

matériau devient plus fragile. La mobilité moléculaire du linker semble être le point clé pour adapter la capacité de procesabilité multiple. Les réseaux polymères obtenus présentent des propriétés d'auto-reparation après avoir été rayés et durcis à 110/130 ° C indiquant la réversibilité des liaisons D-A. Les matériaux lorsqu'ils sont coupés, reassociés et durcis à 130 ° C, sont capables de se réparer et de s'interconnecter ensemble.

References du chapitre 3

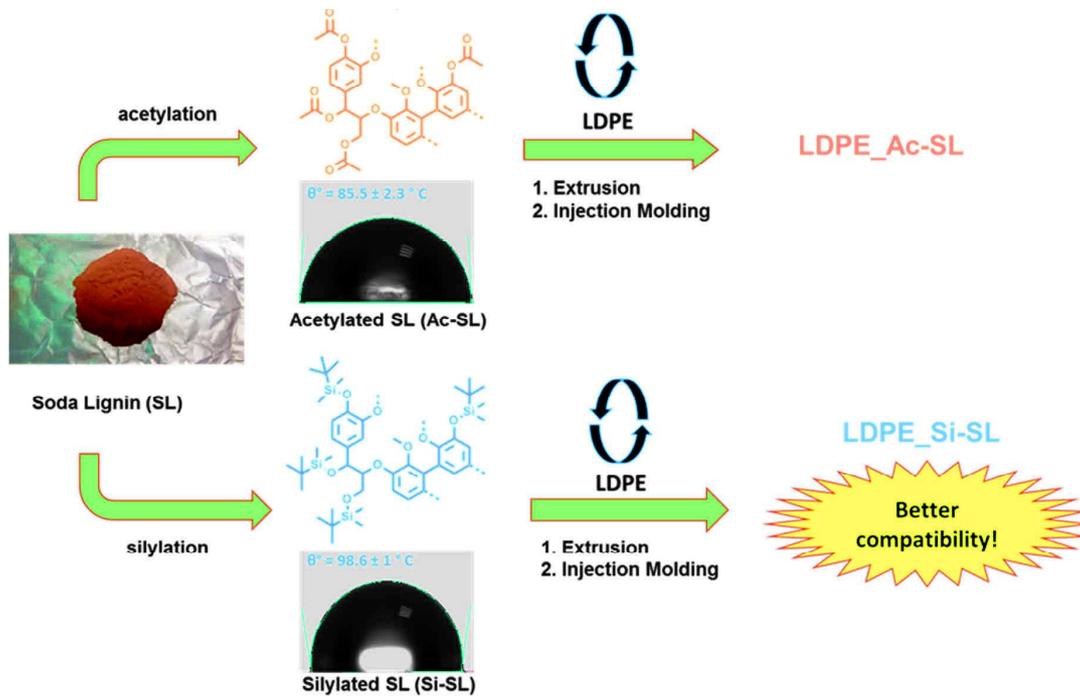
- (1) Rethinking the future of plastics <http://newplasticseconomy.org/report-2016> date access.
- (2) Suarez, H.; Barlow, J. W.; Paul, D. R. Mechanical properties of ABS/polycarbonate blends. *J. Appl. Polym. Sci.* **1984**, *29* (11), 3253–3259.
- (3) Kulich, D. M.; Gaggar, S. K.; Lowry, V.; Stepien, R. Acrylonitrile–Butadiene–Styrene Polymers. In *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc., 2002.
- (4) Laoutid, F.; Bonnaud, L.; Alexandre, M.; Lopez-Cuesta, J.-M.; Dubois, P. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Mater. Sci. Eng. R Rep.* **2009**, *63* (3), 100–125.
- (5) Gandini, A.; Lacerda, T. M.; Carvalho, A. J. F.; Trovatti, E. Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. *Chem. Rev.* **2016**, *116* (3), 1637–1669.
- (6) Belgacem, M. N.; Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*; Elsevier, 2011.
- (7) Kai, D.; Tan, M. J.; Chee, P. L.; Chua, Y. K.; Yap, Y. L.; Loh, X. J. Towards lignin-based functional materials in a sustainable world. *Green Chem.* **2016**, *18* (5), 1175–1200.
- (8) Upton, B. M.; Kasko, A. M. Strategies for the Conversion of Lignin to High-Value Polymeric Materials: Review and Perspective. *Chem. Rev.* **2016**, *116* (4), 2275–2306.
- (9) Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijninx, P. C. A.; Weckhuysen, B. M. Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew. Chem. Int. Ed.* **2016**, *55* (29), 8164–8215.
- (10) Argyropoulos, D. S.; Crestini, C. A Perspective on Lignin Refining, Functionalization, and Utilization. *ACS Sustain. Chem. Eng.* **2016**, *4* (10), 5089–5089.
- (11) Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Davison, B. H.; Dixon, R. A.; Gilna, P.; Keller, M.; et al. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* **2014**, *344* (6185), 1246843.

- (12) Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* **2014**, *39* (7), 1266–1290.
- (13) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Click Chemistry: Diverse Chemical Function from a Few Good Reactions. *Angew. Chem. Int. Ed.* **2001**, *40* (11), 2004–2021.
- (14) Qin, A.; Lam, J. W. Y.; Tang, B. Z. Click polymerization. *Chem. Soc. Rev.* **2010**, *39* (7), 2522–2544.
- (15) Han, Y.; Yuan, L.; Li, G.; Huang, L.; Qin, T.; Chu, F.; Tang, C. Renewable polymers from lignin via copper-free thermal click chemistry. *Polymer* **2016**, *83*, 92–100.
- (16) Buono, P.; Duval, A.; Averous, L.; Habibi, Y. Lignin-Based Materials Through Thiol–Maleimide “Click” Polymerization. *ChemSusChem* **2017**, *10* (5), 984–992.
- (17) Duval, A.; Lange, H.; Lawoko, M.; Crestini, C. Reversible crosslinking of lignin via the furan–maleimide Diels–Alder reaction. *Green Chem.* **2015**, *17* (11), 4991–5000.
- (18) Duval, A.; Couture, G.; Caillol, S.; Avérous, L. Biobased and Aromatic Reversible Thermoset Networks from Condensed Tannins via the Diels–Alder Reaction. *ACS Sustain. Chem. Eng.* **2017**, *5* (1), 1199–1207.
- (19) Kötteritzsch, J.; Stumpf, S.; Hoepfner, S.; Vitz, J.; Hager, M. D.; Schubert, U. S. One-Component Intrinsic Self-Healing Coatings Based on Reversible Crosslinking by Diels–Alder Cycloadditions. *Macromol. Chem. Phys.* **2013**, *214* (14), 1636–1649.
- (20) Liu, Y.-L.; Chuo, T.-W. Self-healing polymers based on thermally reversible Diels–Alder chemistry. *Polym. Chem.* **2013**, *4* (7), 2194–2205.
- (21) Oehlenschlaeger, K. K.; Mueller, J. O.; Brandt, J.; Hilf, S.; Lederer, A.; Wilhelm, M.; Graf, R.; Coote, M. L.; Schmidt, F. G.; Barner-Kowollik, C. Adaptable Hetero Diels–Alder Networks for Fast Self-Healing under Mild Conditions. *Adv. Mater.* **2014**, *26* (21), 3561–3566.
- (22) Gandini, A. The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis. *Prog. Polym. Sci.* **2013**, *38* (1), 1–29.

- (23) Syrett, J. A.; Becer, C. R.; Haddleton, D. M. Self-healing and self-mendable polymers. *Polym. Chem.* **2010**, *1* (7), 978–987.
- (24) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A Thermally Re-mendable Cross-Linked Polymeric Material. *Science* **2002**, *295* (5560), 1698–1702.
- (25) Chen, X.; Wudl, F.; Mal, A. K.; Shen, H.; Nutt, S. R. New Thermally Remendable Highly Cross-Linked Polymeric Materials. *Macromolecules* **2003**, *36* (6), 1802–1807.
- (26) Plaisted, T. A.; Nemat-Nasser, S. Quantitative evaluation of fracture, healing and re-healing of a reversibly cross-linked polymer. *Acta Mater.* **2007**, *55* (17), 5684–5696.
- (27) Liu, H.; Chung, H. Self-Healing Properties of Lignin-Containing Nanocomposite: Synthesis of Lignin-graft-poly(5-acetylaminopentyl acrylate) via RAFT and Click Chemistry. *Macromolecules* **2016**, *49* (19), 7246–7256.
- (28) Abächerli, A.; Doppenberg, F. Method for preparing alkaline solutions containing aromatic polymers. US6239198 B1, May 29, 2001.
- (29) Buono, P.; Duval, A.; Verge, P.; Averous, L.; Habibi, Y. New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation. *ACS Sustain. Chem. Eng.* **2016**, *4* (10), 5212–5222.
- (30) Gadwal, I.; Stuparu, M. C.; Khan, A. Homopolymer bifunctionalization through sequential thiol–epoxy and esterification reactions: an optimization, quantification, and structural elucidation study. *Polym. Chem.* **2015**, *6* (8), 1393–1404.
- (31) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* **1995**, *43* (6), 1538–1544.
- (32) Crawford, R. J. *Plastics Engineering*; Butterworth-Heinemann, 1998.
- (33) McCrum, N. G.; Buckley, C. P.; Bucknall, C. B. *Principles of Polymer Engineering*; Oxford University Press, 1997.

- (34) Park, S. A.; Lim, C. H.; Chung, K.-H. Epoxide opening with tetrabutylammonium fluoride (TBAF). *Bull. Korean Chem. Soc.* **2007**, *28* (10), 1834–1836.
- (35) Yao, Z.; Dai, B.; Yu, Y.; Ji, H.; Zhou, L.; Cao, K. Kinetics based on the base-catalyzed mechanism of a click reaction between glycol dimerthioacetate and glycidyl phenyl ether. *RSC Adv.* **2017**, *7* (18), 10881–10884.
- (36) Froidevaux, V.; Borne, M.; Laborbe, E.; Auvergne, R.; Gandini, A.; Boutevin, B. Study of the Diels–Alder and retro-Diels–Alder reaction between furan derivatives and maleimide for the creation of new materials. *RSC Adv.* **2015**, *5* (47), 37742–37754.
- (37) Adzima, B. J.; Aguirre, H. A.; Kloxin, C. J.; Scott, T. F.; Bowman, C. N. Rheological and Chemical Analysis of Reverse Gelation in a Covalently Cross-Linked Diels–Alder Polymer Network. *Macromolecules* **2008**, *41* (23), 9112–9117.
- (38) Scheltjens, G.; Diaz, M. M.; Brancart, J.; Van Assche, G.; Van Mele, B. A self-healing polymer network based on reversible covalent bonding. *React. Funct. Polym.* **2013**, *73* (2), 413–420.
- (39) Stirn, Z.; Rucigaj, A.; Krajnc, M. Characterization and kinetic study of Diels–Alder reaction: Detailed study on N-phenylmaleimide and furan based benzoxazine with potential self-healing application. *Express Polym. Lett.* **2016**, *10* (7), 537–547.
- (40) Bai, N.; Saito, K.; Simon, G. P. Synthesis of a diamine cross-linker containing Diels–Alder adducts to produce self-healing thermosetting epoxy polymer from a widely used epoxy monomer. *Polym. Chem.* **2013**, *4* (3), 724–730.

Chapitre 4 : Modification chimique de la lignine : acétylation versus silylation



Introduction du chapitre 4

Le quatrième et dernier chapitre de cette thèse illustre une nouvelle modification chimique de la lignine qui a été utilisée pour la synthèse d'additifs à base de lignine et ceci pour des matrices polymères hydrophobes.

Cette étude, publiée dans *ACS Sustainable Chemistry & Engineering* sous le titre « New insights on the chemical modification of lignin: acetylation vs silylation », visait initialement au développement d'une modification chimique capable de masquer partiellement les groupes hydroxyle de la lignine et en même temps de lui conférer une hydrophobicité et une solubilité plus élevées dans des solvants organiques.

Encouragé par l'hydrophobicité beaucoup plus élevée présentée par la lignine silylée, nous avons montré qu'elle pourrait être incorporée de manière très efficace dans du polyéthylène basse densité à hauteur de 10% avec une excellente compatibilité.

New insights on the chemical modification of lignin: acetylation versus silylation

Pietro Buono,^[a] Antoine Duval,^[b] Luc Averous^[b] and Youssef Habibi*^[a]

^a Department of Materials Research and Technology (MRT), Luxembourg Institute of Science and Technology (LIST), 5 avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

^b BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, Strasbourg Cedex 2 67087, France

*e-mail: youssef.habibi@list.lu

Abstract

Soda lignin was functionalized with *tert*-butyldimethylsilyl groups by the reaction with *tert*-butyldimethylsilyl chloride. The reaction conditions leading to a quantitative derivatization of lignin, hydroxyl groups were determined by ³¹P and ¹H NMR and compared with those of acetylation. The functionalization was also confirmed by FTIR and Size Exclusion Chromatography. The silylation enhances the thermal stability and lowers the T_g of lignin as compared to the acetylation. In addition, the silylated lignins are soluble in a wider range of organic solvents, including solvents of low polarity, and show a clear hydrophobic character with a contact angle with water higher than 100°. Neat, acetylated and silylated lignin were then blended with low density polyethylene, and injection molded materials were analyzed with tensile tests, DMA, DSC and Scanning Electron Microscopy (SEM). This study reveals the higher compatibility of the silylated lignin with the polyolefin matrix and hence the great potential of the silylated lignin for a use as additive in apolar polymer matrices.

1. Introduction

Lignin is, after cellulose, the second most abundant polymer from biomass, and the main renewable source of aromatic units.¹ The lignin macromolecule is formed by the radical polymerization of phenylpropane precursors, *p*-hydroxyphenyl, guaiacyl and sinapyl units, respectively denominated as H, G and S units.² The botanical origin of lignin determines the ratio of H/G/S units, leading to a large diversity, further increased by the great variety of interunit linkages (ethers or condensed C-C bonds).³ Furthermore, the extraction process largely modifies the structure of the final lignin, by cleaving ether bonds but also generating new condensed linkages.⁴

Despite significant achievements in the past decade, the wide diversity and structural complexity of lignin still constitutes a major drawback for its use in high value applications. Among the 50 Mt lignin fractionated from biomass per year,⁵ only about 100 kt is commercially available as either Kraft, soda or organosolv lignins,⁶ the majority being burnt in plants for energy production. However, its particular chemical structure and abundance would make it a key renewable raw material to replace petrochemical derivatives.⁷ Nowadays, new processes for Kraft lignin isolation⁸ and fractionation into low polydispersity fractions^{9,10} contribute to the renewed interest for its use in polymer materials. Processes such as soda or organosolv are further able to furnish sulfur-free, low molar mass lignin fragments from annual plants, which also show great potential in polymer chemistry.^{11,12}

As such, the poor thermal stability and difficult melt processing of lignin precludes its direct use as material. Many studies focused on the blending of lignin with various polymers to produce materials.¹³ Its polyphenolic nature makes it a good anti-oxidant additive to limit the degradation of polyolefins during their thermo-mechanical process and usages.¹⁴⁻¹⁶ Because of its numerous OH groups, lignin usually presents a better affinity for polar polymer matrices.¹⁷ It is immiscible with non-polar matrices, such as polyolefins,^{15,18} poly(vinyl acetate) (PVAc)¹⁹ or poly(vinyl chloride)

(PVC),²⁰ generally leading to poor mechanical properties. However, the OH groups can readily be used as a platform for chemical modifications.²¹ Their derivatization can help to decrease the hydrophilic character, thus enhancing lignin compatibility with apolar polymers and later increasing its dispersion into the matrix. The most common reactions used for this purpose are alkylation and acetylation, which have been shown to enhance the miscibility of lignin with polyolefins^{22–25} or aliphatic polyesters,^{26,27} for instance.

In this work, we attempted for the first time to derivatize lignin OH groups with *tert*-butyldimethylsilyl groups (TBDMS), as shown on Scheme 1a. TBDMS group is known to be stable against hydrolysis in a wide pH range as well as under harsh basic, oxidative and reductive conditions.²⁸ It was already explored on others biopolymers, such as cellulose, starch or chitosan, and found to increase their thermal stability and solubility in a wide range of organic solvents.^{29,30} The silylation of soda lignin (SL) was studied and compared with acetylation (Scheme 1b), using a set of spectroscopic techniques (¹H and ³¹P NMR, FTIR). The physico-chemical and thermal properties of the acetylated and silylated lignin were then determined, before extrusion blending with low-density polyethylene (LDPE). LDPE was chosen given its partially amorphous nature, which should facilitate the incorporation of lignin derivatives, and because its relatively low melting point (around 110° C) allows processing far below the degradation temperature of the lignins. Injection-molded LDPE-lignin blends were finally characterized with tensile tests, DMA, DSC and SEM, to evaluate the particular potential of the silylated lignin.

2. Experimental Section

2.1 Reagents and Materials

Alcaline soda lignin (Protobind 1000) was obtained from Green Value SA (Switzerland). It is a sulfur-free lignin obtained after extraction and fractionation from a mix of wheat straw (*Triticum sp.*) and Sarkanda grass (*Saccharum officinarum*), according to the corresponding patented process.³¹ SL is a

low molar mass lignin (M_n below 1000 g.mol⁻¹),³² with a high degree of condensation and low content in residual ether bonds.³³ The lignin was used as received without further purification.

tert-Butyldimethylsilyl chloride (97%), imidazole (>99%), acetic anhydride (>98%), 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), Chromium(III) acetylacetonate (99.99%), Cholesterol (>99%), chloroform-*d* (100%, 99.96 atom% D) and dimethyl sulfoxide-*d*₆ (100%, 99.96 atom% D) were purchased from Sigma-Aldrich, pyridine (99.5%, extra dry over molecular sieve) and dimethylformamide (99.8%, extra dry over molecular sieve) from Acros Organics. All chemicals were used as received without further purification. LDPE was purchased from Scientific Polymer Products (USA) in form of pellets. It has an approximate M_w of 50 000 g mol⁻¹ (data from the supplier). It was dried in a vacuum oven at 40°C for 24 h prior to use.

2.2 Syntheses and materials processing

Acetylation

For acetylation, 2 g of lignin were dissolved in 8 mL of pyridine in a 100 mL flame dried round bottom flask flushed with Argon. Acetic anhydride (0.25 to 5 equivalents with respect to lignin OH groups) was added, and the reaction mixture was stirred at room temperature for 18 h. For partially acetylated products (1.2 eq. or less acetic anhydride), ethanol was then added and all by-products were removed under vacuum. Fully acetylated products (2.5 eq. or more acetic anhydride) could be recovered more easily by precipitation: 10 volumes of 1% HCl were added at 0 °C, and the resulting precipitate was filtered off and washed with deionized water to neutral pH. The acetylated lignin was finally dried in a vacuum oven at 40° C overnight.

Silylation

1 g of previously dried SL were weighted in a flame dried round bottom flask and flushed with Argon. 5 mL of dry DMF was added and the mixture was stirred until full dissolution of lignin. Imidazole (2.5 equivalents with respect to lignin OH groups) and TBDMSCI (0.4 to 5 equivalents) were then added

and the reaction mixture stirred at room temperature for the desired time (1 to 18 h). For partially silylated products (1.2 eq or less TBDMSCl), DMF was first removed under vacuum and the product washed with methanol. Fully silylated products (2.5 eq. or more TBDMSCl) could be recovered more easily after precipitation: deionized water was added to precipitate the product, which was then filtered off and washed with methanol. Finally the silylated lignins were dried in a vacuum oven at 40° C overnight. 1.450 g (94.5% yield) of fully silylated product (Si-SL_05) were recovered. The yield was calculated considering the mass gained from the reaction of 4.67 mmol g⁻¹ of lignin OH groups reacted with TBDMSCl, computed indirectly by residual OH groups detected by ³¹P NMR (Table S1).

Processing of Lignin-polyethylene blends

Extrusion step

LDPE was extruded with 10% (w/w) lignin in a twin screw micro-compounder (Xplore 15 cc, DSM, Geleen, Netherlands) with a nitrogen purge. The processing temperature was set to 110°C and the screw speed was 100 rpm. In total 10 g per batch were introduced in the micro-compounder for a total extrusion time of 5 min (with recirculation) to produce strands of diameter 3 to 5 mm.

Injection molding step

The extruded strands were cut in pieces of 5 mm length and injection molded with a Thermo Scientific HAAKE MiniJet II to obtain dumbbell specimens. The cylinder temperature was set to 130°C and the mold temperature to 65°C. After melting the LDPE – lignin blends in the cylinder for 2 min, the sample was injected with a pressure of 700 bar for 5 s, followed by a post pressure of 100 bar for 3 s.

2.3 Characterization

NMR spectroscopy

All NMR spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer. ³¹P NMR analysis was performed on lignin samples phosphorylated with 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, using cholesterol as internal standard, according to standard protocols.³⁴ 128 scans were recorded with a 15 s delay and a spectral width of 80 ppm (180-100 ppm). For quantitative ¹H-NMR analysis, about 20 mg of lignin were dissolved in 0.5 mL of DMSO-*d*₆ before the addition of 100 μL of a standard solution of pentafluorobenzaldehyde (PFB) in DMSO-*d*₆. 32 scans were collected with a 10 s delay.

FTIR

The FTIR analyses were conducted on a Bruker Tensor 27 (Ettlingen, Germany) in attenuated total reflection (ATR) mode. 40 scans were collected between 400 and 4000 **cm**⁻¹.

SEC measurements

Size Exclusion Chromatography analysis were performed with a size exclusion chromatography (SEC) system from Shimadzu equipped with a pre-column PLGel 5μ, two PLGel 5μ Mixed-C 300 mm columns, one PL 100 Å 300 mm column and refractive index (RI) and ultra-violet (UV) detectors. Chloroform (CHCl₃) was used as the eluent at a flow rate of 1 mL min⁻¹. All determinations of molar mass were performed relative to linear polystyrene standards from 580 to 1 650 000 g mol⁻¹.

Solubility properties

25 mg of lignin were mixed with a solvent (250 μL) forming a 10% w/v solution that was stirred for 5 min. Finally the solubility properties were evaluated by visual inspection. The samples that could not dissolve were diluted to 2.5% w/v, stirred and again inspected as previously described. The solubility was defined by the following categories: fully dissolved in 10% w/v concentration (+++), fully dissolved in 2.5% w/v concentration (++) , partially soluble (+/-), insoluble (-).

Lignin Film Preparation and Water Contact Angle measurements

Thin lignin films were prepared by spin-coating from solutions in DMF, as previously reported.³⁵ Lignin samples (80 mg) were dissolved in DMF (0.2 mL). Then, 50 μL of lignin solution was spin-coated on 1.5 cm \times 1.5 cm silicon wafers at 1000 rpm for 120 s. The lignin coated-glasses were dried in vacuum oven for 24 h at 50 $^{\circ}\text{C}$ to ensure the full removal of DMF. Prior to measurement, the dried films were preconditioned for 3 h under the environmental conditions of measurement. The dynamic contact angle of sessile drops of water on the lignins films was measured with an OCA20 automated and software-controlled Video-Based Contact Angle Meter (DataPhysics Instruments GmbH, Filderstadt, Germany). 6 to 7 measurements were carried out on each film and imaged after 20 s, and the average and standard deviation of the measurements calculated.

Thermogravimetric Analysis (TGA) coupled to Mass Spectrometry (MS)

Thermogravimetric analyses (TGA) were performed on a STA 409PC Luxx apparatus from NETZSCH at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ up to 800 $^{\circ}\text{C}$ under an Argon atmosphere (flow rate = 90 mL min^{-1}). About 30 mg for each sample were analyzed and the evolved species were continuously collected through a heated transfer line to a quadrupole mass spectrometer (NETZSCH Aeolos QMS 403C).

Differential scanning calorimetry (DSC)

DSC thermograms of previously dried lignin samples were recorded on a TA DSC Q200 calorimeter (TA Instruments). The samples were first heated to 105 $^{\circ}\text{C}$ and maintained at this temperature for 15 min to erase thermal history. They were then cooled to 0 $^{\circ}\text{C}$ and heated to 200 $^{\circ}\text{C}$. Glass transition temperatures (T_g) were recorded on the second heating run.

Thermograms of LDPE – lignin blends were obtained on a Netzsch DSC 204 F1 (Selb, Germany). The samples were heated from -150 to 200 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$. T_g , melting temperature (T_m) and the melting enthalpy (ΔH_m) were measured on the second heating run, while the cold crystallization enthalpy (ΔH_{cc}) was obtained on the cooling run. The degree of crystallinity (X_c) is calculated using the equation (4.1):

$$X_c (\%) = \frac{\Delta H_m}{x_{PE} \times \Delta H_m^\circ} \times 100 \quad (4.1)$$

with ΔH_m the experimental melting enthalpy of the sample, ΔH_m° the theoretical melting enthalpy of 100% crystalline PE (293 J g⁻¹ as provided by the *Proteus*[®] database), and x_{PE} the weight percent of PE in the material.

Uniaxial tensile test

Tensile tests were performed at room temperature on an universal testing machine Instron model 5967 (Norwood, MA, USA), equipped with a load cell of 1 kN at 5 mm min⁻¹ crosshead speed. Dumbbells samples were tested and obtained by injection molding as detailed above. They were dried in a vacuum oven for 24 h at 40° C and successively pre-conditioned overnight under the environmental conditions of measurement. 3 to 4 measurements were performed for each LDPE lignin blends at room temperature and 50% relative humidity.

Izod impact test

Izod impact test were performed at room temperature with an Instron CEAST 9050 impact pendulum using a hammer of 2.75 J. Samples of 10 mm x 60 mm x 3 mm were obtained by injection molding, dried in a vacuum oven for 24 h at 40° C and preconditioned overnight under the environmental conditions prior testing.

Dynamic mechanical analysis (DMA)

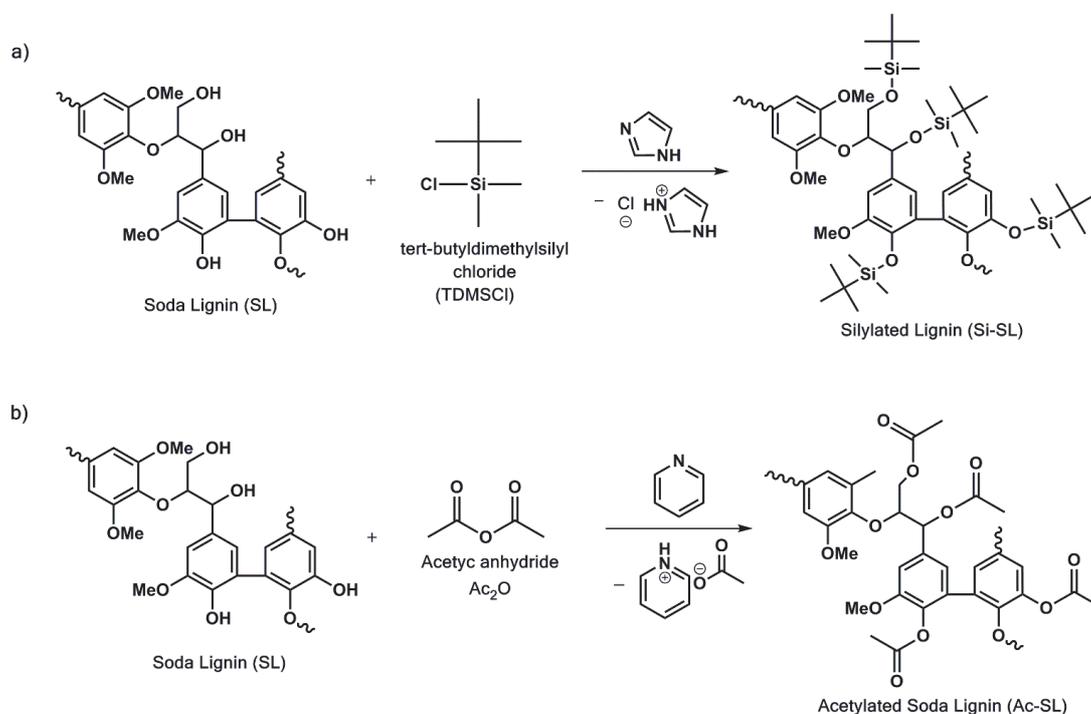
DMA was measured on a Netzsch DMA 42 C equipment (Selb, Germany). Samples of 10 mm x 60 mm x 3 mm were obtained by injection molding. DMA was conducted in the 3-point bending mode from -150 °C to 130 °C at a 2 °C min⁻¹ heating rate and frequency of 10 Hz. Storage modulus E' , loss modulus E'' , and loss factor $\tan \delta = E''/E'$ were continuously recorded as a function of the temperature.

Scanning electron microscopy (SEM)

The microstructure of LDPE – lignin blends was studied by means of a pressure-controlled scanning electron microscope (SEM) Quanta FEG 200 from FEI (Eindhoven, The Netherlands). The processed samples were cryo-fractured in liquid nitrogen and their section analyzed. SEM observations were performed at a water pressure of 100 Pa.

3. Results and discussions

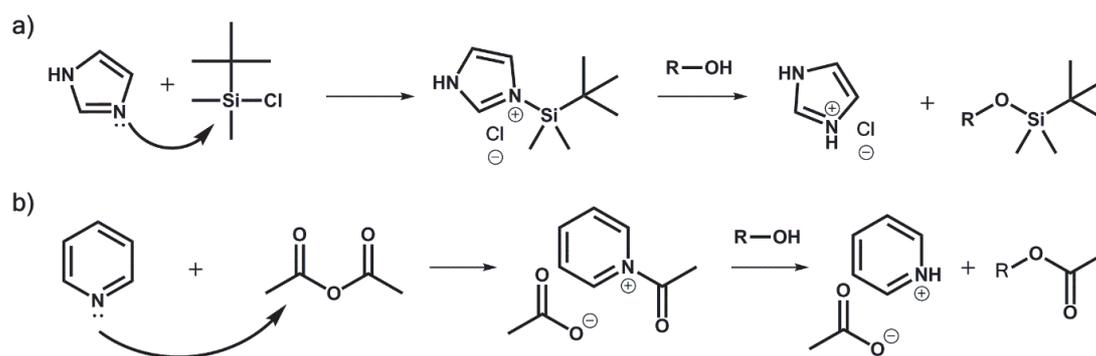
3.1 Comparison on lignin reactivity toward silylation and acetylation



Scheme 4.1. Schematic illustration for lignin silylation (a) and acetylation (b)

SL was reacted with TBDMSCl using imidazole as catalyst, as reported on Scheme 4.1a. The reaction mechanism was first described by Corey,²⁸ who assumed that the reaction proceeds via a reactive *N*-tert-butyldimethylsilylimidazole intermediate (Scheme 4.2a), prior to the nucleophilic attack to the silicon atom by the alcoholic hydroxyl group. However, Patschinski et al.³⁶ recently reported that the

solvent DMF may also catalyze the reaction by forming an additional very reactive silylated – DMF intermediate, even though an auxiliary base is always needed to avoid catalyst deactivation through protonation. The mechanism of silylation presents similarities with the acetylation reaction with Ac₂O catalyzed by pyridine, which proceeds via *N*-acetylpyridinium intermediate (Scheme 4.2b). Since both reactions consume OH groups in lignin, ³¹P NMR was used to evaluate their progress.



Scheme 4.2: Details of the silylation mechanism *via N-tert-butyldimethylsilylimidazole* intermediate (a) and acetylation mechanism *via N-acetylpyridinium* intermediate (b)

The kinetic of the silylation reaction was first evaluated for two TBDMSCl contents, 1.2 and 2.5 equivalents, respectively. The decrease of the OH content with the reaction time is reported on Figure 4.1. With 2.5 equivalents TBDMSCl, phenolic OH groups are very quickly consumed, and are quantitatively derivatized after 3 h. The maximum derivatization of aliphatic OH groups is also reached after 3 h, but they fail to be fully derivatized. When 1.2 equivalents TBDMSCl are used, the reaction rate is similar but the derivatization is incomplete. In all cases, an overnight reaction (18 h) is far enough to reach the maximum derivatization rate for a given content in reagent.

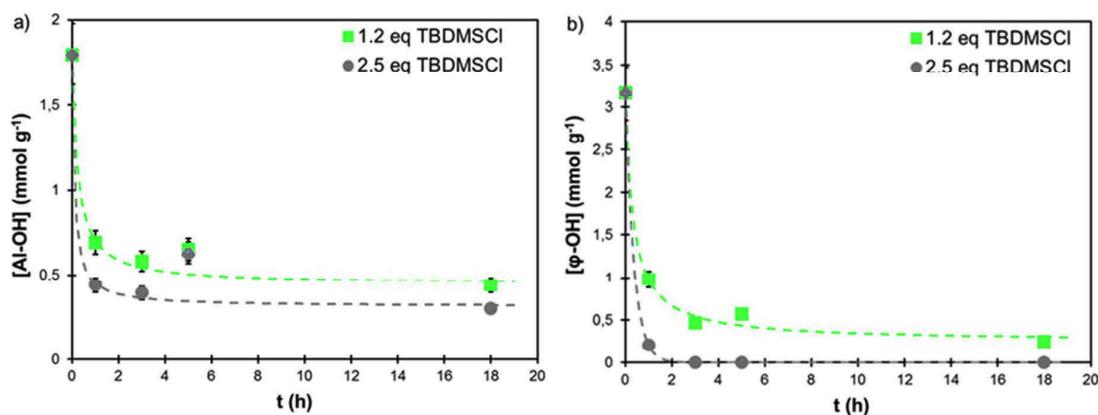


Figure 4.1. Evolution of the OH content (measured by quant. ³¹P NMR) with reaction time during silylation with 1.2 or 2.5 eq TBDMSCl: aliphatic OH groups (a), phenolic OH groups (b).

The influence of the amount of TBDMSCl was later evaluated. For comparison, acetylations with various amounts of acetic anhydride (Ac₂O) were performed under similar conditions. The results are reported on Figure 4.2. In both cases, phenolic OH groups react more easily than their aliphatic counterpart. With 1 equivalent of reagent, about 70 to 80% of them have been converted, whereas the conversion of aliphatic is only between 40 and 60%. This greater reactivity could result from the lower pK_a of phenolic OH, since both imidazole and pyridine act not only as catalysts but also as bases,³⁷ facilitating the deprotonation of the phenols into phenolates, which are effective nucleophiles. Similarly, higher reactivity of phenolic OH groups from lignins has been shown in various base-catalyzed reactions.^{38,39}

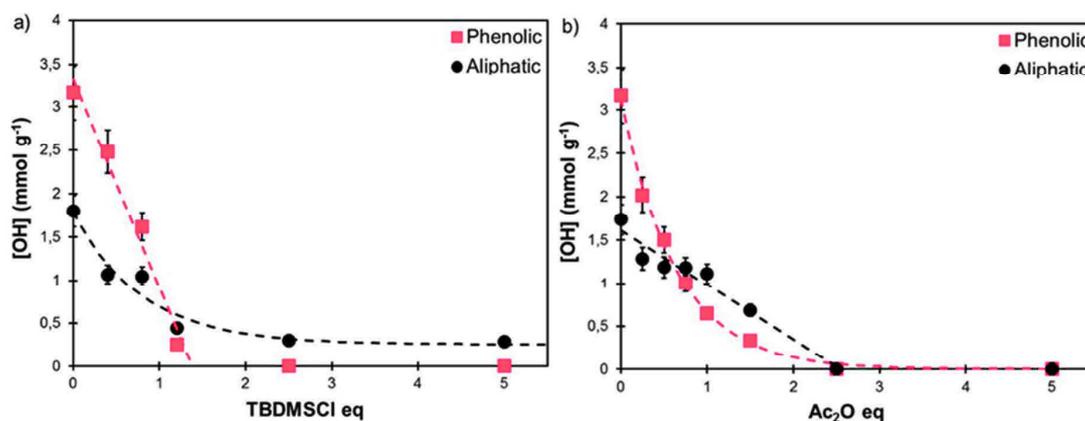


Figure 4.2. Influence of the amount of reagent used for the derivatization on the OH content measured by ³¹P NMR (18 h reaction at room temperature): silylation with TBDMSCl (a), acetylation with Ac₂O (b)

2.5 equivalents of Ac₂O appear sufficient to fully acetylate the lignin in good agreement with previous studies.^{25,40} There is a linear decrease in the content in phenolic OH with the amount of TBDMSCl used for the reaction. 2.5 equivalents allow their full conversion into silyl ethers. About 15% of the aliphatic OH groups cannot be derivatized, even for high excess of reagent. The increase from 2.5 to 5 equivalents does not bring any significant change. Since these groups can be converted into acetyls but not into silyl ethers, this suggests that the limitation might arise from steric hindrance, because the TBDMS group is much bulkier than the acetyl group (Scheme 4.1).

SL also contains a significant amount of COOH groups (0.9 mmol g⁻¹), which may also react with TBDMSCl.⁴¹ However, the derivatized SL shows only a slight decrease in COOH content (Annexe III, Tables S3.2 and S3.1). This could be explained by a partial hydrolysis of the labile TBDMS anhydride during the work up. On the contrary, COOH groups cannot react with Ac₂O, and fully acetylated lignin indeed doesn't show any change in COOH content.

All the modified lignins were also analyzed by ¹H NMR. The spectra of the fully derivatized samples (Ac-SL_06 and Si-SL_05) are shown on Figure 4.3a. The acetylation causes the apparition of two groups of signals in the 1.7 – 2.1 and 2.1 – 2.4 ppm regions, corresponding to aliphatic and phenolic

acetyls, respectively.⁴² The silylation was confirmed by the appearance of two strong signals assigned to the methyl and *t*-butyl groups at -0.5 – 0.5 and 0.5 – 1.5 ppm, respectively. The successful modifications of SL were further confirmed by FTIR experiments (Figure 4.3b), which show the complete disappearance of the O-H stretch signal between 3000 and 3600 cm⁻¹. For the Ac-SL, the C=O stretch in phenolic and aliphatic acetyls appears at 1760 and 1740 cm⁻¹, respectively.⁴³ For the Si-SL, distinct C-H stretch at 2880 cm⁻¹ corresponding to the alkyl groups of the TBDMS group and Si-CH₃ vibrations at 1250, 830 and 780 cm⁻¹ are visible.⁴⁴

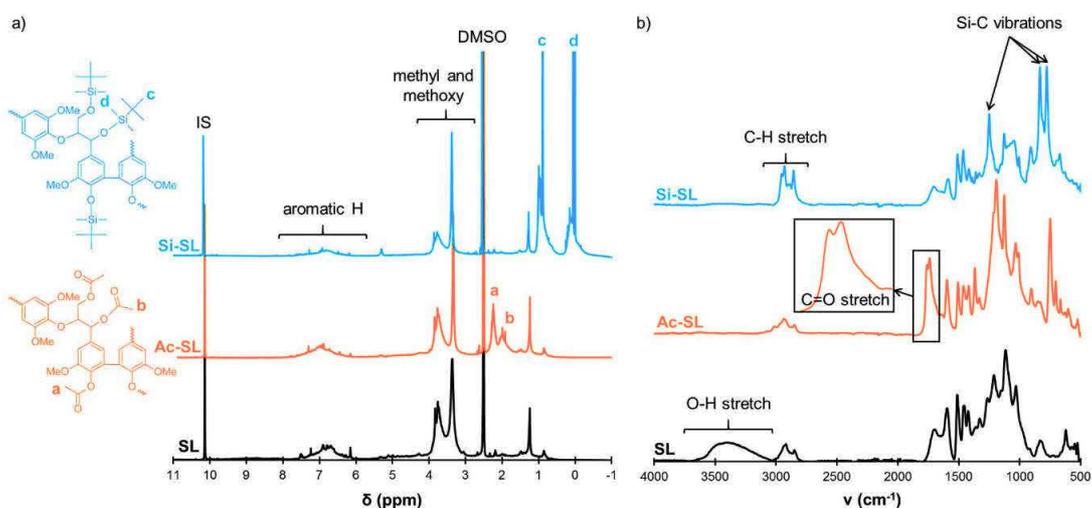


Figure 3. ¹H NMR (a) and FTIR (b) spectra of neat (SL), acetylated (Ac-SL₀₆) and silylated (Si-SL₀₅) lignins. ¹H NMR were recorded in DMSO-*d*₆.

In the presence of a suitable internal standard, the quantification of the acetyl or silyl groups that have been introduced is possible through ¹H NMR. Figure 4 shows the correlation between the amounts of functional groups quantified by ¹H NMR and the decrease in OH groups measured by ³¹P NMR, ΔOH, which is obtained by the formula (2):

$$\Delta OH = [OH]_{init} - [OH]_{deriv} \quad (4.2)$$

where [OH]_{init} and [OH]_{deriv} represent the OH content of the initial and derivatized lignins, respectively.

A linear correlation is observed, but ΔOH is always slightly higher than the content in functional groups detected by ^1H NMR. It arises from the fact that $[\text{OH}]_{\text{derivatized}}$ is obtained in mmol g^{-1} of derivatized lignin. The mass of the derivatized lignin corresponds to the initial mass of lignin increased by the mass of the newly introduced groups. With respect to the initial lignin, this leads to an underestimation of the OH content in the derivatized lignin, and later to an overestimation of the ΔOH . However, the linear correlation attests for a fine agreement between both measurements (Figure 4.4).

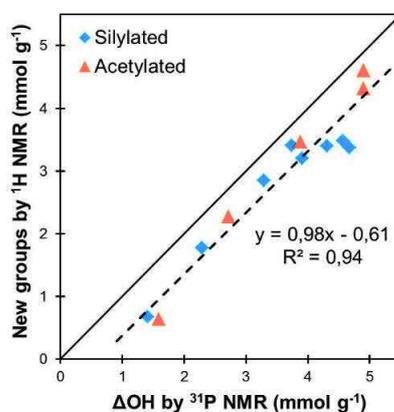


Figure 4.4. Correlation between the amount of functional groups (silyl or acetyl) measured by ^1H NMR and the decrease in OH groups obtained by ^{31}P NMR.

3.2 Physico-chemical properties of silylated and acetylated lignins

The molar mass distribution of the fully derivatized samples Si-SL_05 and Ac-SL_06 were measured by SEC in chloroform (Figure 4.5). Partially derivatized samples could not be analyzed because of solubility issues. Acetylation is commonly used prior to measure the molar mass distribution of lignin, to enhance its solubility in the solvent used as eluent.^{45,46} It is assumed that the acetylation doesn't affect the lignin structure, so that the results obtained on the acetylated lignin are representative of the neat lignin. The molar mass distribution of the silylated lignin is almost identical to the one of acetylated lignin (M_n are 855 and 838 g mol^{-1} , respectively). Despite the fact that the TBDMS group is bulkier than the acetyl group, the differences in terms of hydrodynamic

radius thus seem to be rather limited. This also confirms that the silylation does not induce any side reaction on the lignin backbone, such as condensations or crosslinking reactions. Small differences are however observed in the low molar mass region, and could result from different behaviors of low molar mass residues during the precipitation.

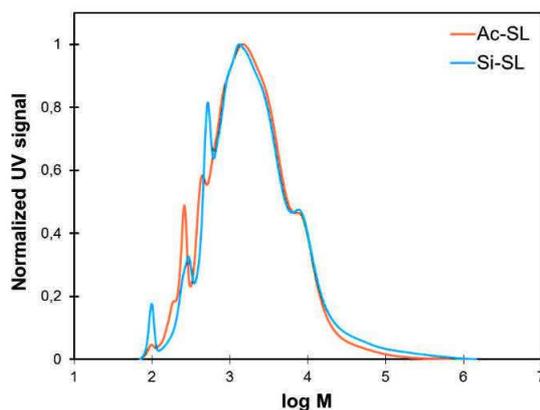


Figure 4.5. Molar mass distributions of fully acetylated (Ac-SL_06) and silylated lignins (Si-SL_05), measured by SEC in chloroform (calibration with PS standards).

The solubility of Si-SL_05 and Ac-SL_06 in various solvents was then evaluated and compared to the solubility of the neat SL. Initially, SL is poorly soluble in organic solvents: only polar aprotic solvents (DMSO, DMF, pyridine) can fully dissolve it. It is also soluble under basic conditions, when phenolic OH groups are deprotonated. Both acetylation and silylation drastically modifies this behavior, as reported in the Annexe III (Table S3.3), but better results are obtained for Si-SL, which is highly soluble in common organic solvents, such as acetone, ethyl acetate, dichloromethane, chloroform, diethyl ether or THF.

The hydrophobic behavior of the silylated lignin was revealed by the measurements of contact angle against water. Figure 6a shows the water droplet deposited on the surface of a film of neat SL, and fully acetylated (Ac-SL_06) or silylated lignins (Si-SL_05). For neat SL, a contact angle of $35.5 \pm 2.7^\circ$ is measured, lower than previously reported on Kraft or milled wood lignins ($46 - 56^\circ$).⁴⁷ This is

probably related to the high content of SL in phenolic OH groups, since their content has been shown to directly influence the contact angle with water.³⁵

Acetylated lignin (Ac-SL_06) exhibit a contact angle with water of $85.5 \pm 2.3^\circ$, in good agreement with previous studies.⁴⁸ For the silylated lignin (Si-SL_05), a greatly enhanced value of $98.6 \pm 1.0^\circ$ is measured. The contact angle was then measured on films of partially silylated lignins. Fig 4.6b presents the evolution of the contact angle with the percentage of derivatized OH groups. Interestingly, the contact angle increases very quickly with the introduction of silyl group: when only 30% of the OH groups are derivatized as silyl ethers, the contact angle is already $84.6 \pm 1.1^\circ$, a value similar to the one obtained for fully acetylated lignin. The contact angle increases then linearly with the quantity of introduced TBDMS groups, as a result of their highly hydrophobic character. When 50% or more of the OH groups are derivatized as silyl ethers, the contact angle becomes higher than 90° , *i.e.* the silylated lignin derivatives become hydrophobic.

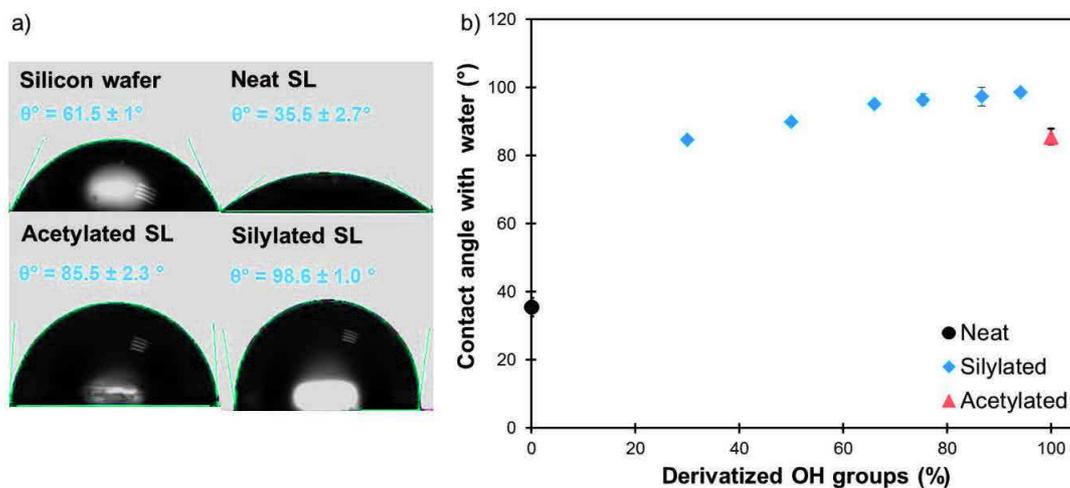


Figure 4.6. (a) Water contact angle of silicon wafer reference, neat SL, and fully acetylated (Ac-SL_06) or silylated (Si-SL_05) lignins. (b) Evolution of the contact angle with the percentage of derivatized OH groups (calculated by ³¹P NMR)

3.3 Thermal properties of silylated and acetylated lignins

TGA was used to investigate the influence of the derivatizations on the thermal sensitivity and degradation of lignins (Figure 4.7). The fully derivatized lignins (Ac-SL_06 and Si-SL_05) were compared to neat SL. They all show small mass loss between 90 and 120 °C, corresponding mainly to the removal of residual water. The onset of the thermal degradation is practically the same for the neat and acetylated lignins, but is markedly increased for the silylated one, at 190 °C (Figure 4.7a). The thermal stability is thus enhanced by silylation, which increases the window of processability and the range of applications of this derivative.

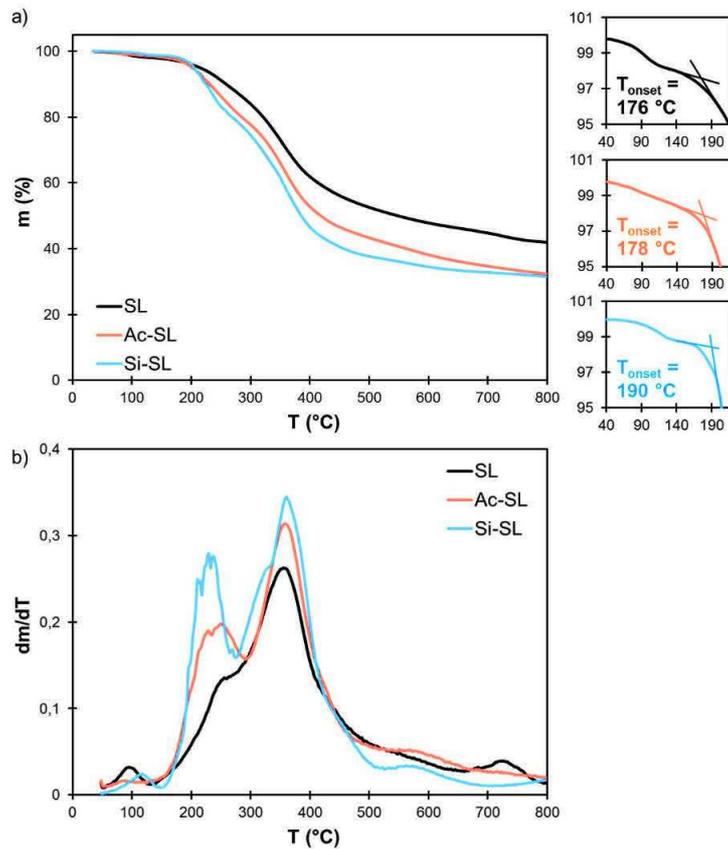


Figure 4.7. TGA (a) and DTG (b) curves of the neat SL, and fully acetylated (Ac-SL_06) or silylated (Si-SL_05) lignins.

The coupling of TGA with mass spectrometry allows the determination of the species that are released during degradation. The curves of the total ion current depending on the temperature are given in the Annexe III. Both silylated and acetylated lignins degrade in two main steps (Figure 4.7b). The first step is located around 230 – 250 °C. For Si-SL, TBDMS methyl ether (m/z 147) is released. It corresponds to the unreacted TBDMSCl quenched with methanol that has not been washed out. The total ion current (TIC) shows that it represents 5% of the total volatiles, corresponding to 3% of the total material weight. Other detected species include dimethylsiloxane fragments (m/z 73 and 75) and methylium ions CH_3^+ (m/z 15), showing that the *t*-butyldimethylsilyl lignin ethers also degrade during this first step. Additionally, CO_2 (m/z 44) is also detected. For the acetylated lignin, the first step is mainly associated with methylium ions and CO_2 release, indicating a probable degradation of the acetyl groups.

The second degradation step is measured at the same temperature for the neat, acetylated and silylated lignins, around 360 °C. The species that are detected include methylium ions (CH_3^+ , m/z 15), probably originating from demethoxylation, as well as carbon monoxide and dioxide. This step rather corresponds to the degradation of the lignin side chains, and is not much affected by the derivatization.

The T_g of lignin has been extensively studied and found to be comprised between 90 and 160° C, depending on many factors, such as the lignin origin, the molar mass or the corresponding extraction process.⁴⁹ The T_g of SL was here measured at 126 ± 2 °C. Acetylation causes a decrease of the T_g , which is measured at 102 ± 2 °C for the acetylated lignin, as a result of the blocking of hydrogen bonds and concomitant increase in free volume due to the presence of the acetyl groups. The decrease is even more pronounced for silylated lignin, which exhibit a T_g of 71 ± 2 °C, because of the bulkier TBDMS group that impact more the global mobility with respect to the acetyl group. However, the T_g spreads over a wide temperature range making its precise detection difficult (DSC traces are available in the Annexe III).

3.4 Blends of lignins derivatives with low-density polyethylene (LDPE)

Neat SL, and fully acetylated (Ac-SL_06) or silylated lignins (Si-SL_05) were melt-blended with LDPE at 10% loading and the resulting composite materials were analyzed, to evaluate the influence of the chemical modifications on the compatibility of lignin with an apolar polymer matrix. SEM images of cryo-fractured surfaces are presented on Figure 4.8. It clearly appears that the neat SL is poorly compatible with LDPE since large lignin aggregates (50 – 100 μm) are visible, and voids around lignin particles attests for a relatively poor interfacial interaction. With acetylated lignin, the lignin particles appear smaller (< 50 μm) and the adhesion to the LDPE matrix is higher. This confirms that acetylation of lignin enhances its compatibility with PE, as previously reported.^{25,50} Best results are obtained with silylated lignin since very fine particles appear well-dispersed in the LDPE matrix. Because of the heavy Si atoms, the silylated lignin appears as brilliant dots when images are taken with back-scattered electrons (Figure 4.8d).

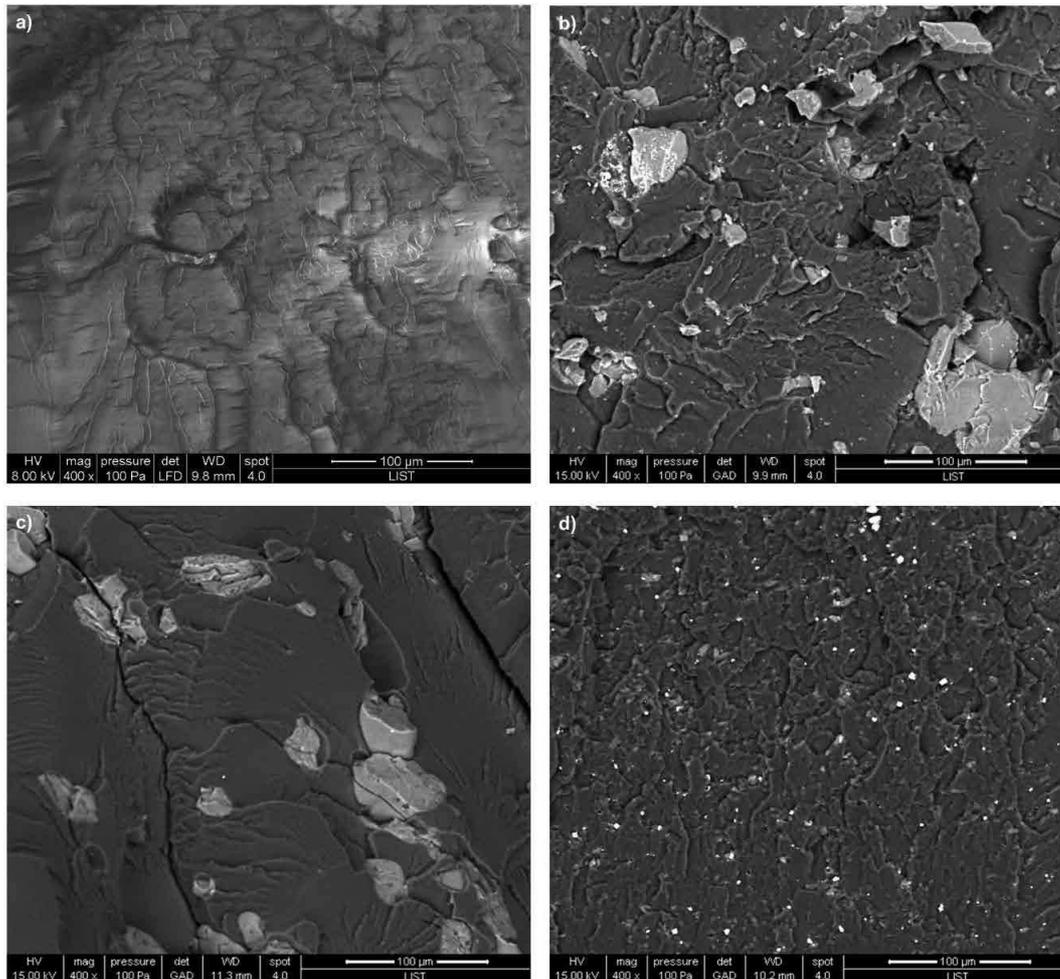


Figure 4.8. SEM images of cryo-fractures of LDPE (a), LDPE – neat SL blend (b), LDPE – acetylated SL (Ac-SL_06) blend (c) and LDPE – silylated SL (Si-SL_05) blend (d). All the blends contain 10% wt of lignin.

Mechanical properties of the LDPE – lignin blends were then measured. Despite clear differences in blend morphology, the results of the tensile tests show only small differences between neat, acetylated and silylated lignins (Table 4.1). As already reported in the literature, lignin with its amorphous 3D structure and the aromatic backbone generally impacts the mechanical properties of polyolefins by increasing the Young’s modulus and reducing the elongation at break.^{16,50,51} The elongation at break is slightly reduced for the three systems, even though acetylated and silylated lignin derivatives allow a better preservation of the ductility. Young’s moduli were observed to

increase. However, taking into account the standard deviations, the value of the system based on silylated lignin is equivalent to the neat LDPE due to a good dispersion and integration of this derivate into the matrix. Same behavior can be observed also for the tensile strength values. Impact tests reveal higher resistance for all the LDPE – lignin blends.

Table 4.1. Results of tensile tests and Izod impact tests for LDPE – lignin blend (10% lignin content). Average values and standard deviation of 3-4 measurements per system.

	Tensile Test			Izod Impact test
	σ Maximum strength (MPa)	ϵ Elongation at break (%)	E Young's modulus (MPa)	Resistance (kJ m^{-2})
PE	15.2 ± 1.7	37.4 ± 1.9	179.7 ± 6.7	45.3 ± 2.1
PE – neat SL	14.7 ± 0.4	25.8 ± 3.4	227.8 ± 46.9	54.4 ± 1.2
PE – acetylated SL	13.4 ± 0.6	31.3 ± 4.2	230.8 ± 2.3	54.9 ± 1.7
PE – silylated SL	14.8 ± 1.2	30.1 ± 3.4	197.2 ± 10.5	50.5 ± 0.3

Results from DSC and DMA measurements are given in Table 4.3. DSC shows a net decrease of T_g for the system with the silylated lignin. It could be explained by strong interactions between the corresponding lignins derivatives and the LDPE polymer chains. The crystallinity slightly increase for the blends with acetylated and silylated lignins, but T_m are almost unaffected, in agreement with previous study.¹⁶

DMA curves available as supporting information show 3 distinct relaxations, commonly described in PE samples as γ , β , and α relaxations.⁵²⁻⁵⁴ T_γ and T_α are reported in Table 4.2. The γ relaxation, which involves chains motion in the amorphous phase and can be associated with the T_g ,⁵³ is unaffected by any of the lignins-based compounds. The T_α increases markedly with the introduction of the neat or acetylated SL. The α relaxation is attributed to the molecular motion in the crystalline phase, and its temperature has been shown to increase with the crystallinity and crystallites size.^{52,54} The results thus suggest that the introduction of neat or acetylated lignins modifies the crystalline structure, which is consistent with the increase of the Young's modulus and decrease of the elongation (Table

4.1). No T_{α} change occurs when the silylated lignin is blended with LDPE. Once again, this can be related a better dispersion of the silylated within LDPE, which does not influence the LDPE crystallization behavior.

Table 4.2. Results of DSC and DMA measurements for LDPE – lignin blends (10% wt of lignin).

	DSC				DMA		
	ΔH_{cc} (J g ⁻¹)	ΔH_m (J g ⁻¹)	X_c (%)	T_m (° C)	T_g (° C)	T_v (° C)	T_{α} (° C)
LDPE	135.3	- 139.7	47.7	112	- 113	- 122	81
LDPE - SL	127.7	- 127.6	48.3	112	- 111	- 122	91
LDPE – Ac-SL_06	135.3	-131.5	49.9	113	- 110	- 121	87
LDPE – Si-SL_05	128.6	-125.3	47.6	113	- 127	- 122	81

4. Conclusion

In this study, a silylation process of soda lignin (SL) was developed, and compared to acetylation. SL was reacted with *tert*-butyldimethylsilyl chloride (TBDMSCl) to produce the corresponding silyl ethers. Phenolic OH groups reacted very quickly and were quantitatively derivatized in the presence of a slight excess of TBDMSCl. About 15% of the aliphatic OH groups could not be accessed because of steric hindrance. 2.5 eq TBDMSCl were sufficient to achieve the highest functionalization of OH groups in lignin, a similar value was found for the acetylation with acetic anhydride. The silylated and acetylated lignin derivatives were then compared. The silylated lignin was found to have a similar molar mass distribution and a better thermal stability than the acetylated lignin. Furthermore, it is soluble in a wider range of organic solvents, including solvents of low polarity, and hydrophobic, as shown by contact angle measurements. To evaluate the potential of the newly developed lignin derivatives, blends with LDPE were prepared and characterized. The silylated lignin showed better compatibility with the LDPE matrix than the neat or acetylated lignins, as revealed by SEM and thermal analysis. The enhanced thermal stability, hydrophobicity and solubility of the silylated lignin

appear very promising to use it into hydrophobic polymer matrices, thus potentially leading to a major and more useful utilization of this abundant biopolymer, although its relatively high cost (TBDMSCl is about 10 times more costly than acetic anhydride) might be limitant. In a close future, the potential of this lignin derivative could be analyzed as antioxidant additive for polyolefins, through specific thermal ageing study.

Conclusion et perspectives du chapitre 4

Dans ce chapitre, nous avons illustré une nouvelle modification chimique de la lignine : la silylation de soda lignine (SL) à travers la réaction avec du chlorure de tert-butyldiméthylsilyle (TBDMSCl) pour produire les éthers de silyle correspondants.

Les dérivés de lignine silylés ont été ensuite comparés avec des équivalents acétylés. Nous avons constaté que la lignine silylée avait une distribution de masse molaire similaire et une meilleure stabilité thermique que la lignine acétylée. En outre, elle est soluble dans une gamme plus large de solvants organiques, y compris des solvants à faible polarité et hydrophobes, comme le montrent les résultats d'angles de contact. Pour évaluer le potentiel des dérivés de lignine nouvellement développés, des mélanges avec du PEBD ont été préparés et caractérisés. La lignine silylée a montré une meilleure compatibilité avec la matrice PEBD que les lignines acétylées, comme le révèlent les résultats de microscopie SEM et les analyses thermiques. La stabilité thermique améliorée, l'hydrophobie et la solubilité de la lignine silylée semblent être des résultats très prometteurs pour l'utiliser comme additif antioxydant pour des polyoléfines.

Références du chapitre 4

- (1) Whetten, R.; Sederoff, R. Lignin Biosynthesis. *Plant Cell* **1995**, *7* (7), 1001–1013.
- (2) Ralph, J.; Lundquist, K.; Brunow, G.; Lu, F.; Kim, H.; Schatz, P. F.; Marita, J. M.; Hatfield, R. D.; Ralph, S. A.; Christensen, J. H.; et al. Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl- propanoids. *Phytochem. Rev.* **2004**, *3* (1–2), 29–60.
- (3) Gellerstedt, G.; Henriksson, G. Lignins: Major Sources, Structure and Properties. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Amsterdam, 2008; pp 201–224.
- (4) Duval, A.; Lawoko, M. A review on lignin-based polymeric, micro- and nano-structured materials. *React. Funct. Polym.* **2014**, *85*, 78–96.
- (5) Lora, J. Industrial Commercial Lignins: Sources, Properties and Applications. In *Monomers, Polymers and Composites from Renewable Resources*; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Amsterdam, 2008; pp 225–241.
- (6) Strassberger, Z.; Tanase, S.; Rothenberg, G. The pros and cons of lignin valorisation in an integrated biorefinery. *RSC Adv.* **2014**, *4* (48), 25310–25318.
- (7) Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Davison, B. H.; Dixon, R. A.; Gilna, P.; Keller, M.; et al. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* **2014**, *344* (6185), 1246843.
- (8) Tomani, P. The Lignoboost Process. *Cellul. Chem. Technol.* **2010**, *44* (1–3), 53–58.
- (9) Sevastyanova, O.; Helander, M.; Chowdhury, S.; Lange, H.; Wedin, H.; Zhang, L.; Ek, M.; Kadla, J. F.; Crestini, C.; Lindström, M. E. Tailoring the molecular and thermo–mechanical properties of kraft lignin by ultrafiltration. *J. Appl. Polym. Sci.* **2014**, *131* (18), 9505–9515.
- (10) Duval, A.; Vilaplana, F.; Crestini, C.; Lawoko, M. Solvent screening for the fractionation of industrial kraft lignin. *Holzforschung* **2015**, *70* (1), 11–20.

- (11) Laurichesse, S.; Avérous, L. Synthesis, thermal properties, rheological and mechanical behaviors of lignins-grafted-poly(ϵ -caprolactone). *Polymer* **2013**, *54* (15), 3882–3890.
- (12) Laurichesse, S.; Huillet, C.; Avérous, L. Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethane synthesis. *Green Chem.* **2014**, *16* (8), 3958–3970.
- (13) Yu, L.; Dean, K.; Li, L. Polymer blends and composites from renewable resources. *Prog. Polym. Sci.* **2006**, *31* (6), 576–602.
- (14) Alexy, P.; Kosíková, B.; Podstránska, G. The effect of blending lignin with polyethylene and polypropylene on physical properties. *Polymer* **2000**, *41* (13), 4901–4908.
- (15) Pouteau, C.; Dole, P.; Cathala, B.; Averous, L.; Boquillon, N. Antioxidant properties of lignin in polypropylene. *Polym. Degrad. Stab.* **2003**, *81* (1), 9–18.
- (16) Pucciariello, R.; Villani, V.; Bonini, C.; D’Auria, M.; Vetere, T. Physical properties of straw lignin-based polymer blends. *Polymer* **2004**, *45* (12), 4159–4169.
- (17) Pouteau, C.; Baumberger, S.; Cathala, B.; Dole, P. Lignin–polymer blends: evaluation of compatibility by image analysis. *C. R. Biol.* **2004**, *327* (9–10), 935–943.
- (18) Kadla, J. F.; Kubo, S. Lignin-based polymer blends: analysis of intermolecular interactions in lignin-synthetic polymer blends. *Compos. Part -Appl. Sci. Manuf.* **2004**, *35* (3), 395–400.
- (19) Teramoto, Y.; Lee, S.-H.; Endo, T. Molecular composite of lignin: Miscibility and complex formation of organosolv lignin and its acetates with synthetic polymers containing vinyl pyrrolidone and/or vinyl acetate units. *J. Appl. Polym. Sci.* **2012**, *125* (3), 2063–2070.
- (20) Yue, X.; Chen, F.; Zhou, X.; He, G. Preparation and Characterization of Poly (vinyl chloride) Polyblends with Fractionated Lignin. *Int. J. Polym. Mater.* **2012**, *61* (3), 214–228.
- (21) Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* **2014**, *39* (7), 1266–1290.
- (22) Sailaja, R. R. N.; Deepthi, M. V. Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin. *Mater. Des.* **2010**, *31* (9), 4369–4379.

- (23) Maldhure, A. V.; Ekhe, J. D.; Deenadayalan, E. Mechanical properties of polypropylene blended with esterified and alkylated lignin. *J. Appl. Polym. Sci.* **2012**, *125* (3), 1701–1712.
- (24) Chen, F.; Dai, H.; Dong, X.; Yang, J.; Zhong, M. Physical properties of lignin-based polypropylene blends. *Polym. Compos.* **2011**, *32* (7), 1019–1025.
- (25) Dehne, L.; Vila Babarro, C.; Saake, B.; Schwarz, K. U. Influence of lignin source and esterification on properties of lignin-polyethylene blends. *Ind. Crops Prod.* **2016**, *86*, 320–328.
- (26) Li, Y.; Sarkanen, S. Alkylated Kraft Lignin-Based Thermoplastic Blends with Aliphatic Polyesters. *Macromolecules* **2002**, *35* (26), 9707–9715.
- (27) Teramoto, Y.; Lee, S.-H.; Endo, T. Phase Structure and Mechanical Property of Blends of Organosolv Lignin Alkyl Esters with Poly([ϵ]-caprolactone). *Polym J* **2009**, *41* (3), 219–227.
- (28) Corey, E. J.; Venkateswarlu, A. Protection of hydroxyl groups as tert-butyldimethylsilyl derivatives. *J. Am. Chem. Soc.* **1972**, *94* (17), 6190–6191.
- (29) Petzold, K.; Koschella, A.; Klemm, D.; Heublein, B. Silylation of Cellulose and Starch – Selectivity, Structure Analysis, and Subsequent Reactions. *Cellulose* **2003**, *10* (3), 251–269.
- (30) Rúnarsson, Ö. V.; Malainer, C.; Holappa, J.; Sigurdsson, S. T.; Mátsson, M. tert-Butyldimethylsilyl O-protected chitosan and chitooligosaccharides: useful precursors for N-modifications in common organic solvents. *Carbohydr. Res.* **2008**, *343* (15), 2576–2582.
- (31) Abächerli, A.; Doppenberg, F. Method for preparing alkaline solutions containing aromatic polymers. US6239198 B1, May 29, 2001.
- (32) Aguié-Béghin, V.; Foulon, L.; Soto, P.; Crônier, D.; Corti, E.; Legée, F.; Cézard, L.; Chabbert, B.; Maillard, M.-N.; Huijgen, W. J. J.; et al. Use of Food and Packaging Model Matrices to Investigate the Antioxidant Properties of Biorefinery Grass Lignins. *J. Agric. Food Chem.* **2015**, *63* (45), 10022–10031.
- (33) Constant, S.; Wienk, H. L. J.; Frissen, A. E.; Peinder, P. de; Boelens, R.; Es, D. S. van; Grisel, R. J. H.; Weckhuysen, B. M.; Huijgen, W. J. J.; Gosselink, R. J. A.; et al. New insights into the

- structure and composition of technical lignins: a comparative characterisation study. *Green Chem.* **2016**, *18* (9), 2651-2665.
- (34) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* **1995**, *43* (6), 1538–1544.
- (35) Chung, H.; Washburn, N. R. Improved Lignin Polyurethane Properties with Lewis Acid Treatment. *ACS Appl. Mater. Interfaces* **2012**, *4* (6), 2840–2846.
- (36) Patschinski, P.; Zhang, C.; Zipse, H. The Lewis Base-Catalyzed Silylation of Alcohols—A Mechanistic Analysis. *J. Org. Chem.* **2014**, *79* (17), 8348–8357.
- (37) Bonner, T. G.; McNamara, P. The pyridine-catalysed acetylation of phenols and alcohols by acetic anhydride. *J. Chem. Soc. B Phys. Org.* **1968**, *0*, 795–797.
- (38) Duval, A.; Lange, H.; Lawoko, M.; Crestini, C. Reversible crosslinking of lignin via the furan–maleimide Diels–Alder reaction. *Green Chem.* **2015**, *17* (11), 4991–5000.
- (39) Sadeghifar, H.; Cui, C.; Argyropoulos, D. S. Toward Thermoplastic Lignin Polymers. Part 1. Selective Masking of Phenolic Hydroxyl Groups in Kraft Lignins via Methylation and Oxypropylation Chemistries. *Ind. Eng. Chem. Res.* **2012**, *51* (51), 16713–16720.
- (40) Thielemans, W.; Wool, R. P. Lignin Esters for Use in Unsaturated Thermosets: Lignin Modification and Solubility Modeling. *Biomacromolecules* **2005**, *6* (4), 1895–1905.
- (41) Huff, B. E. *t*-Butyldimethylchlorosilane. In *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd, 2001.
- (42) Lundquist, K. Proton (¹H) NMR Spectroscopy. In *Methods in Lignin Chemistry*; Lin, S. Y., Dence, C. W., Eds.; Springer-Verlag: Berlin-Heidelberg, 1992.
- (43) Faix, O.; Grünwald, C.; Beinhoff, O. Determination of Phenolic Hydroxyl Group Content of Milled Wood Lignins (MWL's) from Different Botanical Origins Using Selective Aminolysis, FTIR, ¹H-NMR, and UV Spectroscopy. *Holzforschung* **1992**, *46* (5), 425–432.

- (44) Mai, C.; Militz, H. Modification of wood with silicon compounds. Treatment systems based on organic silicon compounds — a review. *Wood Sci. Technol.* **2004**, *37* (6), 453–461.
- (45) Baumberger, S.; Abächerli, A.; Fasching, M.; Gellerstedt, G.; Gosselink, R.; Hortling, B.; Li, J.; Saake, B.; de Jong, E. Molar mass determination of lignins by size-exclusion chromatography: towards standardisation of the method. *Holzforschung* **2007**, *61* (4), 459–468.
- (46) Asikkala, J.; Tamminen, T.; Argyropoulos, D. S. Accurate and Reproducible Determination of Lignin Molar Mass by Acetobromination. *J. Agric. Food Chem.* **2012**, *60* (36), 8968–8973.
- (47) Notley, S. M.; Norgren, M. Surface Energy and Wettability of Spin-Coated Thin Films of Lignin Isolated from Wood. *Langmuir* **2010**, *26* (8), 5484–5490.
- (48) Nadji, H.; Diouf, P. N.; Benaboura, A.; Bedard, Y.; Riedl, B.; Stevanovic, T. Comparative study of lignins isolated from Alfa grass (*Stipa tenacissima* L.). *Bioresour. Technol.* **2009**, *100* (14), 3585–3592.
- (49) Glasser, W. G. Classification of Lignin According to Chemical and Molecular Structure. In *Lignin: Historical, Biological, and Materials Perspectives*; ACS Symposium Series; American Chemical Society, **1999**, *742*, 216–238.
- (50) Toriz, G.; Denes, F.; Young, R. A. Lignin-polypropylene composites. Part 1: Composites from unmodified lignin and polypropylene. *Polym. Compos.* **2002**, *23* (5), 806–813.
- (51) González Sánchez, C.; Alvarez, L. A. E. Micromechanics of lignin/polypropylene composites suitable for industrial applications. *Angew. Makromol. Chem.* **1999**, *272* (1), 65–70.
- (52) Nitta, K. -h; Tanaka, A. Dynamic mechanical properties of metallocene catalyzed linear polyethylenes. *Polymer* **2001**, *42* (3), 1219–1226.
- (53) Matsuo, M.; Bin, Y.; Xu, C.; Ma, L.; Nakaoki, T.; Suzuki, T. Relaxation mechanism in several kinds of polyethylene estimated by dynamic mechanical measurements, positron annihilation, X-ray and ¹³C solid-state NMR. *Polymer* **2003**, *44* (15), 4325–4340.
- (54) Munaro, M.; Akcelrud, L. Correlations between composition and crystallinity of LDPE/HDPE blends. *J. Polym. Res.* **2007**, *15* (1), 83–88.

CONCLUSION GENERALE & PERSPECTIVES

Ce travail de doctorat s'est déroulé dans un contexte d'une collaboration entre le Pr. Luc Avérous, directeur de l'équipe BioTeam au sein de l'Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES / UMR CNRS 7515) à l'Université de Strasbourg (UniStra) à Strasbourg et le Dr Youssef Habibi, chercheur au Luxembourg Institute of Science and Technology du Luxembourg.

L'objectif de ce travail a été l'élaboration de nouveaux polymères et additifs aromatiques renouvelable en utilisant les principes d'une chimie « verte », en évitant quand cela est possible l'utilisation de solvants et catalyseurs. Cet objectif a été réalisé par l'association d'une ressource renouvelable aromatique, complexe et largement disponible : la lignine, et la chimie « clic ».

L'étude bibliographique présentée dans le chapitre 1 dresse un état de l'art des principaux biopolymères/macromères aromatiques et des principaux types de réactions chimiques du type « clic ». Ceci a permis d'appréhender les problématiques principales liées à l'élaboration de matériaux à partir de biopolymères naturels, et pour faire la lumière sur l'application de certaines réactions de clic pour préparer des matériaux à base de lignine. Nous avons également montré qu'il existe encore de nombreux versants de la chimie clic encore inexplorée non seulement sur la lignine, mais aussi sur d'autres composés aromatiques biosourcés. Ce qui pourrait inspirer de nombreuses recherches académiques et industrielles futures.

Dans les chapitres 2 et 3, des matériaux à base de lignine ont été obtenus grâce aux polymérisations de type thiol-ene et Diels-Alder maléimide-furane. Dans ces études, des macromères de lignine ont été greffés par une réaction d'estérification avec de l'acide 11-maleimide-undécénique, sans utilisation de solvants et de catalyseurs. Les dérivés de lignine à base de fonctions maléimides ont été ensuite polymérisés avec différents thiols aliphatique et aromatiques polyfonctionnels. Nous avons montré qu'en dépit de systèmes de polymérisation différents et des « linkers » de longueurs légèrement différentes, nous avons pu obtenir des matériaux avec des propriétés thermo-mécaniques reproductibles avec des propriétés qui vont dans le même sens. L'augmentation de la

fonctionnalité des « linkers » de deux à quatre a donné des matériaux avec une T_g , T_α , une densité de liaison plus élevée ainsi qu'une rigidité et une résistance accrue, mais avec un allongement à la rupture réduit. Les matériaux obtenus grâce à la réaction thermoréversible de Diels-Alder montrent des propriétés d'auto-réparation après avoir été rayés et durcis à 110/130 ° C indiquant la réversibilité des liaisons D-A. Les matériaux lorsqu'ils sont coupés, reassociés et durcis à 130 ° C, sont capables de se réparer et de s'interconnecter ensemble. Nous avons montrés la polymérisation contrôlée avec des « linkers » différents conduit à la synthèse de matériaux ayant des propriétés ajustables. Ceci pourra être poursuivi par l'exploration d'une polymérisation moins chère et donc plus compétitive pour une plus large diffusion. Un aspect que nous prendrons en compte dans l'avenir sera l'extension de nos études également à d'autres types de lignine obtenus par des procédés de fractionnement différents.

Le quatrième et dernier chapitre de cette thèse a illustré un nouveau type de modification chimique de la lignine inexploré pour la synthèse d'additifs à base de lignine, et ceci pour des matrices polymères hydrophobes. La lignine silylée obtenu a une distribution en masses molaires similaire mais avec une meilleure stabilité thermique que la lignine acétylée correspondante. Elle est soluble dans une gamme plus large de solvants organiques, y compris des solvants à faible polarité. Elle est beaucoup plus hydrophobe. En fait, la lignine silylée a montré une excellente compatibilité avec une matrice polyéthylène comme le révèlent les clichés SEM. De plus, l'addition de la lignine silylée n'affecte pas les propriétés mécaniques du polyéthylène final.

Ceci pourrait être étendu dans un avenir proche à d'autres types de lignines obtenus par des procédés de fractionnement différents. Il conviendrait de mettre en exergue les différentes fonctions d'usage complémentaires apportées par cette lignine modifiée. Il conviendrait par exemple d'en étudier l'efficacité sur des tenues et des vieillissement climatiques à long termes. Cette approche par ailleurs pourrait être développée pour d'autres composés aromatiques biosourcés, tels que les tanins.

Cette thèse rédigée sous format d'articles a permis de soumettre 3 publications scientifiques plus un article de synthèse bibliographique (review) dans des journaux à comité de lecture et ainsi valoriser ce travail doctoral. Deux publications scientifiques sont d'ores et déjà été publiées:

1. *ACS Sustainable Chem. Eng.*, **2016**, 4 (10), 5212–5222
2. *ChemSusChem* **2017**, 10 (5), 984–992

ANNEXES

Annexe I: Supporting information du chapitre 2

Synthesis and characterization of maleimido-soda lignin (Mal-SL)

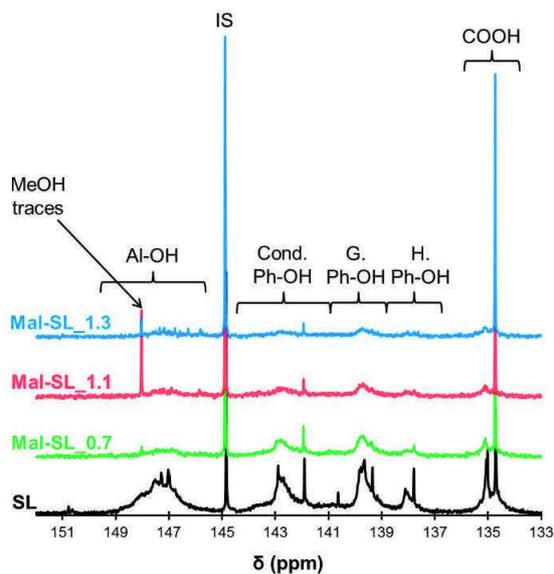


Figure S2.1. ^{31}P NMR of SL and Mal-SL. IS = internal standard (cholesterol).

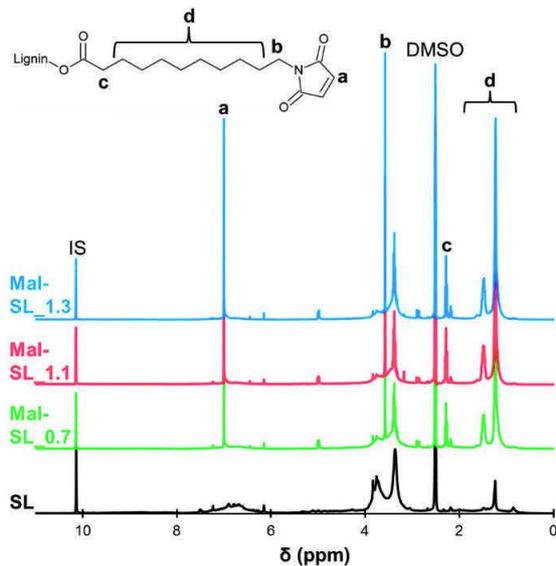


Figure S2.2. ^1H NMR of SL and Mal-SL in $\text{DMSO}-d_6$. IS = internal standard (2,3,4,5,6-pentafluorobenzaldehyde).

Synthesis of thiol-maleimide lignin-based polymeric materials

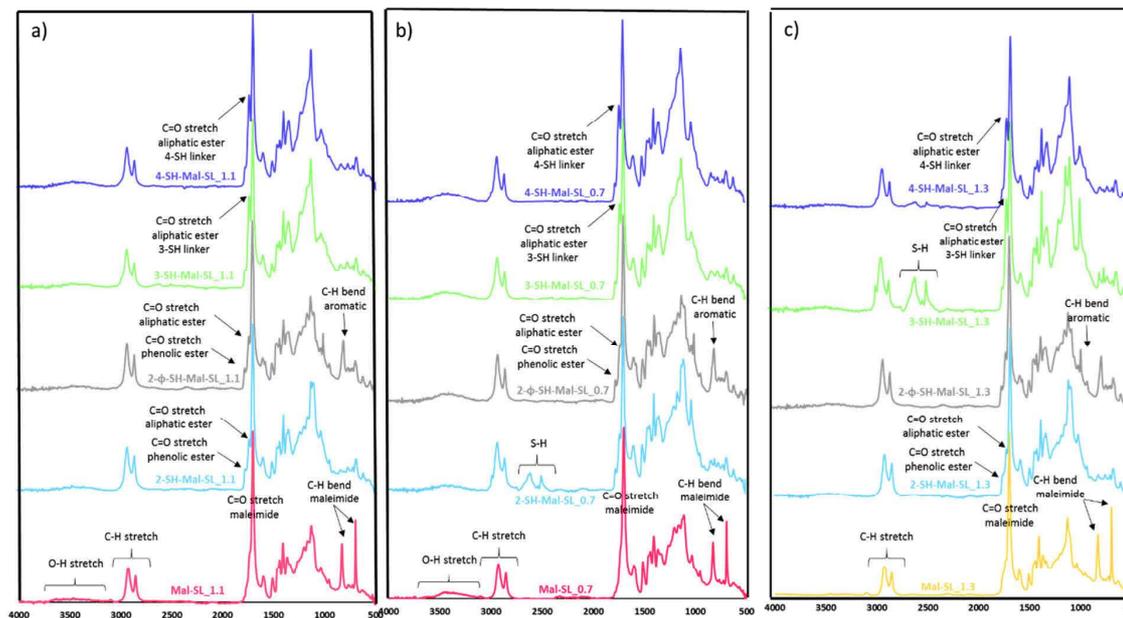


Figure S2.3. FTIR spectra of the materials prepared with Mal-SL_1.1 (a) Mal-SL_0.7 (b) and Mal-SL_1.3 (c). 2-SH-Mal-SL_0.7, 3-SH-Mal-SL_1.3 and 4-SH-Mal-SL_1.3 were not washed prior to analysis because of their partial solubility in methanol, unlike all other materials.

Evaluation of the structure of the thiol-maleimide networks

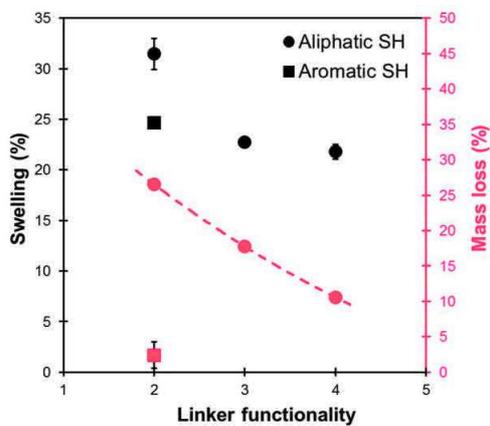


Figure S2.4. Swelling and mass loss in methanol of the materials prepared with Mal-SL_1.1 depending on the linker functionality.

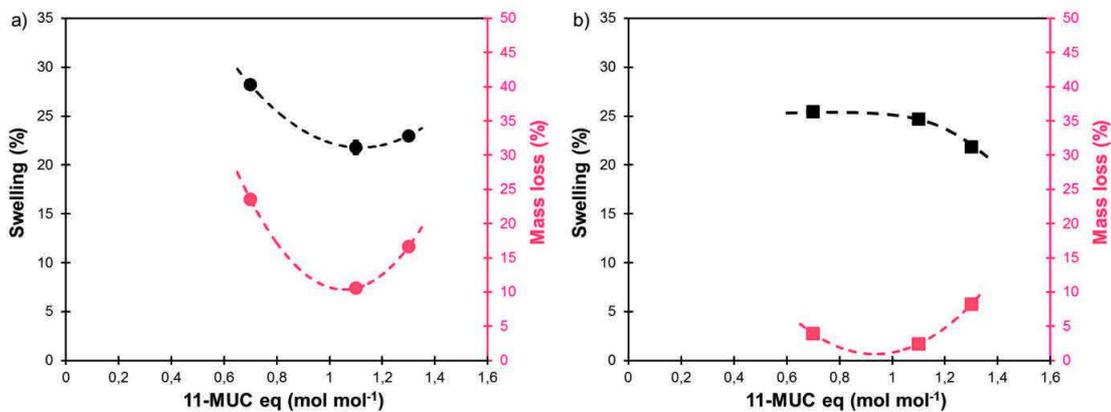


Figure S2.5. Swelling and mass loss in methanol of the materials prepared with 4-SH linker (a) and 2-φ-SH linker (b) depending on the amount of 11-MUC used to derivatize the lignin

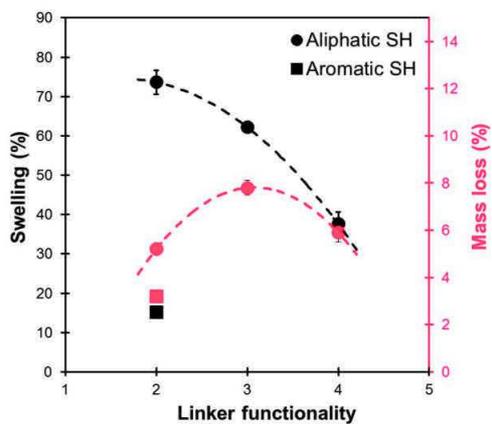


Figure S2.6. Swelling and mass loss in water of the materials prepared with Mal-SL_1.1 depending on the linker functionality.

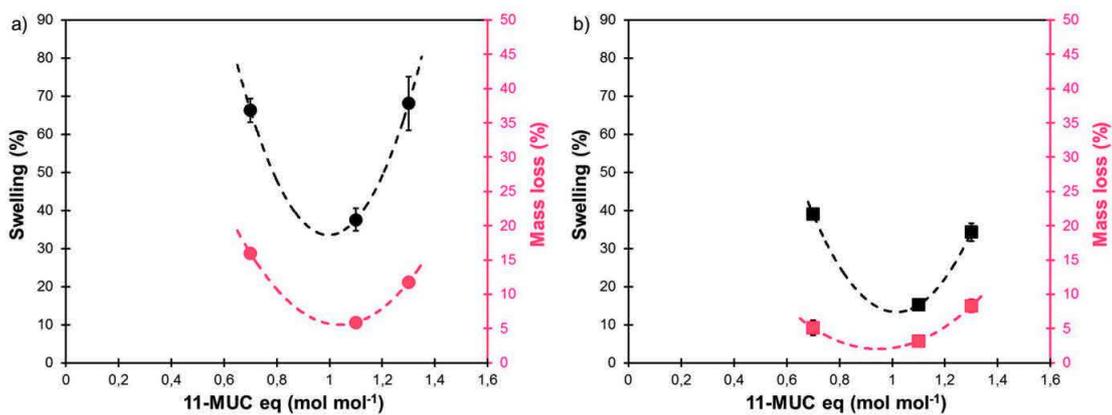


Figure S2.7. Swelling and mass loss in water of the materials prepared with 4-SH linker (a) and 2-φ-SH linker (b) depending on the amount of 11-MUC used to derivatize the lignin.

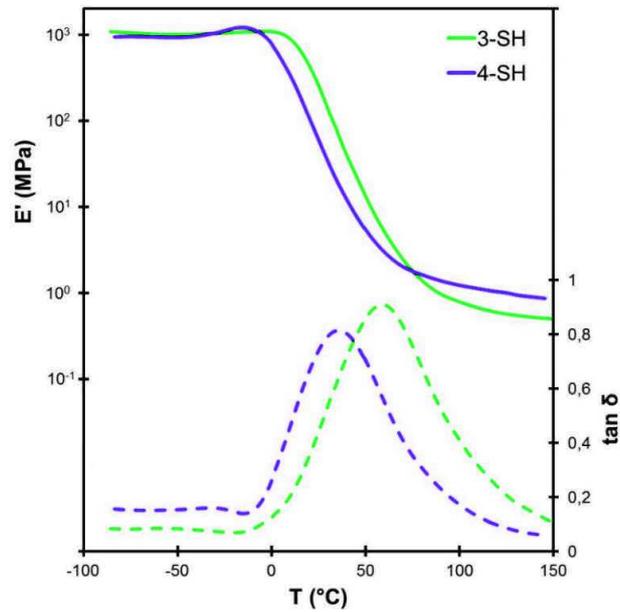


Figure S2.8. DMA of the materials prepared with Mal-SL_0.7: storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature.

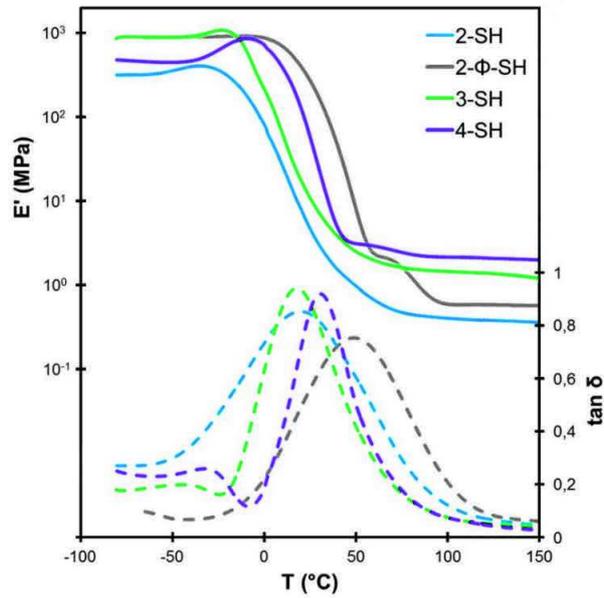


Figure S2.9. DMA of the materials prepared with Mal-SL_1.1: storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature.

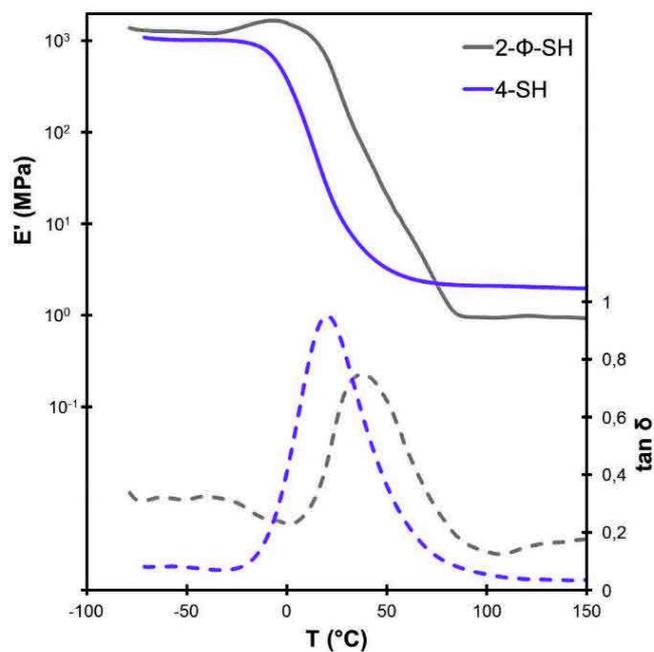


Figure S2.10. DMA of the materials prepared with Mal-SL_1.3: storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature

Thermal and mechanical properties of the thiol-maleimide lignin-based materials

Table S2.1. Thermal properties (TGA, DSC) of the thiol-maleimide lignin-based materials

	TGA		DSC	
	$T_{95\%}$ (° C)		T_g (° C)	
2-SH-Mal-SL_1.3 ^a	227 ± 6		-14.6 ± 0.7	
3-SH-Mal-SL_1.3 ^a	214 ± 9		-8.0 ± 0.9	
4-SH-Mal-SL_1.3	192 ± 3		-1.8 ± 0.8	
2-φ-SH-Mal-SL_1.3	201		5.7 ± 0.4	
2-SH-Mal-SL_1.1	249 ± 3		-14.0 ± 1.5	
3-SH-Mal-SL_1.1	221 ± 7		-2 ± 0.6	
4-SH-Mal-SL_1.1	241 ± 9		6.4 ± 0.6	
2-φ-SH-Mal-SL_1.1	250 ± 9		15.2 ± 1.5	
2-SH-Mal-SL_0.7 ^a	206 ± 7		-8 ± 2.9	
3-SH-Mal-SL_0.7	227 ± 6		5.9 ± 2.6	
4-SH-Mal-SL_0.7	185 ± 3		-3.4 ± 0.9	
2-φ-SH-Mal-SL_0.7 ^b	213 ± 7		21.2 ± 1.7	

Table S2.2. Uniaxial tensile properties of the thiol-maleimide lignin-based materials

	Tensile Test		
	E' (Mpa)	ε (%)	σ _{max} (Mpa)
2-SH-Mal-SL_1.3 ^a			
3-SH-Mal-SL_1.3 ^a			
4-SH-Mal-SL_1.3	3.2 ± 0.2	31.8 ± 3.1	0.5 ± 0.0
2-φ-SH-Mal-SL_1.3	22.8 ± 3.8	47.1 ± 0.7	3.5 ± 0.4
2-SH-Mal-SL_1.1	0.8 ± 0.1	96.2 ± 9.4	0.4 ± 0.0
3-SH-Mal-SL_1.1	2.4 ± 0.1	72.8 ± 3.1	1.0 ± 0.1
4-SH-Mal-SL_1.1	6.2 ± 0.4	58.8 ± 9.2	2.5 ± 0.4
2-φ-SH-Mal-SL_1.1	17.6 ± 2.5	77.4 ± 25.0	3.9 ± 0.6
2-SH-Mal-SL_0.7 ^a			
3-SH-Mal-SL_0.7	68.0 ± 5.2	52.8 ± 5.2	5.7 ± 0.4
4-SH-Mal-SL_0.7	8.4 ± 0.8	78.6 ± 11.5	2.6 ± 0.4
2-φ-SH-Mal-SL_0.7 ^b			

^a Could not be processed in 2 mm film.

^b Successfully processed in 2 mm film, but not analyzable by tensile test due to high brittleness.

Annexe II: Supporting information du chapitre 3

Synthesis of maleimide-functionalized SL (Mal-SL)

The ^{31}P NMR spectra (Figure S3.1b) revealed the almost disappearance of both phenolic and aliphatic OH groups during the reaction.

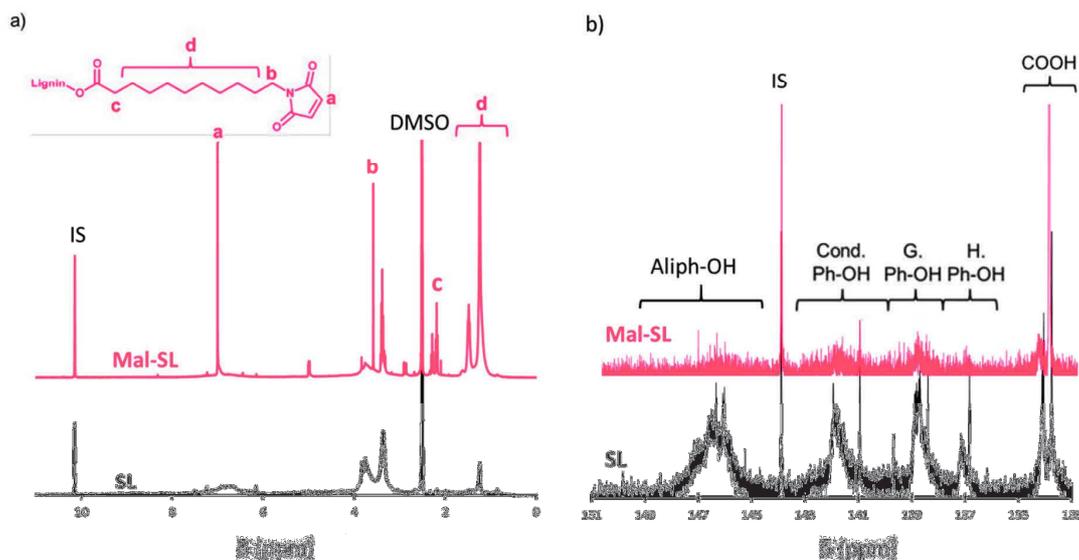


Figure S3.1. a) ^1H NMR of SL and Mal-SL in DMSO-d_6 . IS = internal standard (2,3,4,5,6-pentafluorobenzaldehyde). b) ^{31}P NMR of SL and Mal-SL. IS = internal standard (cholesterol).

Considering the initial content of OH groups in SL (5.2 mmol g^{-1}) and the mass increase caused by the grafting, the content of maleimide groups in the final material can be calculated from the conversion by using Equation (S3.1)

$$x_{\text{maleimide}} (\text{mol g}^{-1}) = \frac{\chi_{\text{OH}} \times [\text{OH}]_{\text{tot}}}{1 + \chi_{\text{OH}} \times [\text{OH}]_{\text{tot}} \times 263.4} \quad (\text{S3.1})$$

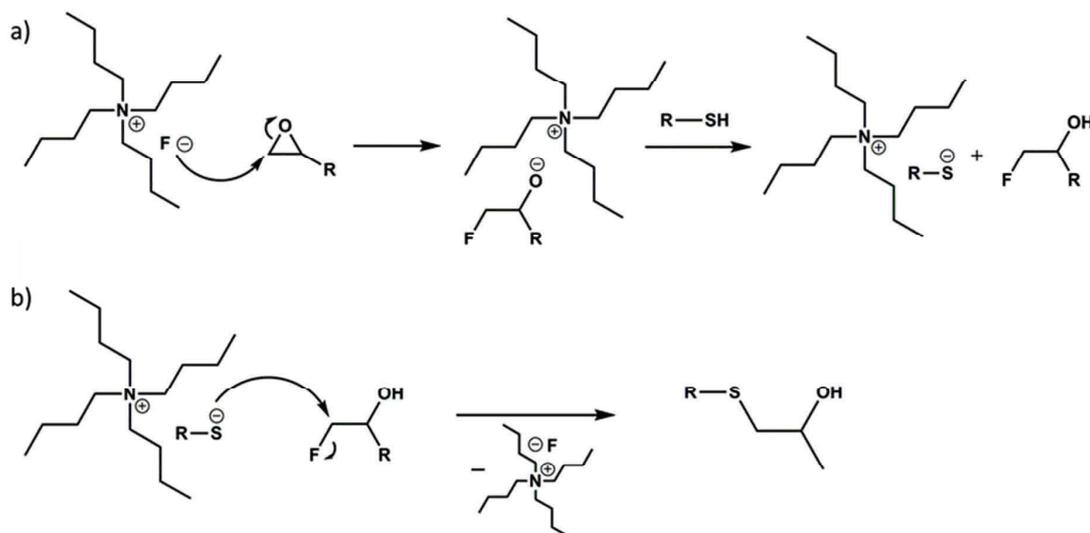
where χ_{OH} stands for the conversion of OH groups, $[\text{OH}]_{\text{tot}}$ is the total content of SL in OH groups (5.2 mmol g^{-1}) and 263.4 g mol^{-1} corresponds to the molar mass of the grafted chain ($= M_{11\text{-MUA}} - 18$). Mal-SL was also analysed by ^1H NMR spectroscopy (Figure S3.1a), which evidences a strong signal at 7.00 ppm belonging to the maleimide ring double-bond protons (2 H, signal a). The saturated side-chain of 11-MUA produces signals in the 0.75–1.75 ppm region (16 H, signal d), whereas the protons

close to the maleimide ring appear at 3.38 ppm (2 H, signal b), and the protons at the position with respect to the ester linkage appear at 2.18 ppm (2 H, signal c). This last signal is free from overlap with other lignin-related signals and was thus used to quantify the amount of grafted 11-MUA (Table S3.1).

Table S3.1. Content of maleimide groups in Mal-SL

	11-MUC [equiv.]	Maleimide content [mmol g ⁻¹]	
		By ³¹ P NMR	By ¹ H NMR
Mal-SL	1.0	1.91	2.10

Synthesis of poly-functional furan linkers



Scheme S3.1. a) Epoxy ring opening by fluoride anion and further formation of thiolate anion b) thioether linkage formation.

The linkers were analyzed by ¹H NMR spectroscopy which shows a significant shift of the proton's signal belonging to the epoxy moiety from 3.3 to 3.7 ppm (Figure S3.2a) after the ring opening, together with the appearance of a signal around 5.0 ppm and underlined in red in Figure S3.2a corresponding to the proton's signals of the newly formed hydroxyl groups. The detailed interpretation of the linker's ¹H and ¹³C NMR spectrum can be found in the following pages.

The furan content was accurately calculated by quantitative ^1H NMR by integrating the furan ring proton's signals and computing the average. The results are summarized below in Table S3.1.

Linker	M (g mol^{-1})	^1H NMR data				Furan content (mmol g^{-1})		Theoretical furan content
		$I_{7,62}$ ppm	$I_{6,42}$ ppm	mmol g^{-1}	mmol g^{-1}	Average	SD	
2 S-Fur	491,2	3,25	6,83	4,69	4,92	4,81	0,12	4,07
3 S-Fur	862,3	1,64	3,44	3,71	3,89	3,80	0,09	3,48
4 S-Fur	1105,3	1,46	3,06	3,66	3,84	3,75	0,09	3,62
2 ϕ S-Fur	558,7	1,54	3,21	3,91	4,07	3,99	0,08	3,58

The reaction was confirmed by FTIR which evidences O-H stretching in the region between 3600 and 3300 cm^{-1} after the epoxy rings opening (Figure S3.2b). Peculiar vibrations are also observed intrinsically depending on the linker's chemical backbone and detailed in Figure S3.2b.

Finally the linkers were also analyzed by HRMS (Figures S3.6, S3.10, S3.14 and S3.18) and for all of them signals corresponding to their $[\text{M}+\text{H}]^+$ were detected.

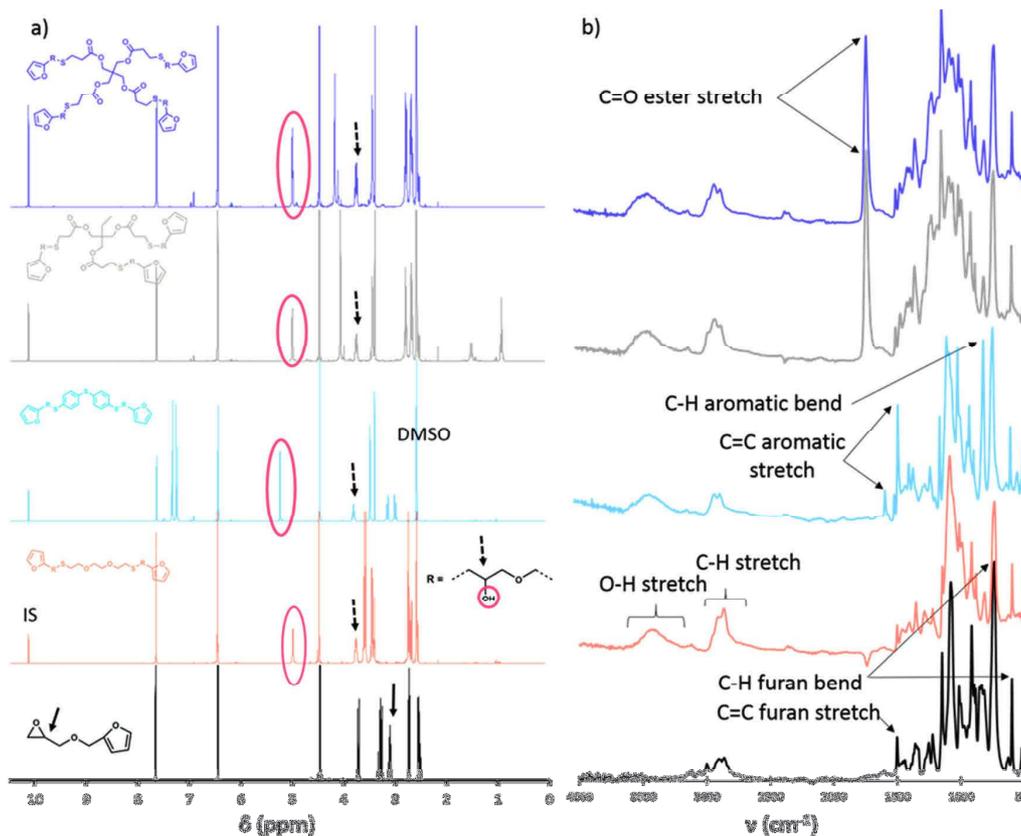


Figure S3.2. a) ^1H NMR and b) FTIR spectrum of polyfunctional furan linkers.

Furfuryl Glycidyl Ether

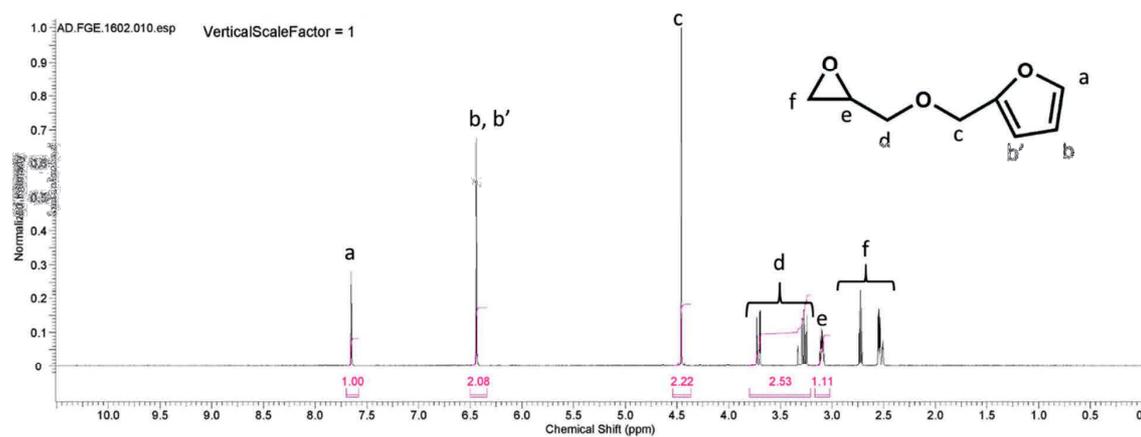


Figure S3.3. ^1H NMR of Furfuryl Glycidyl Ether (FGE).

2 S – Fur characterization

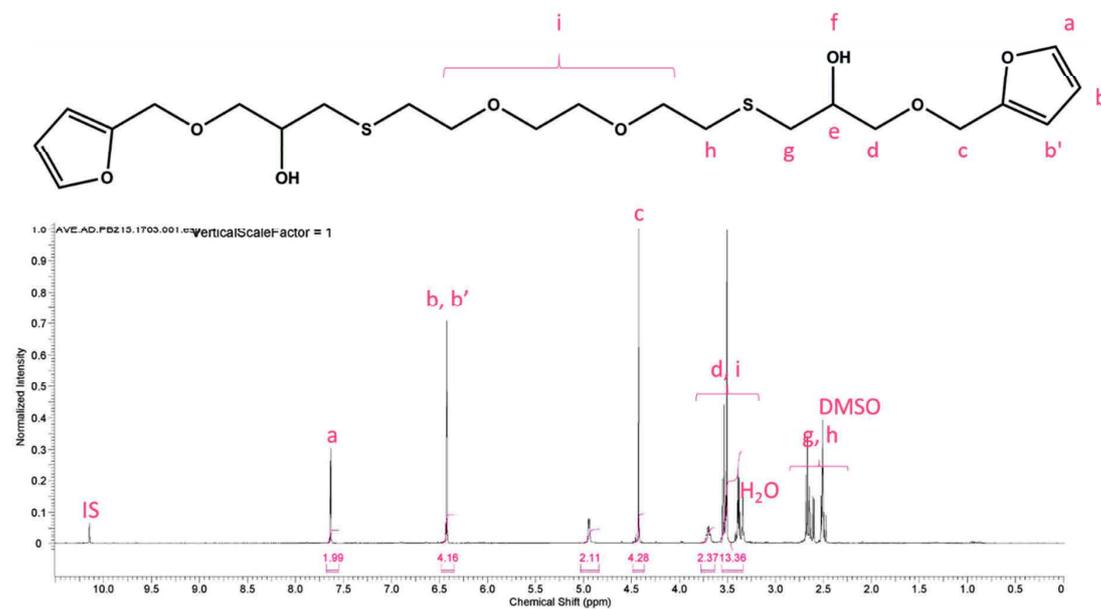


Figure S3.4. ¹H NMR interpretation for of 2 S – Fur

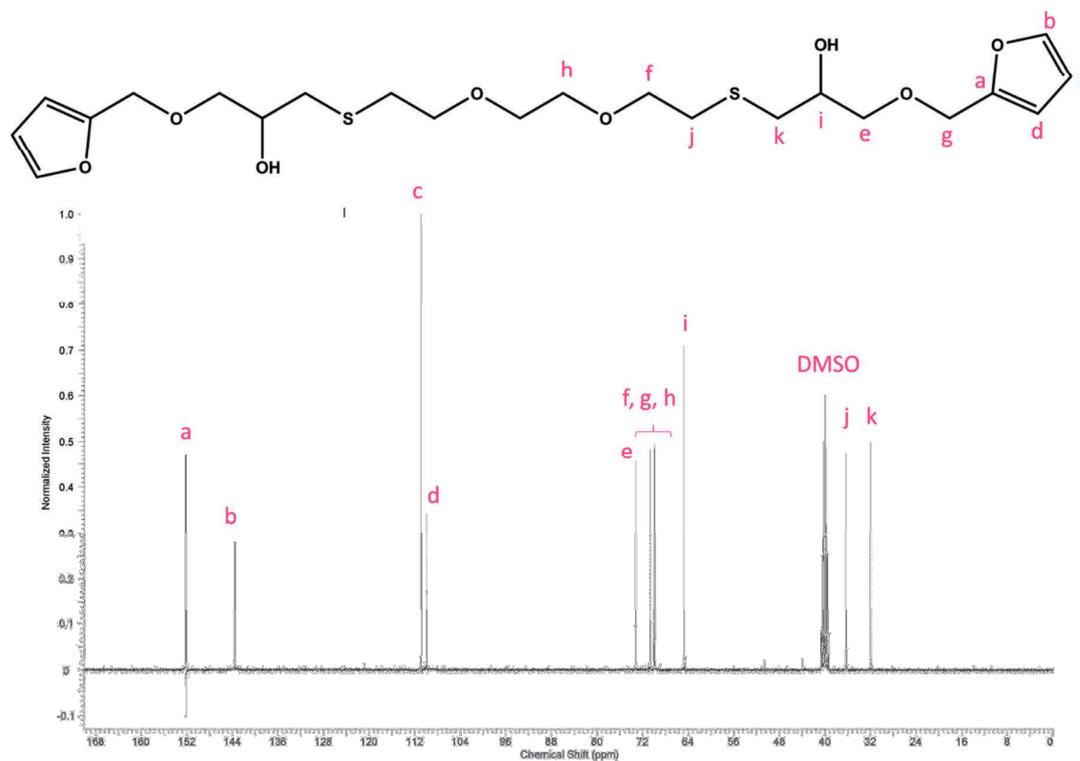


Figure S3.5. ¹³C NMR interpretation for of 2 S – Fur.

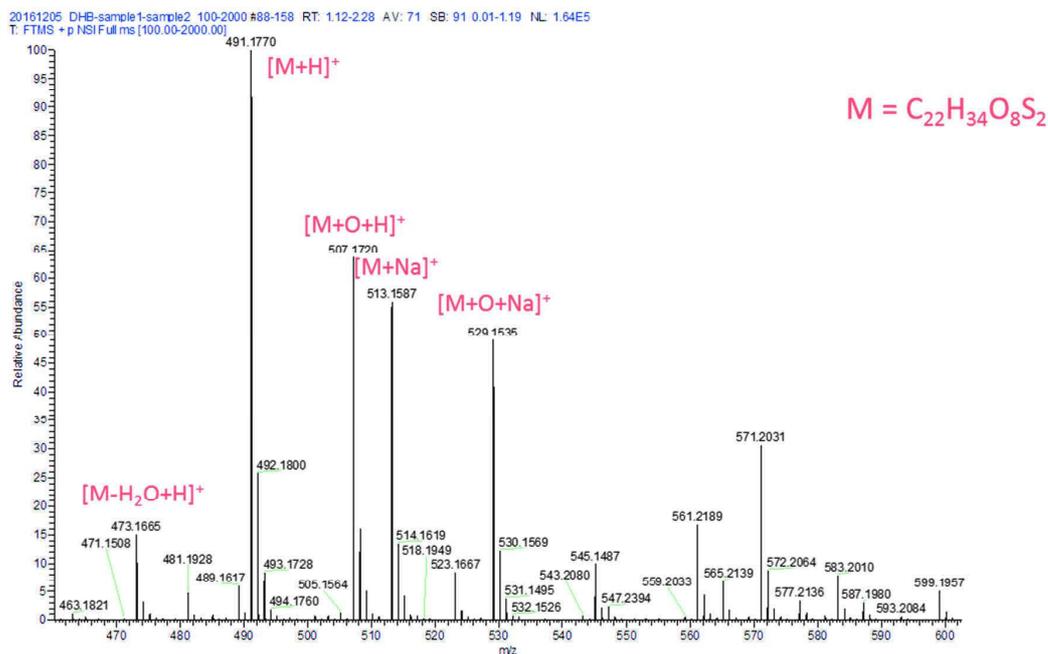


Figure S3.6. HRMS analysis of 2 S – Fur.

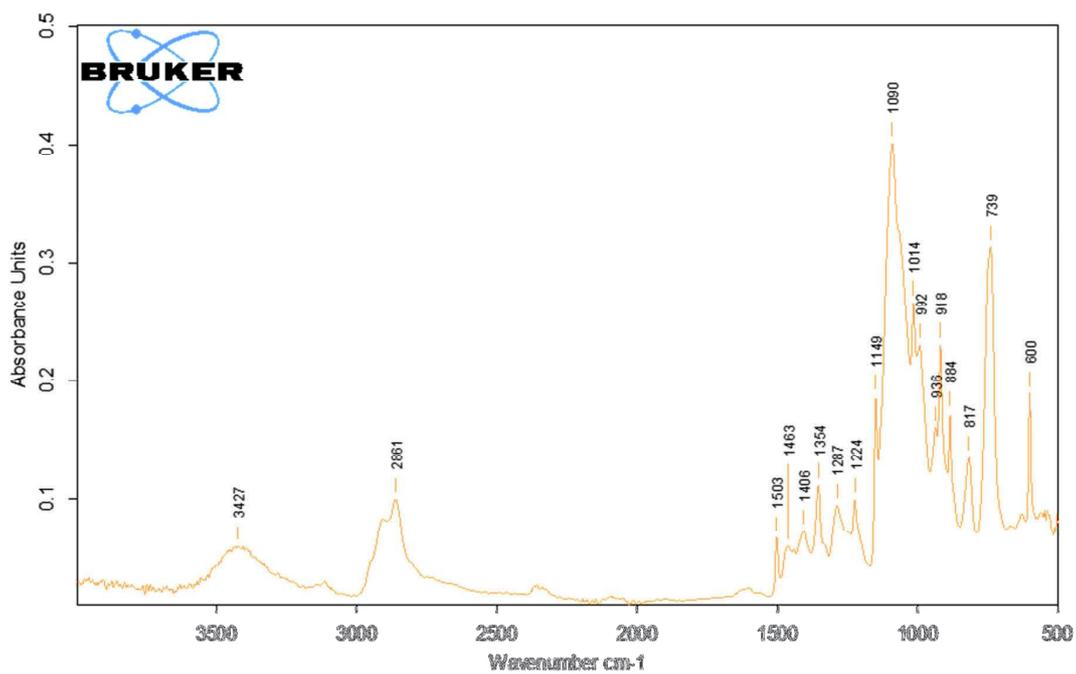


Figure S3.7. FTIR spectrum of 2 S – Fur.

2φ S – Fur Characterization

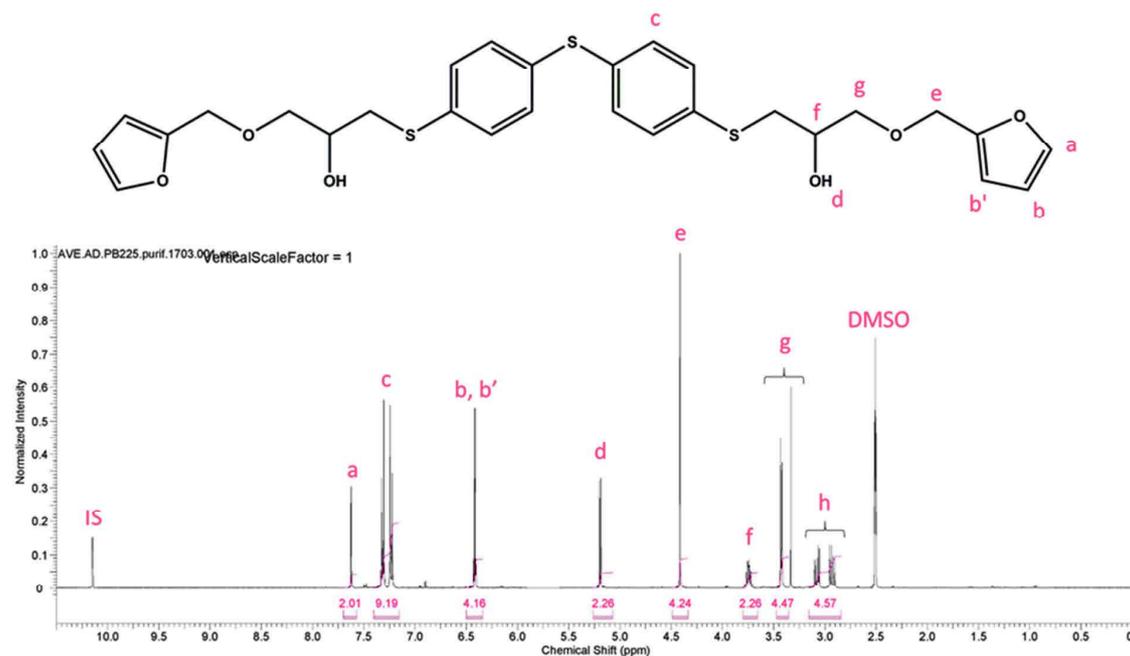


Figure S3.8. ¹H NMR interpretation for of 2φ S – Fur.

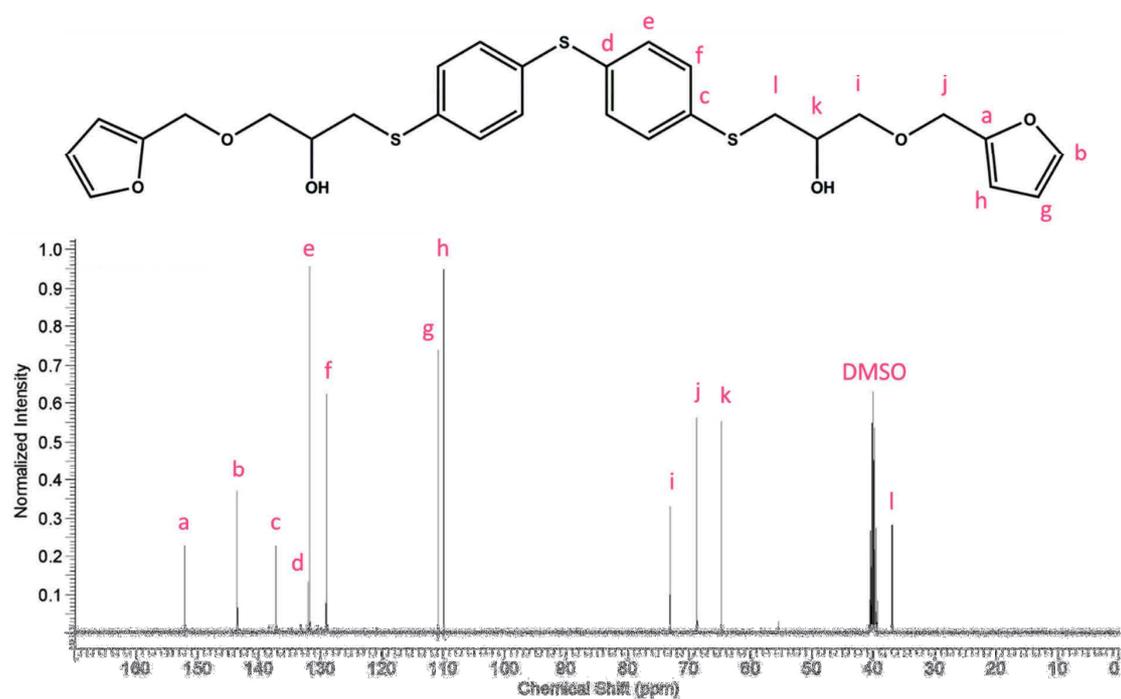


Figure S3.9. ¹³C NMR interpretation of 2 S – Fur.

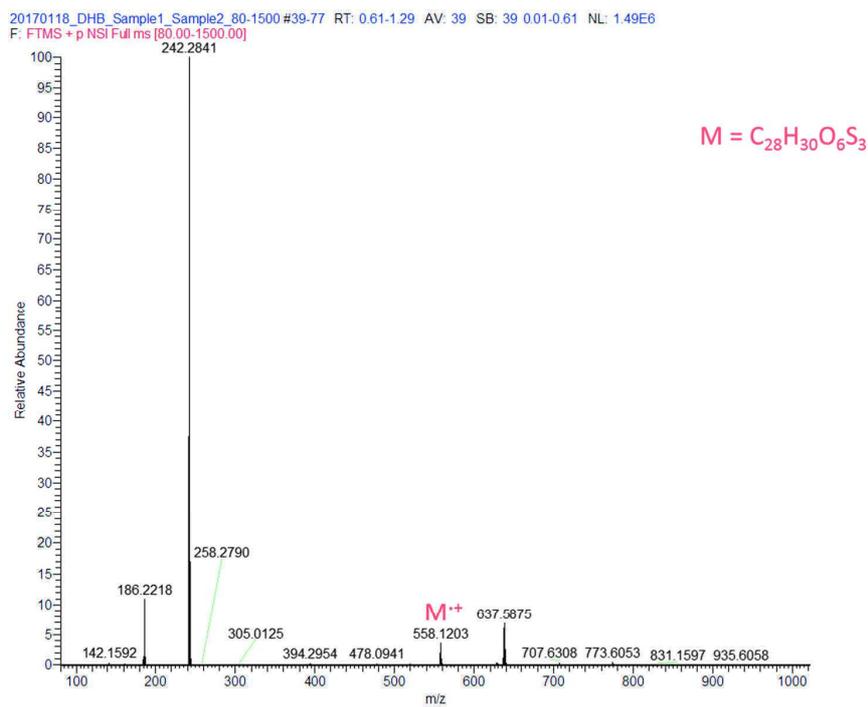


Figure S3.10. HRMS analysis of 2φ S – Fur.

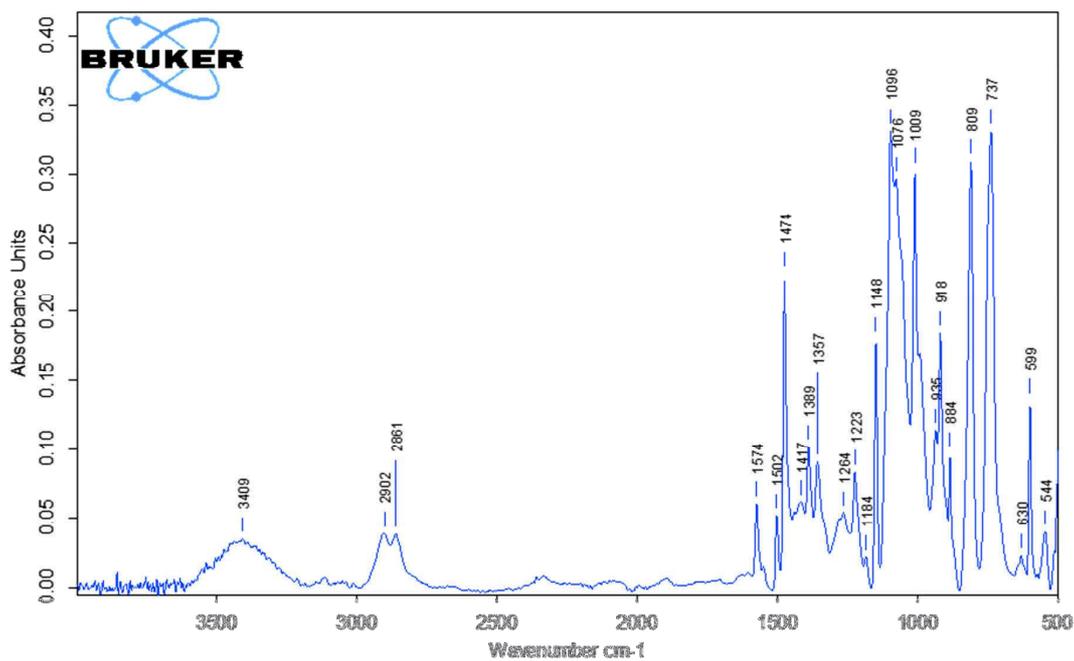


Figure S3.11. FTIR spectrum of 2φ S – Fur.

3 S – Fur characterization

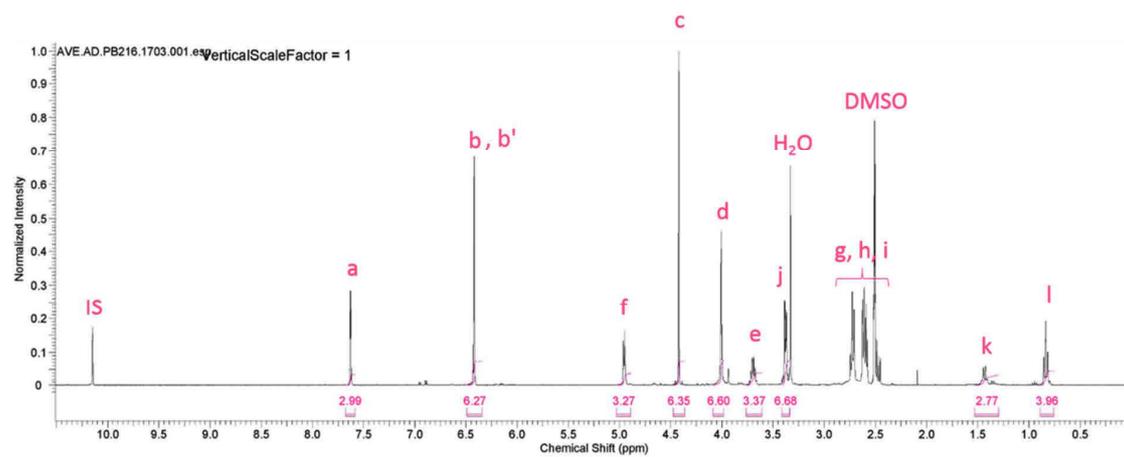
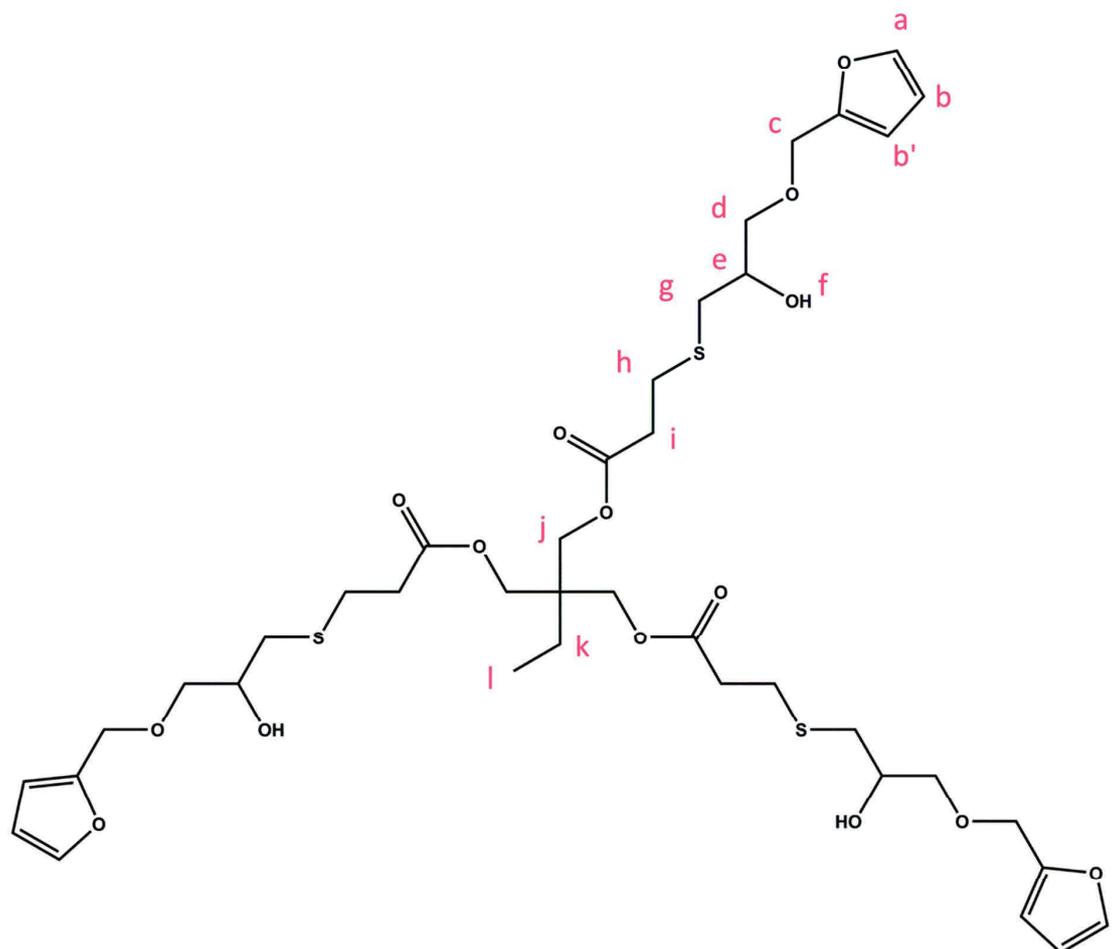


Figure S3.12. ¹H NMR interpretation for of 3 S – Fur.

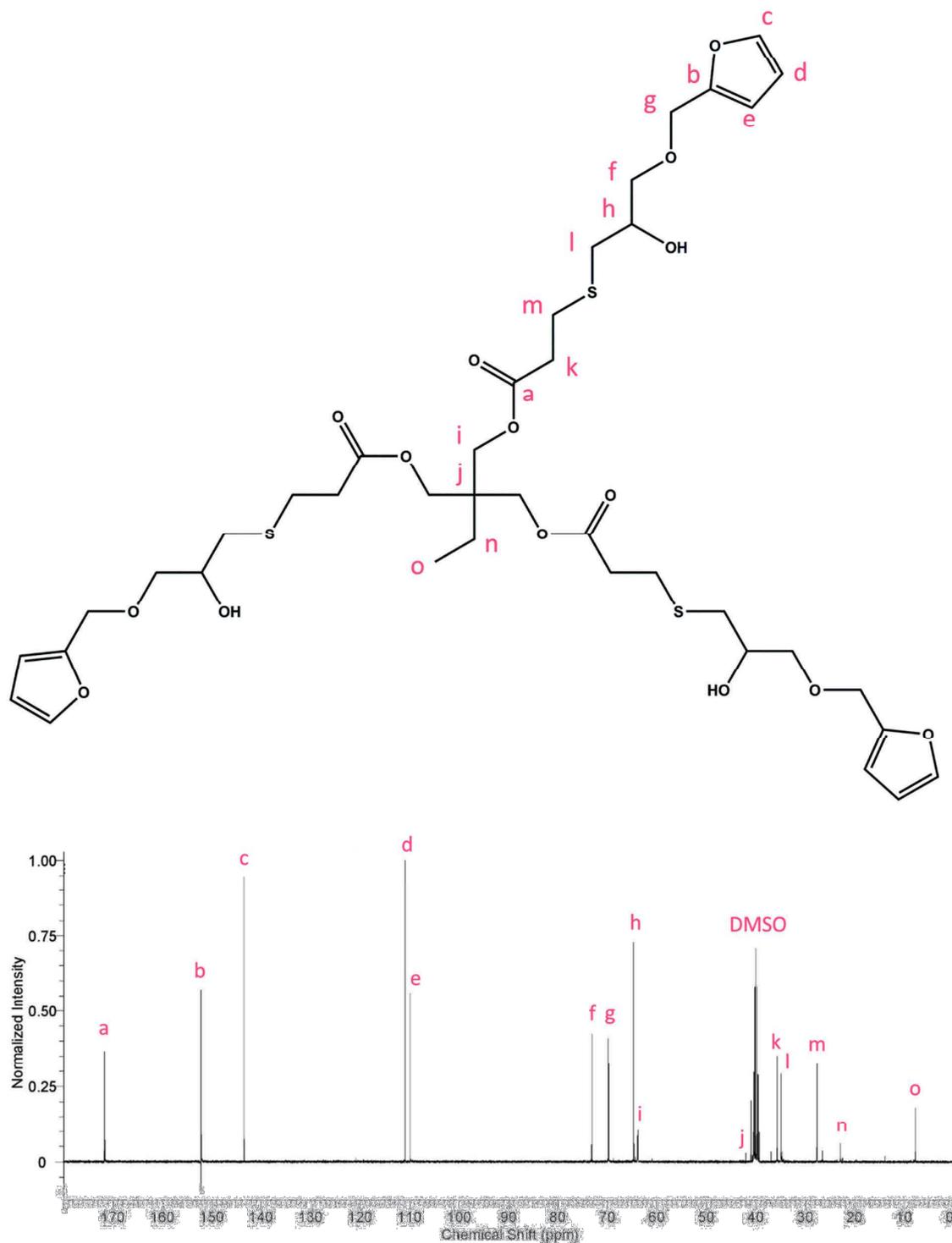


Figure S3.13. ^{13}C NMR interpretation of 3 S - Fur.

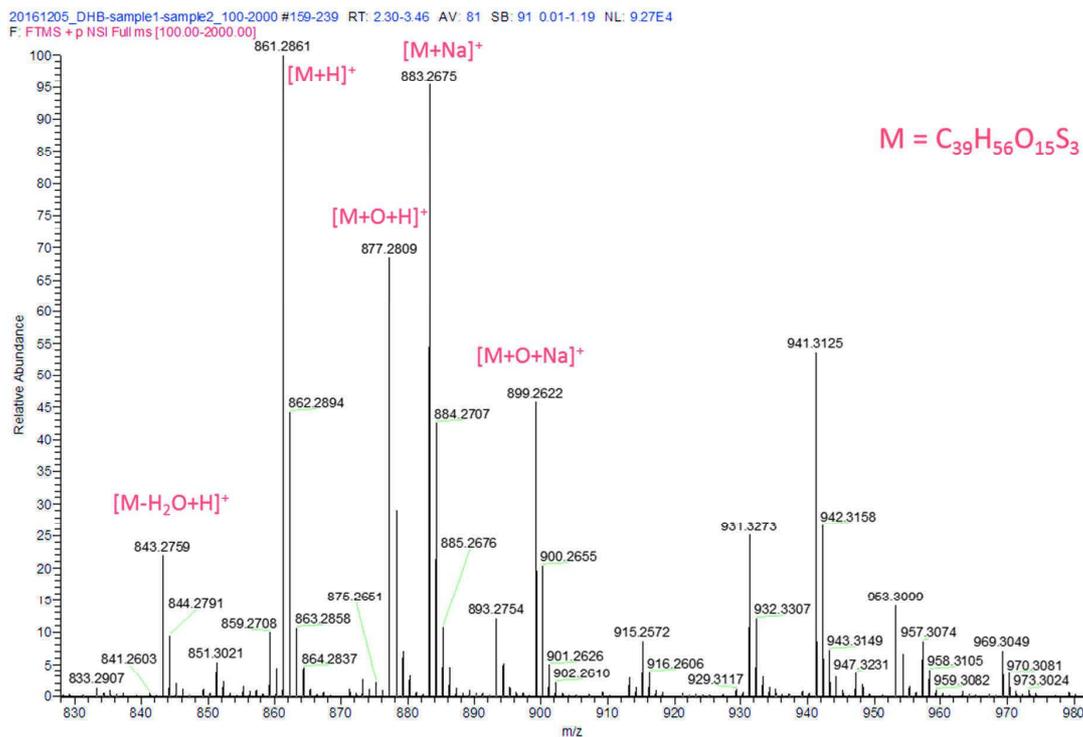


Figure S3.14. HRMS analysis of 3 S – Fur.

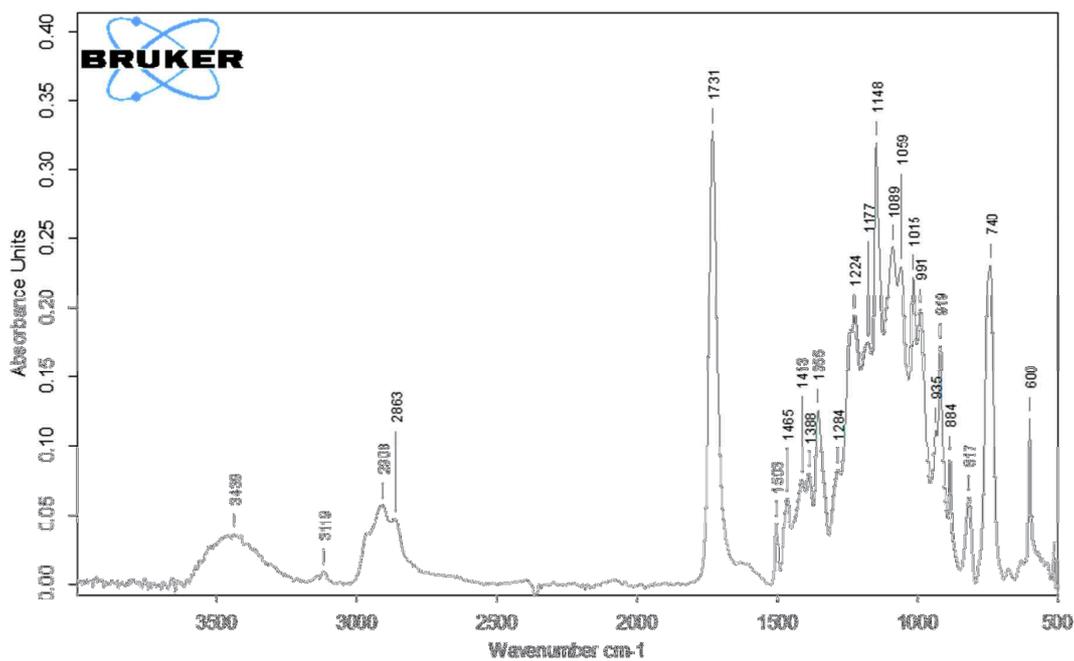


Figure S3.15. FTIR spectrum of 3 S – Fur.

4 S – Fur characterization

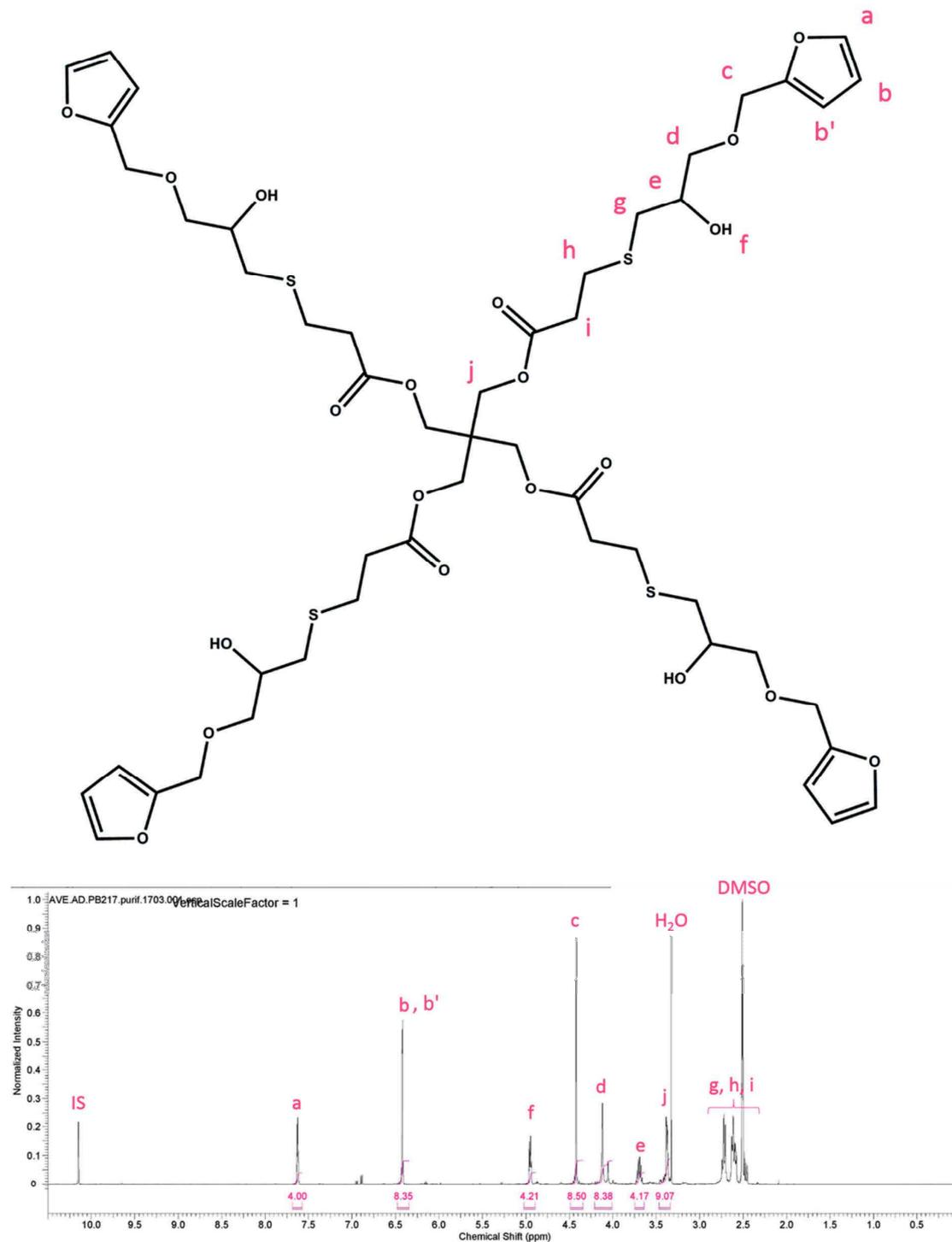


Figure S3.16. ^1H NMR interpretation for of 4 S – Fur.

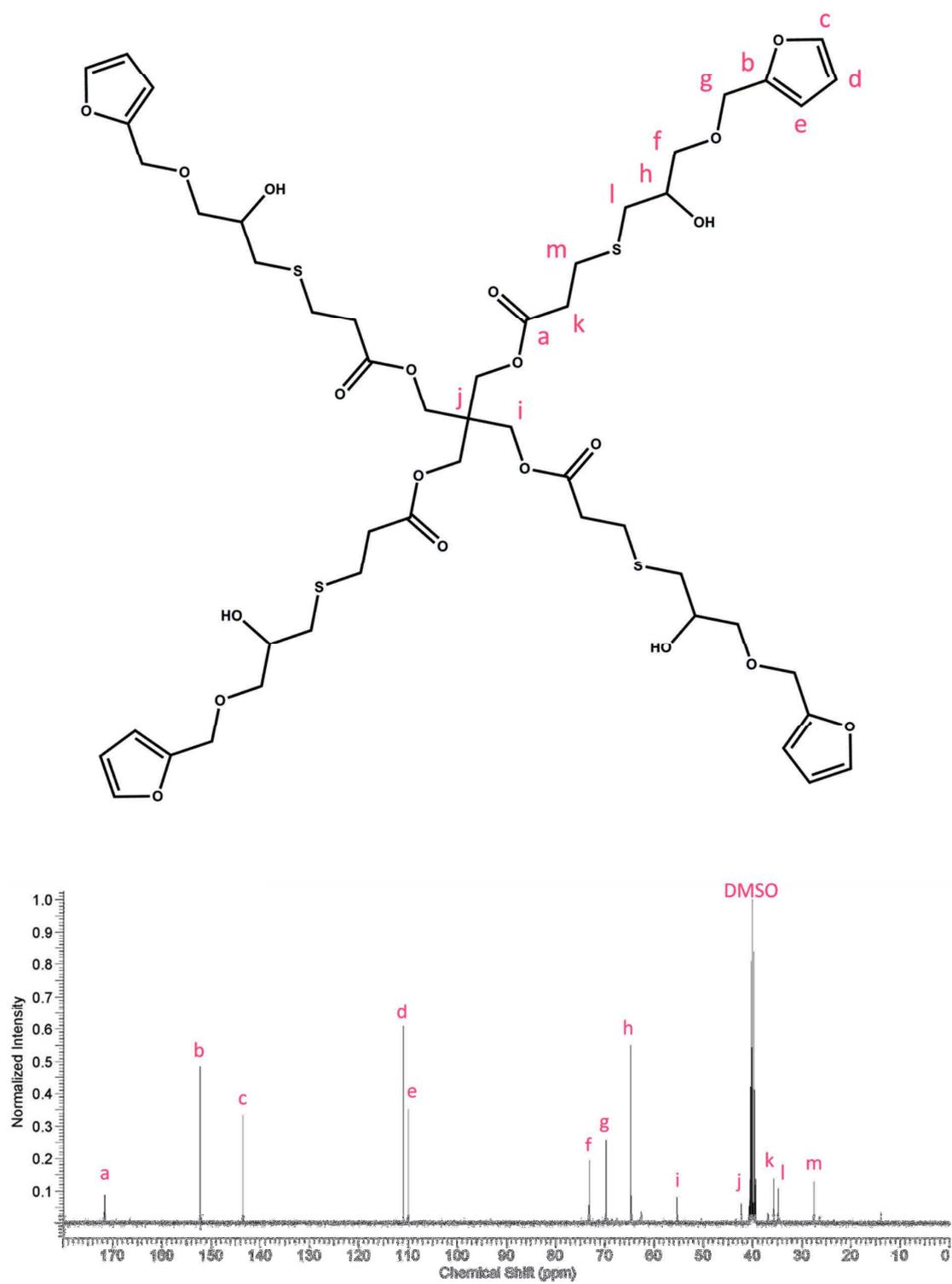


Figure S3.17. ^{13}C NMR interpretation of 4 S – Fur.

20170118_DHB_Sample1_Sample2_80-1500-240k #63-90 RT: 1.52-2.17 AV: 28 SB: 26 0.28-0.86 NL: 2.63E4
 F: FTMS + p NSI Full ms [250.00-1500.00]

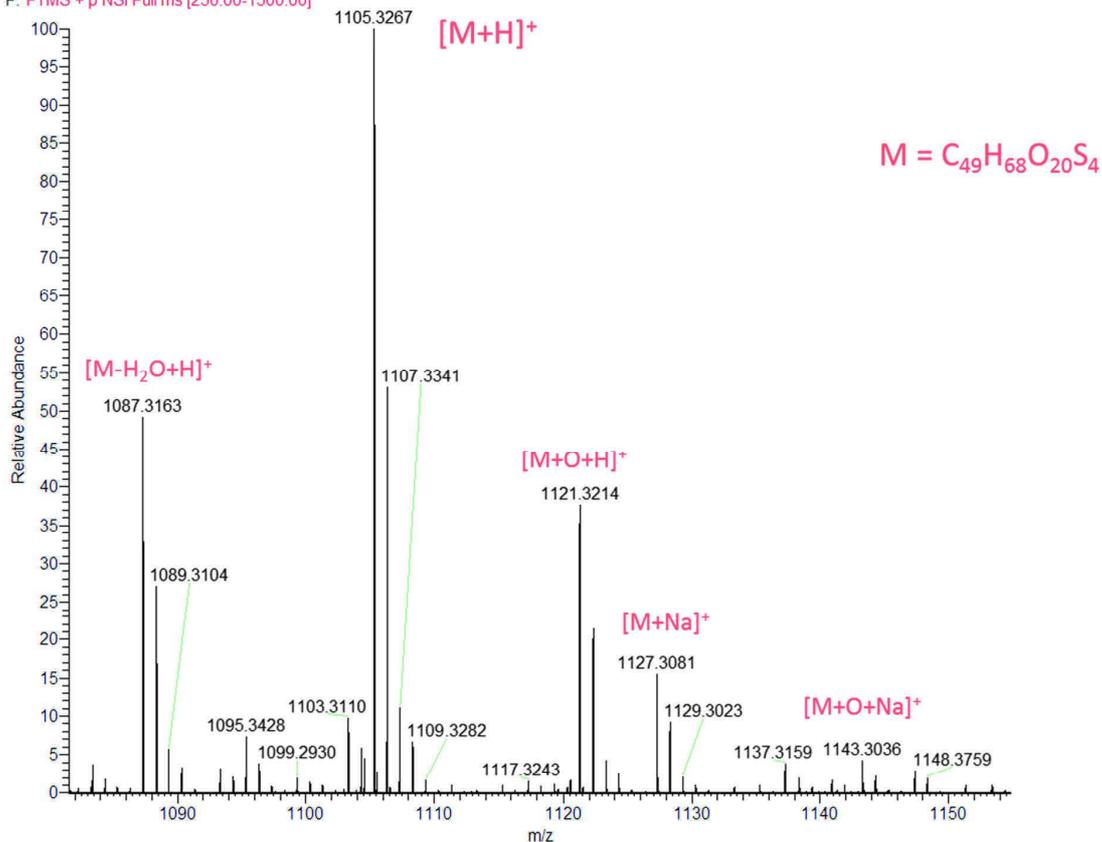


Figure S3.18. HRMS analysis of 4 S – Fur.

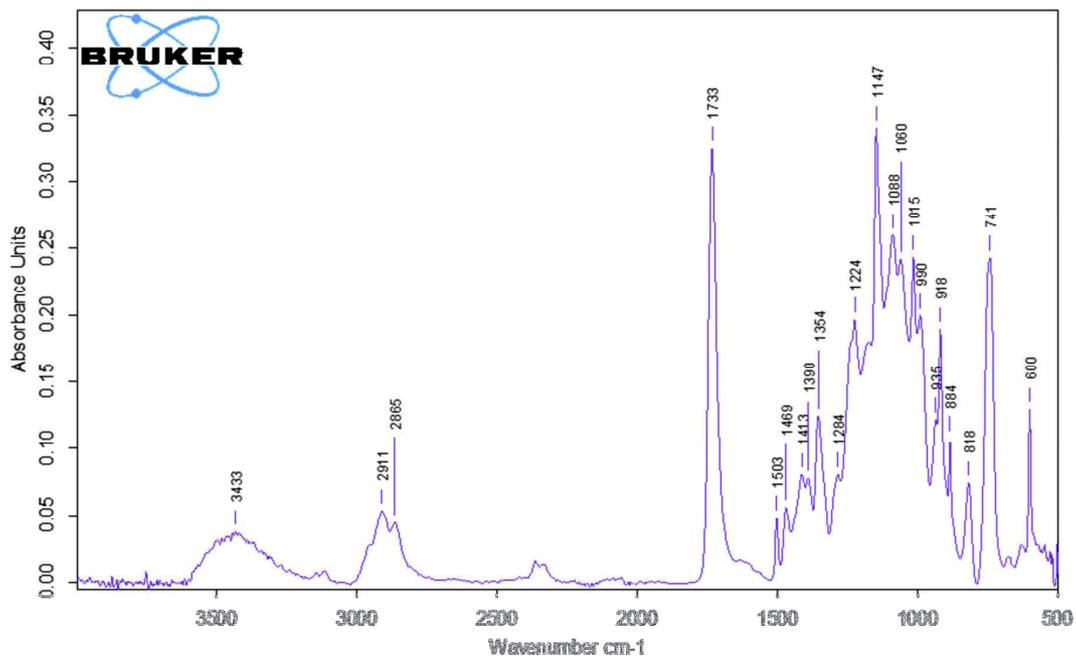


Figure S3.19. FTIR spectrum of 4 S – Fur

D-A polymerization and retro D-A

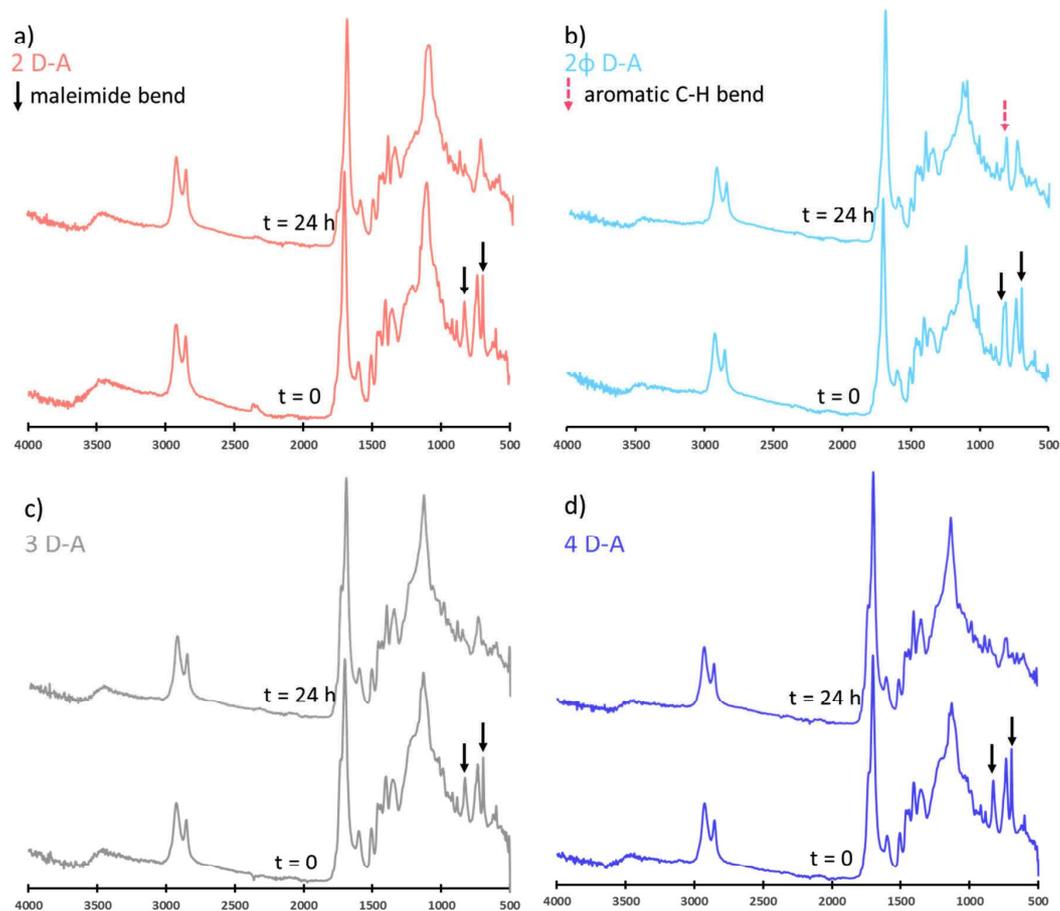


Figure S3.20. FTIR spectrum of the monomers mixture a) $t = 0$ and after 24h at 60°C a) 2 D-A b) 2ϕ D-A c) 3 D-A and d) 4 D-A.

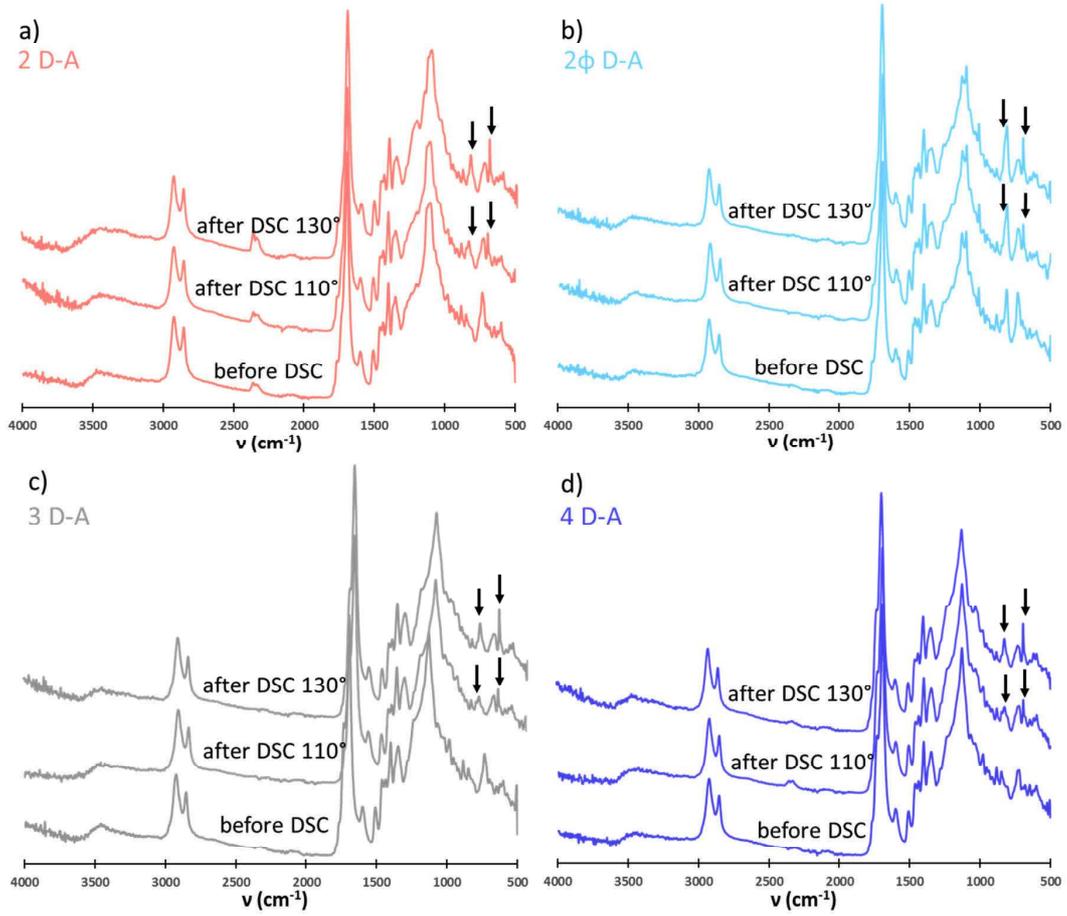


Figure S3.21. FTIR spectrum of the D-A materials before and after DSC analysis performed at 110 and 130 °C a) 2 D-A b) 2 ϕ D-A c) 3 D-A and d) 4 D-A.

Thermo-mechanical properties and reprocessing of lignin based D-A materials

Table S3.2. Thermo-mechanical properties of the lignin based D-A materials

	Tensile test			TGA	DSC	DMA	
	E (Mpa)	ε (%)	σ _{max} (Mpa)	T _{95%} (° C)	T _g (° C)	T _α (° C)	v _e (mol L ⁻¹)
<i>1st processing</i>							
2 D-A	0.4 ± 0.1	139.7 ± 12.3	0.4 ± 0.0	208 ± 2.0	-11.9 ± 2.5	8.0 ± 0.4	1.59
2φ D-A	13.6 ± 3.6	115.1 ± 9.4	1.7 ± 0.1	224 ± 2.5	9.8 ± 0.3	-	-
3 D-A	2.8 ± 0.4	103.2 ± 9.8	2.0 ± 0.2	227 ± 1.0	-0.85 ± 0.3	17.8 ± 0.1	3.25
4 D-A	4.5 ± 0.6	101.4 ± 9.7	3.6 ± 0.4	229 ± 1.0	0.9 ± 0.3	22.9 ± 0.2	4.53
<i>2nd processing</i>							
2 D-A	0.6 ± 0.0	140.2 ± 5.5	0.7 ± 0.0	209 ± 0.0	-5.7 ± 0.0	15.8 ± 1.0	1.25
2φ D-A	25.4 ± 8.1	42.7 ± 22.4	2.3 ± 0.7	214 ± 1.0	12 ± 0.6	-	-
3 D-A	3.8 ± 0.4	80.9 ± 8.9	1.9 ± 0.3	218 ± 1.0	3.5 ± 0.5	22.9 ± 0.3	3.66
4 D-A	9.3 ± 1.1	63.4 ± 17.6	2.7 ± 0.8	219 ± 1.0	5.7 ± 0.5	25.5 ± 0.4	4.20
<i>3rd processing</i>							
2 D-A	0.8 ± 0.1	130.2 ± 6.0	0.8 ± 0.0	224 ± 2.0	-6.30 ± 0.4	17.5 ± 1.2	1.27
2φ D-A	141.8 ± 16.0	10.2 ± 3.8	3.7 ± 0.2	233 ± 1.4	13.0 ± 0.4	-	-
3 D-A	6.7 ± 2.3	84.5 ± 3.4	2.8 ± 0.2	234.5 ± 0.7	5.6 ± 0.1	24.3 ± 0.8	2.94
4 D-A	15.2 ± 3.6	60.1 ± 17.3	4.2 ± 0.9	232 ± 0.0	8.4 ± 0.3	27.6 ± 0.8	3.77

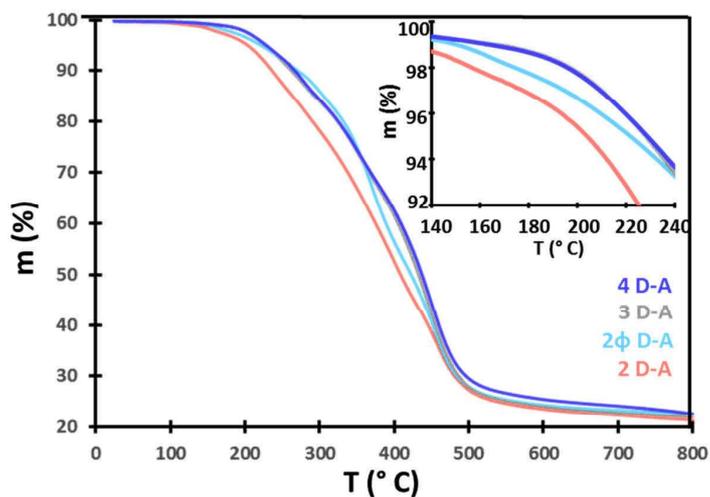


Figure S3.22. TGA analysis of the lignin based D-A materials.

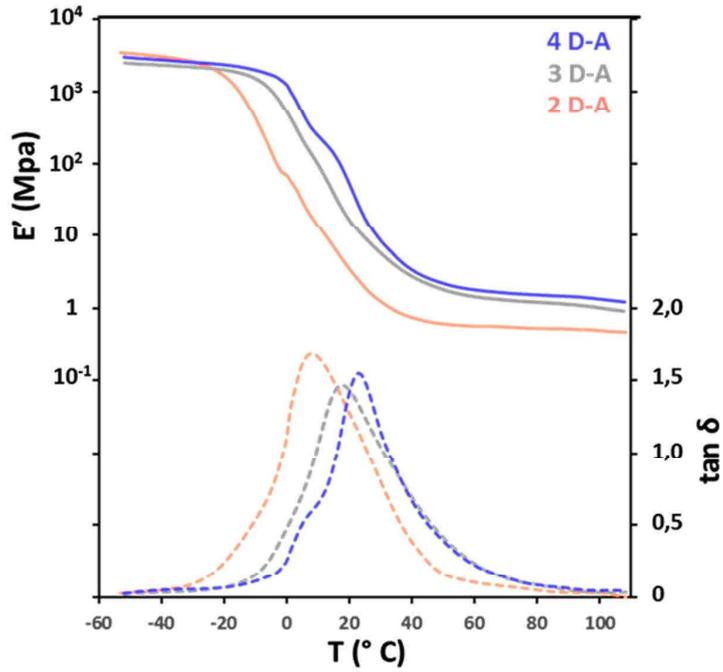


Figure S3.23. Storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature

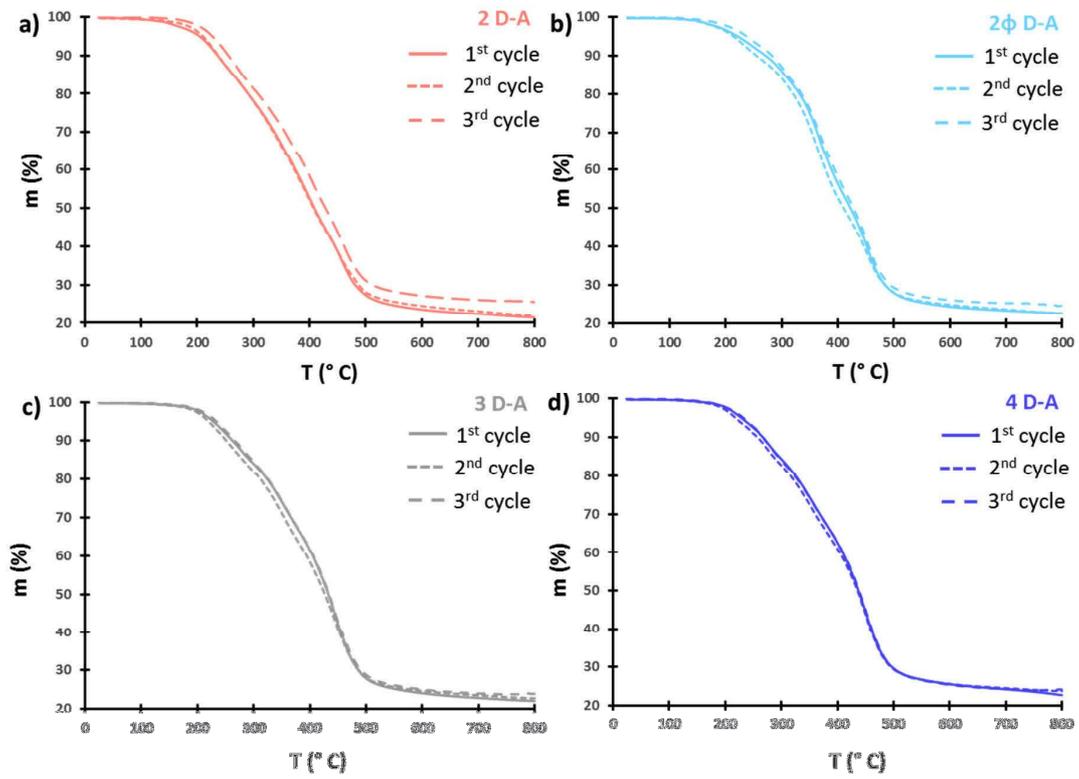


Figure S3.24. TGA curves before and after reprocessing of the D-A lignin based materials.

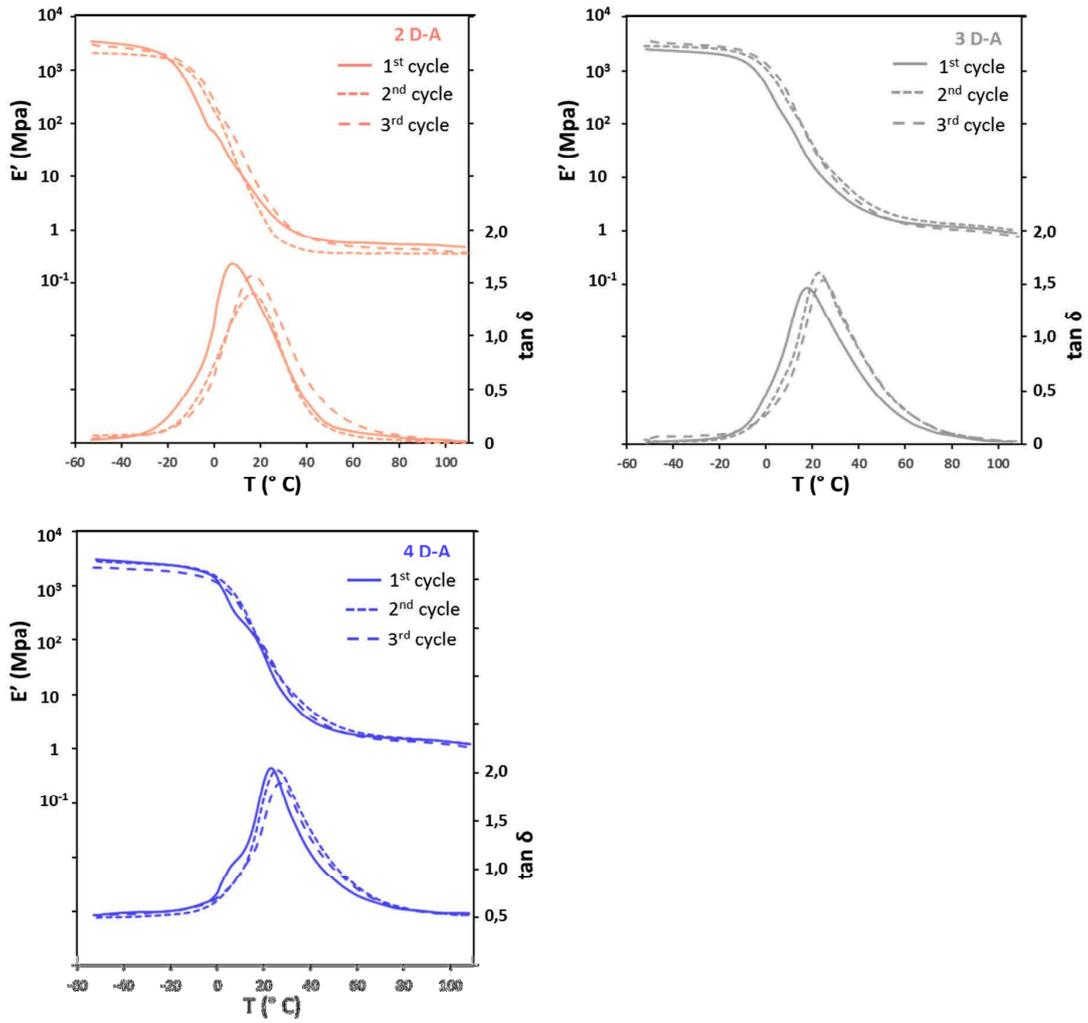


Figure S3.25. Storage modulus E' (solid lines) and loss factor $\tan \delta$ (dashed lines) depending on the temperature before and after reprocessing of the D-A lignin based materials.

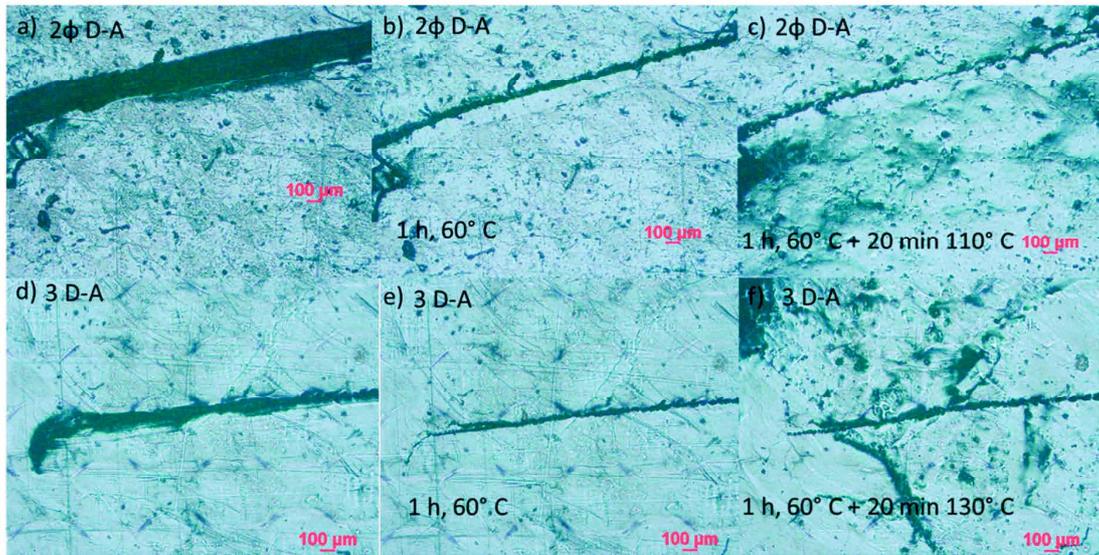


Figure S3.26. Optical microscope picture of a) 2φ D-A after scratch b) 2 D-A after curing at 60 °C for 1h c) 2φ D-A after curing at 60 °C for 1h with additional 20 min at 110 °C d) 3 D-A after scratch e) 3 D-A after curing at 60 °C for 1h f) 3 D-A after curing at 60 °C for 1h with additional 20 min at 130 °C.

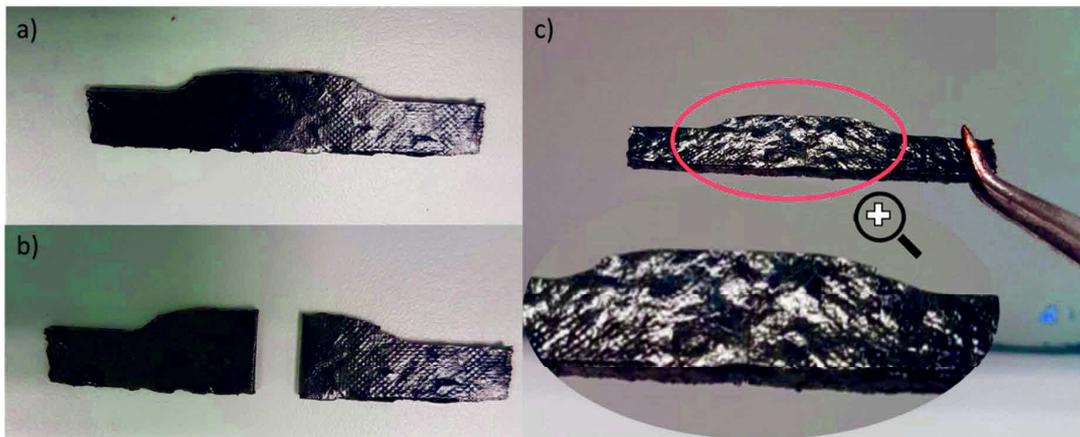


Figure S3.27. 4 D-A a) before the cut b) after the cut c) after the self-healing.

Annexe III: Supporting information du chapitre 4

Table S3.1. Quantification of the functional groups in the silylated lignins by ^{31}P (mmol g^{-1}) and ^1H NMR (mmol g^{-1})

	TBDMSCl eq.	Time (h)	By ^{31}P NMR						By ^1H NMR
			Al-OH	Cond. Ph-OH	G Ph-OH	H Ph-OH	Total Ph-OH	COOH	TBDMS
SL	-	-	1.80	1.61	1.09	0.46	3.16	0.90	-
Si-SL_01	0.4	18	1.07	1.28	0.85	0.35	2.48	0.55	0.67
Si-SL_02	0.8	18	1.05	0.88	0.53	0.21	1.62	0.46	1.78
Si-SL_03	1.2	18	0.44	0.15	0.07	0.03	0.25	0.23	2.71
Si-SL_04	2.5	18	0.30	0.00	0.00	0.00	0.00	0.32	2.38
Si-SL_05	5	18	0.29	0.00	0.00	0.00	0.00	0.45	3.37
Si-SL_06	1.2	1	0.69	0.52	0.30	0.15	0.98	0.35	2.85
Si-SL_07	1.2	3	0.58	0.27	0.15	0.05	0.47	0.28	3.20
Si-SL_08	1.2	5	0.65	0.33	0.16	0.08	0.57	0.36	3.41
Si-SL_09	2.5	1	0.44	0.21	0.00	0.00	0.21	0.41	3.40
Si-SL_10	2.5	3	0.39	0.00	0.00	0.00	0.00	0.33	3.48
Si-SL_11	2.5	5	0.63	0.00	0.00	0.00	0.00	0.46	2.77

Table S3.2. Quantification of the functional groups in the acetylated lignins by ^{31}P (mmol g^{-1}) and ^1H NMR (mmol g^{-1})

	Ac ₂ O eq.	Time (h)	By ^{31}P NMR						By ^1H NMR
			Al-OH	Cond. Ph-OH	G Ph-OH	H Ph-OH	Total Ph-OH	COOH	Acetyl
SL	-	-	1.80	1.61	1.09	0.46	3.16	0.90	-
Ac-SL_01	0.25	18	1.29	1.09	0.68	0.25	2.02	0.33	0.63
Ac-SL_02	0.5	18	1.19	0.82	0.50	0.17	1.50	0.34	<i>nd</i>
Ac-SL_03	0.75	18	1.18	0.58	0.31	0.10	1.00	0.57	2.27
Ac-SL_04	1	18	1.11	0.43	0.17	0.05	0.65	0.40	<i>nd</i>
Ac-SL_05	1.5	18	0.68	0.25	0.06	0.02	0.33	0.44	3.46
Ac-SL_06	2.5	18	0.00	0.00	0.00	0.00	0.00	0.90	4.31
Ac-SL_07	5	18	0.00	0.00	0.00	0.00	0.00	0.88	4.60

nd = not determined

Table S3.3. Solubility test for neat SL, acetylated SL (Ac-SL_06) and silylated SL (Si-SL_05).

Solvent	Boiling Point [° C]	Polarity Index [P]	SL	Ac-SL_06	Si-SL_05
Water	100	9.0	-	-	-
Water (NaOH 10%)	-	-	+++	-	-
DMSO	189	7.2	+++	++	+/-
DMF	155	6.4	+++	+++	+++
Pyridine	115	5.3	+++	+++	+++
Ethanol	78	5.2	+/-	-	-
Acetone	56	5.1	+/-	+++	+++
Methanol	65	5.1	+/-	-	-
1,4 Dioxane	101	4.8	+/-	++	++
Ethyl Acetate	77	4.4	-	+/-	+++
Chloroform	61	4.1	-	+++	+++
THF	65	4.0	+/-	+++	+++
Dichloromethane	41	3.1	-	+++	+++
Diethyl ether	36	2.8	-	-	+++
Hexane	69	0.0	-	-	-

+++ fully dissolved at 10% (w/v)

++ fully dissolved at 2.5% (w/v)

+/- partially soluble

- insoluble

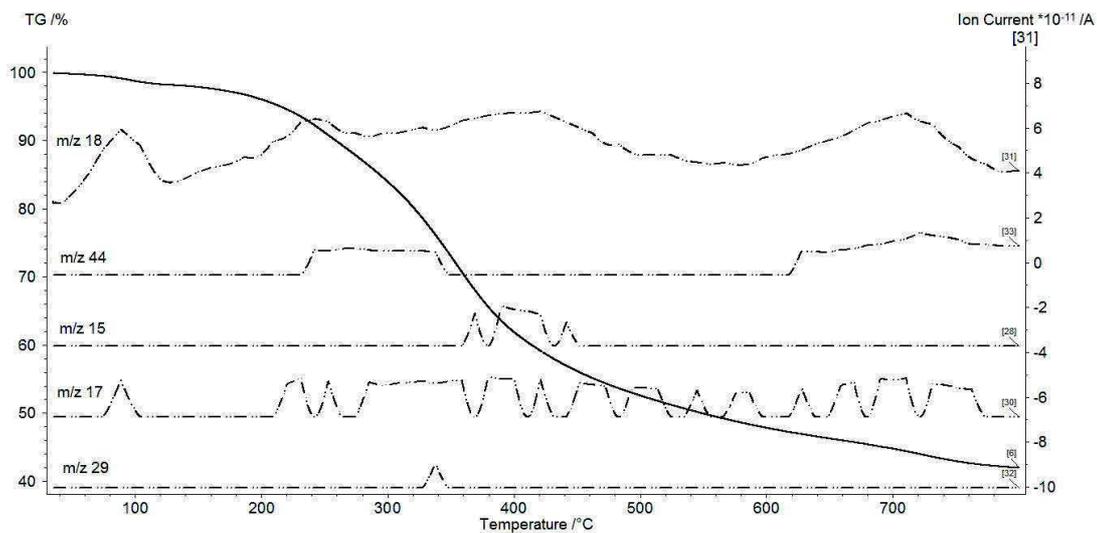


Figure S3.1. TGA coupled to MS of neat soda lignin (SL)

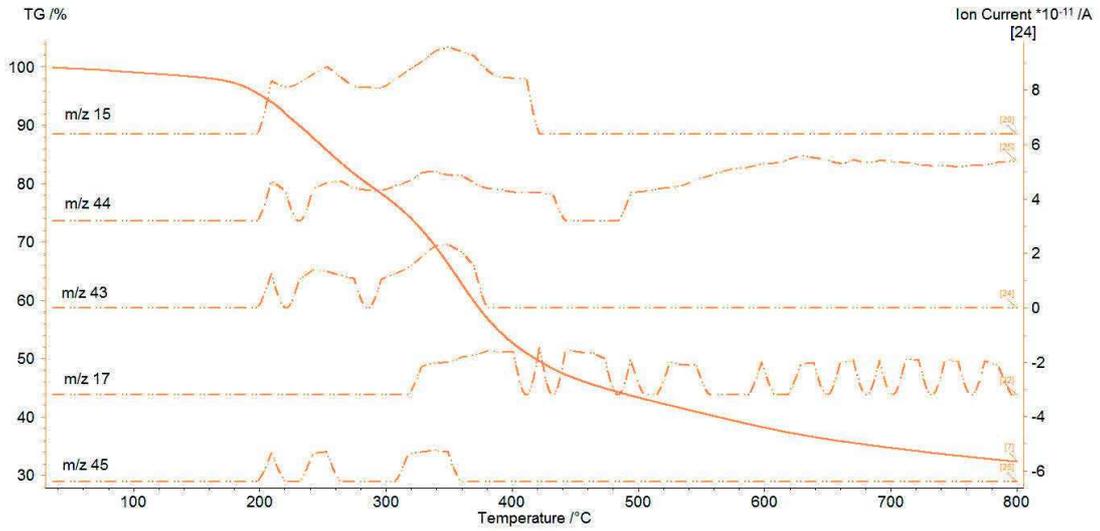


Figure S3.2. TGA coupled to MS of acetylated lignin (Ac-SL_06)

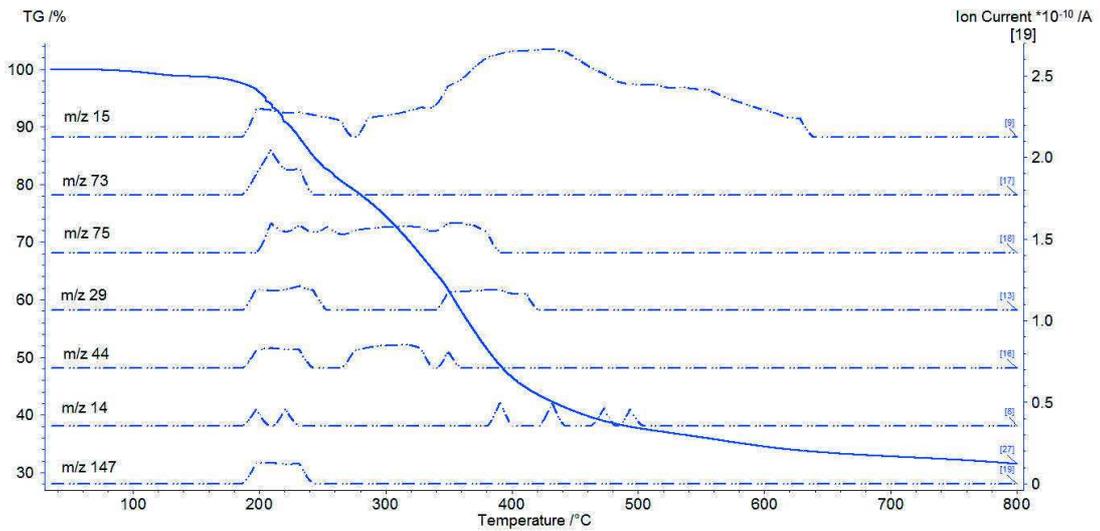


Figure S3.3. TGA coupled to MS of silylated lignin (Si-SL_05)

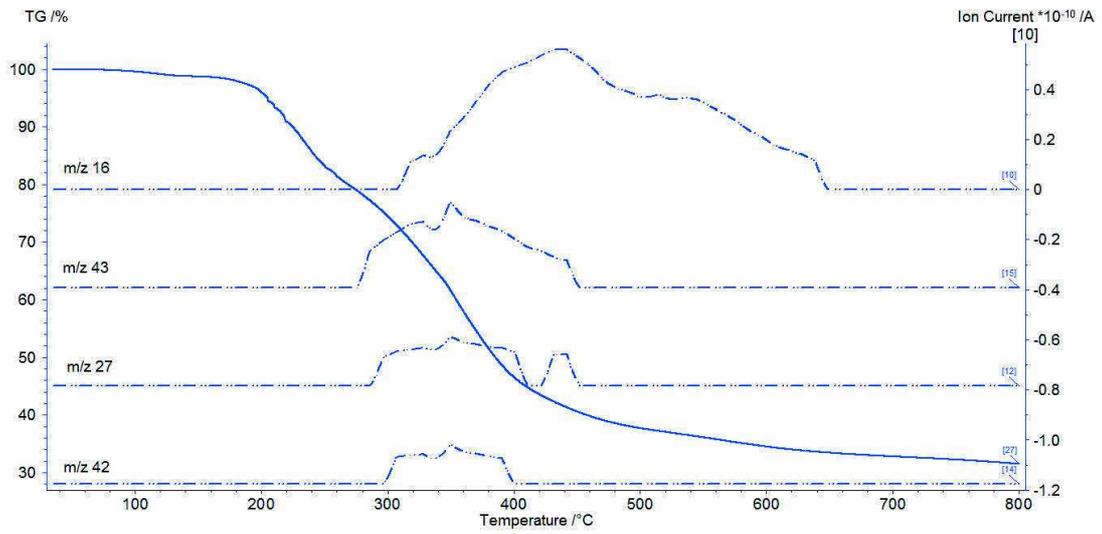


Figure S3.4. TGA coupled to MS of silylated lignin (Si-SL_05) (following)

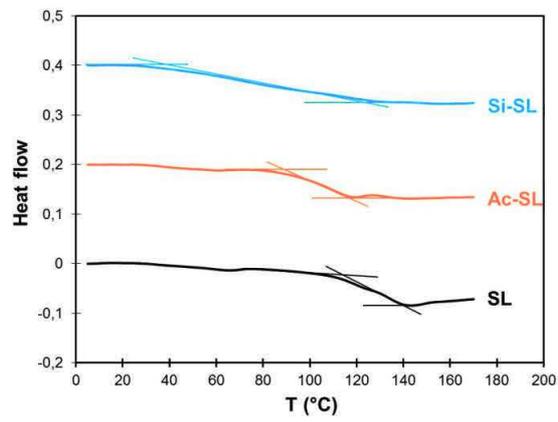


Figure S3.5. DSC traces of the neat (SL), acetylated (Ac-SL_06) and silylated lignins (Si-SL_05)

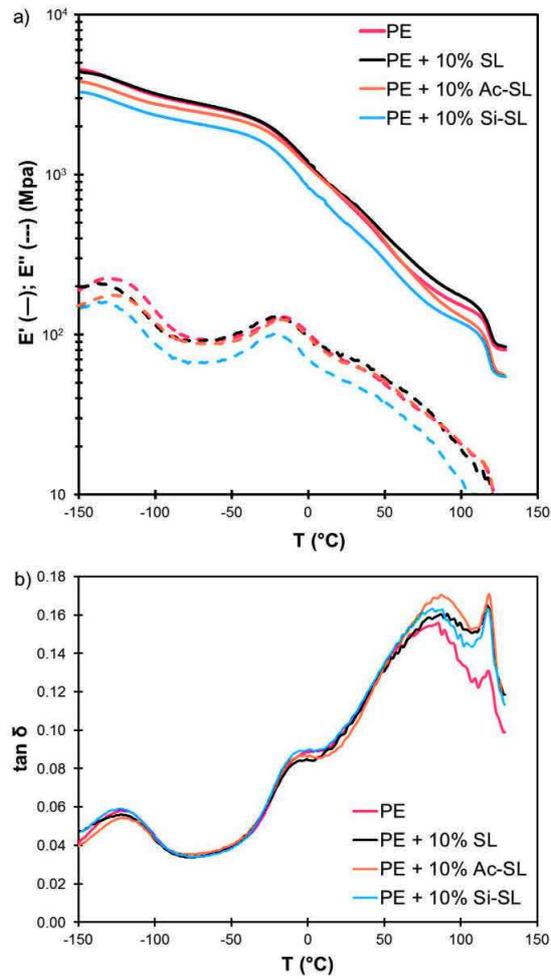


Figure S3.6. Dynamic mechanical analysis: storage E' and loss moduli E'' (a) and loss factor $\tan \delta$ (b) of LDPE and its blends with neat (SL), acetylated (Ac-SL_06) and silylated lignins (Si-SL_05).

LISTE COMPLETE DES REFERENCES BIBLIOGRAPHIQUES

- A, Hayashi, Kinoshita K, Taniguchi A, and Nakamura T. 1975. "Demethylation of lignin during pulping, 3: Correlation between oxidation product of quinones and lignin chromophore." *Journal of the Japan Wood Research Society*, 21 (8), 472-473.
- Abächerli, Alfred, and Frank Doppenberg. 2001. Method for preparing alkaline solutions containing aromatic polymers. US6239198 B1, filed March 20, 1998, and issued May 29, 2001.
- Abascal, Kathy, Lisa Ganora, and Eric Yarnell. 2005. "The Effect of Freeze-Drying and Its Implications for Botanical Medicine: A Review." *Phytotherapy Research* 19 (8): 655–60.
- Adzima, Brian J., H. Alan Aguirre, Christopher J. Kloxin, Timothy F. Scott, and Christopher N. Bowman. 2008. "Rheological and Chemical Analysis of Reverse Gelation in a Covalently Cross-Linked Diels–Alder Polymer Network." *Macromolecules* 41 (23): 9112–9117.
- Aguié-Béghin, Véronique, Laurence Foulon, Paola Soto, David Crônier, Elena Corti, Frédéric Legée, Laurent Cézard, et al. 2015. "Use of Food and Packaging Model Matrices to Investigate the Antioxidant Properties of Biorefinery Grass Lignins." *Journal of Agricultural and Food Chemistry* 63 (45): 10022–10031.
- Ahsan, Haseeb, Amjid Ahad, Jahangir Iqbal, and Waseem A. Siddiqui. 2014. "Pharmacological Potential of Tocotrienols: A Review." *Nutrition & Metabolism* 11: 52-59. doi:10.1186/1743-7075-11-52.
- Ahvazi, Behzad C., Claudia Crestini, and Dimitris S. Argyropoulos. 1999. "19F Nuclear Magnetic Resonance Spectroscopy for the Quantitative Detection and Classification of Carbonyl Groups in Lignins." *Journal of Agricultural and Food Chemistry* 47 (1): 190–201.
- Alexy, P., B. Kosíková, and G. Podstránska. 2000. "The Effect of Blending Lignin with Polyethylene and Polypropylene on Physical Properties." *Polymer* 41 (13): 4901–8.
- Anastas, Paul, and John Warner. 2000. *Green Chemistry: Theory and Practice*. Oxford, New York: Oxford University Press.
- Arbenz, Alice, and Luc Avérous. 2015. "Chemical Modification of Tannins to Elaborate Aromatic Biobased Macromolecular Architectures" 17 (5): 2626–46.

- Argyropoulos, Dimitris S. 1994. "Quantitative Phosphorus-31 NMR Analysis of Lignins, a New Tool for the Lignin Chemist." *Journal of Wood Chemistry and Technology* 14 (1): 45–63.
- Argyropoulos, Dimitris S., and Claudia Crestini. 2016. "A Perspective on Lignin Refining, Functionalization, and Utilization." *ACS Sustainable Chemistry & Engineering* 4 (10): 5089–5089.
- Argyropoulos, Dimitris S., and Liming Zhang. 1998. "Semiquantitative Determination of Quinonoid Structures in Isolated Lignins by 31P Nuclear Magnetic Resonance." *Journal of Agricultural and Food Chemistry* 46 (11): 4628–34.
- Aro, Thomas, and Pedram Fatehi. 2017. "Production and Application of Lignosulfonates and Sulfonated Lignin." *ChemSusChem* 10 (9): 1961-1977.
- Asami, Danny K., Yun-Jeong Hong, Diane M. Barrett, and Alyson E. Mitchell. 2003. "Comparison of the Total Phenolic and Ascorbic Acid Content of Freeze-Dried and Air-Dried Marionberry, Strawberry, and Corn Grown Using Conventional, Organic, and Sustainable Agricultural Practices." *Journal of Agricultural and Food Chemistry* 51 (5): 1237–41.
- Asikkala, Janne, Tarja Tamminen, and Dimitris S. Argyropoulos. 2012. "Accurate and Reproducible Determination of Lignin Molar Mass by Acetobromination." *Journal of Agricultural and Food Chemistry* 60 (36): 8968–8973.
- Atkinson, Jeffrey, Raquel F. Epan, and Richard M. Epan. 2008. "Tocopherols and Tocotrienols in Membranes: A Critical Review." *Free Radical Biology and Medicine* 44 (5): 739–764.
- Auras, Rafael A., Loong-Tak Lim, Susan E. M. Selke, and Hideto Tsuji. 2011. *Poly(lactic Acid): Synthesis, Structures, Properties, Processing, and Applications*. John Wiley & Sons.
- Averous, L., and N. Boquillon. 2004. "Biocomposites Based on Plasticized Starch: Thermal and Mechanical Behaviours." *Carbohydrate Polymers* 56 (2): 111–122.
- Averous, L., N. Fauconnier, L. Moro, and C. Fringant. 2000. "Blends of Thermoplastic Starch and Polyesteramide: Processing and Properties." *Journal of Applied Polymer Science* 76 (7): 1117–1128.

- Avérous, Luc. 2004. "Biodegradable Multiphase Systems Based on Plasticized Starch: A Review." *Journal of Macromolecular Science, Part C* 44 (3): 231–274.
- Awang, Mariyamni, and Goh Meng Seng. 2008. "Sulfonation of Phenols Extracted from the Pyrolysis Oil of Oil Palm Shells for Enhanced Oil Recovery." *ChemSusChem* 1 (3): 210–214.
- Babu, Ramesh P., Kevin O'Connor, and Ramakrishna Seeram. 2013. "Current Progress on Bio-Based Polymers and Their Future Trends." *Progress in Biomaterials* 2 (1): 8-16.
- Bai, Nan, Kei Saito, and George P. Simon. 2013. "Synthesis of a Diamine Cross-Linker Containing Diels–Alder Adducts to Produce Self-Healing Thermosetting Epoxy Polymer from a Widely Used Epoxy Monomer" 4 (3): 724–730.
- Bate-Smith, E. C. 1962. "The Phenolic Constituents of Plants and Their Taxonomic Significance. I. Dicotyledons." *Journal of the Linnean Society of London, Botany* 58 (371): 95–173.
- Baumberger, Stéphanie, Alfred Abächerli, Mario Fasching, Göran Gellerstedt, Richard Gosselink, Bo Hortling, Jiebing Li, Bodo Saake, and Ed de Jong. 2007. "Molar Mass Determination of Lignins by Size-Exclusion Chromatography: Towards Standardisation of the Method." *Holzforschung* 61 (4): 459–468.
- Belgacem, Mohamed Naceur, and Alessandro Gandini. 2011. *Monomers, Polymers and Composites from Renewable Resources*. Amsterdam. Elsevier.
- Berstis, Laura, Thomas Elder, Michael F. Crowley, and Gregg T Beckham. 2016. "The Radical Nature of C-Lignin." *ACS Sustainable Chemistry & Engineering*, 4 (10): 5327–5335.
- Besteti, Marina D., Fernando G. Souza, Denise M.G. Freire, and José Carlos Pinto. 2014. "Production of Core-Shell Polymer Particles-Containing Cardanol by Semibatch Combined Suspension/Emulsion Polymerization." *Polymer Engineering & Science* 54 (5): 1222–1229.
- Bicu, Ioan, and Fanica Mustata. 2007. "Polymers from a Levopimaric Acid–acrylic Acid Diels–Alder Adduct: Synthesis and Characterization." *Journal of Polymer Science Part A: Polymer Chemistry* 45 (24): 5979–5990.

- Bonner, T. G., and P. McNamara. 1968. "The Pyridine-Catalysed Acetylation of Phenols and Alcohols by Acetic Anhydride." *Journal of the Chemical Society B: Physical Organic*, no. 0 (January): 795–797.
- Bräse, Stefan, Carmen Gil, Kerstin Knepper, and Viktor Zimmermann. 2005. "Organic Azides: An Exploding Diversity of a Unique Class of Compounds." *Angewandte Chemie International Edition* 44 (33): 5188–5240.
- Buono, Pietro, Antoine Duval, Luc Averous, and Youssef Habibi. 2017. "Lignin-Based Materials Through Thiol–Maleimide 'Click' Polymerization." *ChemSusChem* 10 (5): 984–992.
- Buono, Pietro, Antoine Duval, Pierre Verge, Luc Averous, and Youssef Habibi. 2016. "New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation." *ACS Sustainable Chemistry & Engineering* 4 (10): 5212–5222.
- C. Ferreira, Edilene, Ana Rita A. Nogueira, Gilberto B. Souza, and Luiz A. R. Batista. 2004. "Effect of Drying Method and Length of Storage on Tannin and Total Phenol Concentrations in Pigeon Pea Seeds." *Food Chemistry* 86 (1): 17–23.
- Calò, Emanuela, Alfonso Maffezzoli, Giuseppe Mele, Francesca Martina, Selma E. Mazzetto, Antonella Tarzia, and Cristina Stifani. 2007. "Synthesis of a Novel Cardanol-Based Benzoxazine Monomer and Environmentally Sustainable Production of Polymers and Bio-Composites." *Green Chemistry* 9 (7): 754–759.
- Canary, Stephen A., and Malcolm P. Stevens. 1992. "Thermally Reversible Crosslinking of Polystyrene via the Furan–maleimide Diels–Alder Reaction." *Journal of Polymer Science Part A: Polymer Chemistry* 30 (8): 1755–1760.
- Candolle, Augustin Pyramus de. 1813. *Théorie Élémentaire de La Botanique; Ou, Exposition Des Principes de La Classification Naturelle et de L'art de Décrire et D'étudier Les Végétaux*. Paris,: Déterville.
- Chen, Feng, Honghu Dai, Xiaoli Dong, Jintao Yang, and Mingqiang Zhong. 2011. "Physical Properties of Lignin-Based Polypropylene Blends." *Polymer Composites* 32 (7): 1019–1025.

- Chen, Xiangxu, Matheus A. Dam, Kanji Ono, Ajit Mal, Hongbin Shen, Steven R. Nutt, Kevin Sheran, and Fred Wudl. 2002. "A Thermally Re-Mendable Cross-Linked Polymeric Material." *Science* 295 (5560): 1698–1702.
- Chen, Xiangxu, Fred Wudl, Ajit K. Mal, Hongbin Shen, and Steven R. Nutt. 2003. "New Thermally Remendable Highly Cross-Linked Polymeric Materials." *Macromolecules* 36 (6): 1802–1807.
- Chung, Hoyong, and Newell R. Washburn. 2012. "Improved Lignin Polyurethane Properties with Lewis Acid Treatment." *ACS Applied Materials & Interfaces* 4 (6): 2840–2846.
- Chung, Hoyong, and Newell R. Washburn. 2013. "Chemistry of Lignin-Based Materials." *Green Materials* 1 (3): 137–160.
- Collins, Joe, Zeyun Xiao, Markus Müllner, and Luke A. Connal. 2016. "The Emergence of Oxime Click Chemistry and Its Utility in Polymer Science." *Polymer Chemistry* 7 (23): 3812–3826
- Constant, Sandra, Hans L. J. Wienk, Augustinus E. Frissen, Peter de Peinder, Rolf Boelens, Daan S. van Es, Ruud J. H. Grisel, et al. 2016. "New Insights into the Structure and Composition of Technical Lignins: A Comparative Characterisation Study." *Green Chemistry* 18 (9): 2651–2665.
- Corey, E. J., and A. Venkateswarlu. 1972. "Protection of Hydroxyl Groups as Tert-Butyldimethylsilyl Derivatives." *Journal of the American Chemical Society* 94 (17): 6190–6191.
- Crawford, Roy J. 1998. *Plastics Engineering*. Butterworth-Heinemann.
- Crestini, Claudia, Federica Melone, Marco Sette, and Raffaele Saladino. 2011. "Milled Wood Lignin: A Linear Oligomer." *Biomacromolecules* 12 (11): 3928–3935.
- Da Cunha, C., A. Deffieux, and M. Fontanille. 1992. "Synthesis and Polymerization of Lignin Macromonomers. II. Effects of Lignin Fragments on Methyl Methacrylate Radical Polymerization." *Journal of Applied Polymer Science* 44 (7): 1205–1212.
- Da Cunha, C., A. Deffieux, and M. Fontanille. 1993. "Synthesis and Polymerization of Lignin-Based Macromonomers. III. Radical Copolymerization of Lignin-Based Macromonomers with Methyl Methacrylate." *Journal of Applied Polymer Science* 48 (5): 819–831.

- Darroman, Emilie, Léa Bonnot, Remi Auvergne, Bernard Boutevin, and Sylvain Caillol. 2015. "New Aromatic Amine Based on Cardanol Giving New Biobased Epoxy Networks with Cardanol." *European Journal of Lipid Science and Technology* 117 (2): 178–189.
- De Oliveira, W., and W. G. Glasser. 1989. "Engineering Plastics from Lignin .16. Starlike Macromers with Propylene-Oxide." *Journal of Applied Polymer Science* 37 (11): 3119–3135.
- Dehne, Laura, Carlos Vila Babarro, Bodo Saake, and Katrin U. Schwarz. 2016a. "Influence of Lignin Source and Esterification on Properties of Lignin-Polyethylene Blends." *Industrial Crops and Products* 86 (August): 320–328.
- Diels, Otto, and Kurt Alder. 1928. "Synthesen in Der Hydroaromatischen Reihe." *Justus Liebigs Annalen Der Chemie* 460 (1): 98–122.
- Dizhbite, Tatiana, Galina Telysheva, Vilhelmina Jurkjane, and Uldis Viesturs. 2004. "Characterization of the Radical Scavenging Activity of Lignins—natural Antioxidants." *Bioresource Technology* 95 (3): 309–317.
- Domenek, Sandra, Abderrahim Louaifi, Alain Guinault, and Stéphanie Baumberger. 2013. "Potential of Lignins as Antioxidant Additive in Active Biodegradable Packaging Materials." *Journal of Polymers and the Environment* 21 (3): 692–701.
- Du, Pengfei, Meiyin Wu, Xuanxuan Liu, Zhen Zheng, Xinling Wang, Peiyu Sun, Thomas Joncheray, and Yuefan Zhang. 2014. "Synthesis of Linear Polyurethane Bearing Pendant Furan and Cross-Linked Healable Polyurethane Containing Diels–Alder Bonds" 38 (2): 770–776.
- Duval, Antoine, and Luc Averous. 2017. "Solvent and Halogen-Free Modification of Biobased Polyphenols to Introduce Vinyl Groups: Versatile Aromatic Building Blocks for Polymer Synthesis." *ChemSusChem*. 10 (8): 1813–1822.
- Duval, Antoine, Guillaume Couture, Sylvain Caillol, and Luc Avérous. 2017. "Biobased and Aromatic Reversible Thermoset Networks from Condensed Tannins via the Diels–Alder Reaction." *ACS Sustainable Chemistry & Engineering* 5 (1): 1199–1207.

- Duval, Antoine, Heiko Lange, Martin Lawoko, and Claudia Crestini. 2015a. "Modification of Kraft Lignin to Expose Diazobenzene Groups: Toward pH- and Light-Responsive Biobased Polymers." *Biomacromolecules* 16 (9): 2979–2989.
- Duval, Antoine, Heiko Lange, Martin Lawoko, and Claudia Crestini. 2015b. "Reversible Crosslinking of Lignin via the Furan–maleimide Diels–Alder Reaction." *Green Chemistry* 17 (11): 4991–5000.
- Duval, Antoine, and Martin Lawoko. 2014. "A Review on Lignin-Based Polymeric, Micro- and Nano-Structured Materials." *Reactive and Functional Polymers* 85: 78–96.
- Duval, Antoine, Francisco Vilaplana, Claudia Crestini, and Martin Lawoko. 2015. "Solvent Screening for the Fractionation of Industrial Kraft Lignin." *Holzforschung* 70 (1): 11–20.
- EUBIO_Admin. 2017. "Market." *European Bioplastics e.V.* Accessed March 20. <http://www.european-bioplastics.org/market/> Data access 17 March 2017
- Fache, Maxence, Bernard Boutevin, and Sylvain Caillol. 2016. "Vanillin Production from Lignin and Its Use as a Renewable Chemical." *ACS Sustainable Chemistry & Engineering* 4 (1): 35–46.
- Fache, Maxence, Emilie Darroman, Vincent Besse, Rémi Auvergne, Sylvain Caillol, and Bernard Boutevin. 2014. "Vanillin, a Promising Biobased Building-Block for Monomer Synthesis." *Green Chemistry* 16 (4): 1987–1998.
- Fairbanks, Benjamin D., Timothy F. Scott, Christopher J. Kloxin, Kristi S. Anseth, and Christopher N. Bowman. 2009. "Thiol–Yne Photopolymerizations: Novel Mechanism, Kinetics, and Step-Growth Formation of Highly Cross-Linked Networks." *Macromolecules* 42 (1): 211–217.
- Faix, O., C. Grünwald, and O. Beinhoff. 1992. "Determination of Phenolic Hydroxyl Group Content of Milled Wood Lignins (MWL's) from Different Botanical Origins Using Selective Aminolysis, FTIR, ¹H-NMR, and UV Spectroscopy." *Holzforschung* 46 (5): 425–432.
- Fire-resistant plasticizer for the plastic material industry and method of making thereof. US8349924.
- Foo, L. Yeap, and Richard W. Hemingway. 1985. "Condensed Tannins: Reactions of Model Compounds with Furfuryl Alcohol and Furfuraldehyde." *Journal of Wood Chemistry and Technology* 5 (1): 135–158.

- Froidevaux, V., M. Borne, E. Laborbe, R. Auvergne, A. Gandini, and B. Boutevin. 2015. "Study of the Diels–Alder and Retro-Diels–Alder Reaction between Furan Derivatives and Maleimide for the Creation of New Materials." *RSC Advances* 5 (47): 37742–37754.
- Fu, Changqing, Jiancheng Liu, Hongying Xia, and Liang Shen. 2015. "Effect of Structure on the Properties of Polyurethanes Based on Aromatic Cardanol-Based Polyols Prepared by Thiol–Ene Coupling." *Progress in Organic Coatings* 83: 19–25.
- Gadwal, Ikhlas, Mihaiela C. Stuparu, and Anzar Khan. 2015. "Homopolymer Bifunctionalization through Sequential Thiol–epoxy and Esterification Reactions: An Optimization, Quantification, and Structural Elucidation Study" 6 (8): 1393–1404.
- Gandini, Alessandro. 2013. "The Furan/Maleimide Diels–Alder Reaction: A Versatile Click–unclick Tool in Macromolecular Synthesis." *Progress in Polymer Science, Topical Issue on Polymer Chemistry*, 38 (1): 1–29.
- Gandini, Alessandro, and Mohamed Naceur Belgacem. 1997. "Furans in Polymer Chemistry." *Progress in Polymer Science* 22 (6): 1203–1379.
- Gandini, Alessandro, Talita M. Lacerda, Antonio J. F. Carvalho, and Eliane Trovatti. 2016. "Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides." *Chemical Reviews* 116 (3): 1637–1669.
- García, Danny E., Wolfgang G. Glasser, Antonio Pizzi, Sebastian P. Paczkowski, and Marie-Pierre Laborie. 2016. "Modification of Condensed Tannins: From Polyphenol Chemistry to Materials Engineering" 40 (1): 36–49.
- Garlotta, Donald. 2001. "A Literature Review of Poly(Lactic Acid)." *Journal of Polymers and the Environment* 9 (2): 63–84.
- Gartner. 1999. "Determination of Phenolic Hydroxyl Groups in Residual Lignin Using a Modified UV-Method." *Nordic Pulp and Paper Research Journal* 14 (2): 163–170.

- Gellerstedt, Göran, and Gunnar Henriksson. 2008. "Lignins: Major Sources, Structure and Properties." In *Monomers, Polymers and Composites from Renewable Resources*, edited by Mohamed Naceur Belgacem and Alessandro Gandini, 201–224. Amsterdam: Elsevier.
- Glasser, W. G., C. A. Barnett, T. G. Rials, and V. P. Saraf. 1984. "Engineering Plastics from Lignin .2. Characterization of Hydroxyalkyl Lignin Derivatives." *Journal of Applied Polymer Science* 29 (5): 1815–1830.
- Glasser, Wolfgang G. 1999. "Classification of Lignin According to Chemical and Molecular Structure." In *Lignin: Historical, Biological, and Materials Perspectives*, 742:216–238. ACS Symposium Series 742. American Chemical Society.
- Glasser, Wolfgang G., and Hong-Xue Wang. 1989. "Derivatives of Lignin and Ligninlike Models with Acrylate Functionality." In *Lignin*, 397: 515–522. ACS Symposium Series 397. American Chemical Society.
- González Sánchez, Carlos, and L. A. Expósito Alvarez. 1999. "Micromechanics of Lignin/Polypropylene Composites Suitable for Industrial Applications." *Die Angewandte Makromolekulare Chemie* 272 (1): 65–70.
- Gou, Lijing, Blaine Opheim, Chris N. Coretsopoulos, and Alec B. Scranton. 2006. "Consumption of the Molecular Oxygen in Polymerization Systems Using Photosensitized Oxidation of Dimethylantracene." *Chemical Engineering Communications* 193 (5): 620–627.
- Granata, Alessandro, and Dimitris S. Argyropoulos. 1995a. "2-Chloro-4,4,5,5-Tetramethyl-1,3,2-Dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins." *Journal of Agricultural and Food Chemistry* 43 (6): 1538–1544.
- Hambardzumyan, Arayik, Laurence Foulon, Brigitte Chabbert, and Véronique Aguié-Béghin. 2012. "Natural Organic UV-Absorbent Coatings Based on Cellulose and Lignin: Designed Effects on Spectroscopic Properties." *Biomacromolecules* 13 (12): 4081–4088.

- Han, Yanming, Liang Yuan, Gaiyun Li, Luohua Huang, Tefu Qin, Fuxiang Chu, and Chuanbing Tang. 2016. "Renewable Polymers from Lignin via Copper-Free Thermal Click Chemistry." *Polymer* 83 (January): 92–100.
- Hannoda, Yoshiki, Yuki Akasaka, and Mitsuhiro Shibata. 2015. "Bio-Based Thermosetting Bismaleimide Resins Using Cardanyl Linolenate and Allyl Cardanyl Ether." *Reactive and Functional Polymers* 97 (December): 96–104.
- Hayashi, A., K. Kinoshita, and A. (Ritsumeikan Univ Taniguchi. 1975. "Demethylation of lignin during pulping, 2: Correlation between demethylation and coloring with soda cooking." *Journal of the Japan Wood Research Society* 21 (8): 480-484.
- Hensarling, Ryan M., Vanessa A. Doughty, Justin W. Chan, and Derek L. Patton. 2009. "'Clicking' Polymer Brushes with Thiol-Yne Chemistry: Indoors and Out." *Journal of the American Chemical Society* 131 (41): 14673–14675.
- Hermann, B. G., K. Blok, and M. K. Patel. 2007. "Producing Bio-Based Bulk Chemicals Using Industrial Biotechnology Saves Energy and Combats Climate Change." *Environmental Science & Technology* 41 (22): 7915–7921.
- Hilburg, Shayna L., Allison N. Elder, Hoyong Chung, Rachel L. Ferebee, Michael R. Bockstaller, and Newell R. Washburn. 2014. "A Universal Route towards Thermoplastic Lignin Composites with Improved Mechanical Properties." *Polymer* 55 (4): 995–1003.
- Hocking, Martin B. 1997. "Vanillin: Synthetic Flavoring from Spent Sulfite Liquor." *Journal of Chemical Education* 74 (9): 1055-1059.
- Hofmann, K., and W. G. Glasser. 1993. "Engineering Plastics from Lignin .21. Synthesis and Properties of Epoxidized Lignin-Poly(propylene Oxide) Copolymers." *Journal of Wood Chemistry and Technology* 13 (1): 73–95.
- Holmberg, Angela L., Ngoc A. Nguyen, Michael G. Karavolias, Kaleigh H. Reno, Richard P. Wool, and Thomas H. Epps. 2016. "Softwood Lignin-Based Methacrylate Polymers with Tunable Thermal and Viscoelastic Properties." *Macromolecules* 49 (4): 1286–1295.

- Hoogenboom, Richard. 2010. "Thiol–Yne Chemistry: A Powerful Tool for Creating Highly Functional Materials." *Angewandte Chemie International Edition* 49 (20): 3415–3417.
- Hoyle, Charles E., Andrew B. Lowe, and Christopher N. Bowman. 2010. "Thiol-Click Chemistry: A Multifaceted Toolbox for Small Molecule and Polymer Synthesis." *Chemical Society Reviews* 39 (4): 1355–1387.
- Hoyle, Charles E., and Christopher N. Bowman. 2010. "Thiol–Ene Click Chemistry." *Angewandte Chemie International Edition* 49 (9): 1540–1573.
- Huang, Kun, Yan Zhang, Mei Li, Jianwei Lian, Xiaohua Yang, and Jianling Xia. 2012. "Preparation of a Light Color Cardanol-Based Curing Agent and Epoxy Resin Composite: Cure-Induced Phase Separation and Its Effect on Properties." *Progress in Organic Coatings* 74 (1): 240–247.
- Huff, Bret E. 2001. "T-Butyldimethylchlorosilane." In *Encyclopedia of Reagents for Organic Synthesis*. John Wiley & Sons: New York.
- I, Suresh Kattimuttathu, Gesche Foerst, Rolf Schubert, and Eckhard Bartsch. 2012. "Synthesis and Micellization Properties of New Anionic Reactive Surfactants Based on Hydrogenated Cardanol." *Journal of Surfactants and Detergents* 15 (2): 207–215.
- Inoue, Kazuhiko, Midori Yamashiro, and Masatoshi Iji. 2009. "Recyclable Shape-Memory Polymer: Poly(lactic Acid) Crosslinked by a Thermoreversible Diels–Alder Reaction." *Journal of Applied Polymer Science* 112 (2): 876–885.
- Jahanshahi, Shayesteh, Antonio Pizzi, Ali Abdulkhani, and Alireza Shakeri. 2016. "Analysis and Testing of Bisphenol A—Free Bio-Based Tannin Epoxy-Acrylic Adhesives." *Polymers* 8 (4): 143–157.
- Jaillet, Fanny, Emilie Darroman, Amédée Ratsimihety, Rémi Auvergne, Bernard Boutevin, and Sylvain Caillol. 2014. "New Biobased Epoxy Materials from Cardanol." *European Journal of Lipid Science and Technology* 116 (1): 63–73.
- Jawerth, M., M. Lawoko, S. Lundmark, C. Perez-Berumen, and M. Johansson. 2016. "Allylation of a Lignin Model Phenol: A Highly Selective Reaction under Benign Conditions towards a New Thermoset Resin Platform." *RSC Advances* 6 (98): 96281–96288.

- Jin, Can, Xueyan Zhang, Junna Xin, Guifeng Liu, Guomin Wu, Zhenwu Kong, and Jinwen Zhang. 2017. "Clickable Synthesis of 1,2,4-Triazole Modified Lignin-Based Adsorbent for the Selective Removal of Cd(II)." *ACS Sustainable Chemistry & Engineering* 5 (5): 4086–4093.
- John, George, and C. K. S. Pillai. 1993. "Synthesis and Characterization of a Self-Crosslinkable Polymer from Cardanol: Autooxidation of Poly(cardanyl Acrylate) to Crosslinked Film." *Journal of Polymer Science Part A: Polymer Chemistry* 31 (4): 1069–1073.
- John, George, and Chennakkattu Krishna Sadasivan Pillai. 1992. "Self-Crosslinkable Monomer from Cardanol: Crosslinked Beads of Poly(cardanyl Acrylate) by Suspension Polymerization." *Die Makromolekulare Chemie, Rapid Communications* 13 (5): 255–259.
- Kade, Matthew J., Daniel J. Burke, and Craig J. Hawker. 2010. "The Power of Thiol-Ene Chemistry." *Journal of Polymer Science Part A: Polymer Chemistry* 48 (4): 743–50. doi:10.1002/pola.23824.
- Kadla, J. F., and S. Kubo. 2004. "Lignin-Based Polymer Blends: Analysis of Intermolecular Interactions in Lignin-Synthetic Polymer Blends." *Composites Part a-Applied Science and Manufacturing* 35 (3): 395–400.
- Kai, Dan, Mein Jin Tan, Pei Lin Chee, Yun Khim Chua, Yong Liang Yap, and Xian Jun Loh. 2016. "Towards Lignin-Based Functional Materials in a Sustainable World." *Green Chemistry* 18 (5): 1175–1200.
- Kelley, S. S., W. G. Glasser, and T. C. Ward. 1988. "Engineering Plastics from Lignin .14. Characterization of Chain-Extended Hydroxypropyl Lignins." *Journal of Wood Chemistry and Technology* 8 (3): 341–359.
- Kelley, Stephen S., Wolfgang G. Glasser, and Thomas C. Ward. 1988. "Engineering Plastics from Lignin XIV. Characterization of Chain-Extended Hydroxypropyl Lignins." *Journal of Wood Chemistry and Technology* 8 (3): 341–359.

- Kempe, Kristian, Andreas Krieg, C. Remzi Becer, and Ulrich S. Schubert. 2011a. "'Clicking' On/With Polymers: A Rapidly Expanding Field for the Straightforward Preparation of Novel Macromolecular Architectures" 41 (1): 176–191.
- Koivu, Klaus Asko Yrjänä, Hasan Sadeghifar, Paula Nousiainen, Dimitris S. Argyropoulos, and Jussi Sipila. 2016. "The Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin." *ACS Sustainable Chemistry & Engineering* 4 (10): 5238–5247.
- Kolb, Hartmuth C., M. G. Finn, and K. Barry Sharpless. 2001. "Click Chemistry: Diverse Chemical Function from a Few Good Reactions." *Angewandte Chemie International Edition* 40 (11): 2004–2021.
- Konkolewicz, Dominik, Angus Gray-Weale, and Sébastien Perrier. 2009. "Hyperbranched Polymers by Thiol–Yne Chemistry: From Small Molecules to Functional Polymers." *Journal of the American Chemical Society* 131 (50): 18075–18077.
- Kötteritzsch, Julia, Steffi Stumpf, Stephanie Hoepfner, Juergen Vitz, Martin D. Hager, and Ulrich S. Schubert. 2013. "One-Component Intrinsic Self-Healing Coatings Based on Reversible Crosslinking by Diels–Alder Cycloadditions." *Macromolecular Chemistry and Physics* 214 (14): 1636–1649.
- Kriegel, Robert, Xiaoyan Huang, Mikell W. Schultheis, Doug A. Bippert, Gerard E. Insolia, Brock Kolls, and Scott Summerville. 2010. Bio-based polyethylene terephthalate packaging and method of making thereof. US20100028512 A1, filed October 12, 2009, and issued February 4, 2010.
- Kriegel, Robert M., Xiaoyan Huang, and Mikell W. Schultheis. 2009. Bio-based polyethylene terephthalate polymer and method of making same. US20090246430 A1, filed September 14, 2008, and issued October 1, 2009.
- Kulich, D. M., S. K. Gaggar, V. Lowry, and R. Stepien. 2002a. "Acrylonitrile–Butadiene–Styrene Polymers." In *Encyclopedia of Polymer Science and Technology*. New York: John Wiley & Sons, Inc.

- Ladmiral, Vincent, Renaud Jeannin, Kepa Fernandes Lizarazu, Josephine Lai-Kee-Him, Patrick Bron, Patrick Lacroix-Desmazes, and Sylvain Caillol. n.d. "Aromatic Biobased Polymer Latex from Cardanol." *European Polymer Journal*. in press
- Laoutid, F., L. Bonnaud, M. Alexandre, J. -M. Lopez-Cuesta, and Ph. Dubois. 2009. "New Prospects in Flame Retardant Polymer Materials: From Fundamentals to Nanocomposites." *Materials Science and Engineering: R: Reports* 63 (3): 100–125.
- Laurichesse, Stéphanie, and Luc Avérous. 2013. "Synthesis, Thermal Properties, Rheological and Mechanical Behaviors of Lignins-Grafted-Poly(ϵ -Caprolactone)." *Polymer* 54 (15): 3882–3890.
- Laurichesse, Stéphanie, Cédric Huillet, and Luc Avérous. 2014a. "Original Polyols Based on Organosolv Lignin and Fatty Acids: New Bio-Based Building Blocks for Segmented Polyurethane Synthesis." *Green Chemistry* 16 (8): 3958–3970.
- Li, Shouhai, Xuejuan Yang, Kun Huang, Mei Li, and Jianling Xia. 2014. "Design, Preparation and Properties of Novel Renewable UV-Curable Copolymers Based on Cardanol and Dimer Fatty Acids." *Progress in Organic Coatings* 77 (2): 388–394.
- Li, Yan, and Simo Sarkanen. 2002. "Alkylated Kraft Lignin-Based Thermoplastic Blends with Aliphatic Polyesters." *Macromolecules* 35 (26): 9707–9715.
- Liu, Hailing, and Hoyong Chung. 2016. "Self-Healing Properties of Lignin-Containing Nanocomposite: Synthesis of Lignin-Graft-poly(5-Acetylaminoethyl Acrylate) via RAFT and Click Chemistry." *Macromolecules* 49 (19): 7246–7256.
- Liu, Jingcheng, Ren Liu, Xiaopeng Zhang, Zhiqian Li, Hongtao Tang, and Xiaoya Liu. 2016. "Preparation and Properties of UV-Curable Multi-Arms Cardanol-Based Acrylates." *Progress in Organic Coatings* 90 (January): 126–131.
- Liu, Ren, Xiaopeng Zhang, Jiajia Zhu, Xiaoya Liu, Zhen Wang, and Jingling Yan. 2015. "UV-Curable Coatings from Multiarmed Cardanol-Based Acrylate Oligomers." *ACS Sustainable Chemistry & Engineering* 3 (7): 1313–1320.

- Liu, Ren, Junchao Zheng, Ruixi Guo, Jing Luo, Yan Yuan, and Xiaoya Liu. 2014. "Synthesis of New Biobased Antibacterial Methacrylates Derived from Tannic Acid and Their Application in UV-Cured Coatings." *Industrial & Engineering Chemistry Research* 53 (27): 10835–10840.
- Liu, Ren, Guigang Zhu, Zhiqian Li, Xiaoya Liu, Zhigang Chen, and Sharonie Ariyasivam. 2015. "Cardanol-Based Oligomers with 'hard Core, Flexible Shell' Structures: From Synthesis to UV Curing Applications." *Green Chemistry* 17 (6): 3319–3325.
- Liu, Ren, Jiajia Zhu, Jing Luo, and Xiaoya Liu. 2014. "Synthesis and Application of Novel UV-Curable Hyperbranched Methacrylates from Renewable Natural Tannic Acid." *Progress in Organic Coatings* 77 (1): 30–37.
- Liu, Ying-Ling, and Tsai-Wei Chuo. 2013. "Self-Healing Polymers Based on Thermally Reversible Diels–Alder Chemistry" 4 (7): 2194–2205.
- Lochab, Bimlesh, Swapnil Shukla, and Indra K. Varma. 2014. "Naturally Occurring Phenolic Sources: Monomers and Polymers" 4 (42): 21712–21752.
- Lomonaco, Diego, Francisco Jonas Nogueira Maia, and Selma Elaine Mazzetto. 2013. "Thermal Evaluation of Cashew Nutshell Liquid as New Bioadditives for Poly(methyl Methacrylate)." *Journal of Thermal Analysis and Calorimetry* 111 (1): 619–626.
- Lora, Jairo. 2008. "Industrial Commercial Lignins: Sources, Properties and Applications." In *Monomers, Polymers and Composites from Renewable Resources*, edited by Mohamed Naceur Belgacem and Alessandro Gandini, 225–41. Amsterdam: Elsevier.
- Lora, Jairo H. 2016. "Lignin: A Platform for Renewable Aromatic Polymeric Materials." In *Quality Living Through Chemurgy and Green Chemistry*, edited by Peter C. K. Lau, 221–261. Green Chemistry and Sustainable Technology. Springer Berlin Heidelberg.
- Lowe, Andrew B. 2010. "Thiol-Ene 'click' Reactions and Recent Applications in Polymer and Materials Synthesis." *Polymer Chemistry* 1 (1): 17–36.
- Lu, Fung-Jou, Li-Hsueh Chu, and Rung-Jiun Gau. 1998. "Free Radical-scavenging Properties of Lignin." *Nutrition and Cancer* 30 (1): 31–38.

- Lundquist, Knut. 1992. "Proton (1H) NMR Spectroscopy." In *Methods in Lignin Chemistry*, edited by S. Y. Lin and C. W. Dence. Berlin-Heidelberg: Springer-Verlag.
- Lundquist, Knut, Rainer Sjöholm, Gerd Teien, Tuula Pakkanen, Rolf Servin, Hans Sternerup, Lars-Göran Wistrand, L. Nørskov, and Gustav Schroll. 1979. "NMR Studies of Lignins. 2. Interpretation of the 1H NMR Spectrum of Acetylated Birch Lignin." *Acta Chemica Scandinavica* 33b: 27–30.
- Lunt, James. 1998. "Large-Scale Production, Properties and Commercial Applications of Polylactic Acid Polymers." *Polymer Degradation and Stability, Biodegradable Polymers and Macromolecules*, 59 (1): 145–152.
- Luo, Chunhua, Warren J. Grigsby, Neil R. Edmonds, and Jafar Al-Hakkak. 2013. "Vegetable Oil Thermosets Reinforced by Tannin–lipid Formulations." *Acta Biomaterialia* 9 (2): 5226–5233.
- Mai, Carsten, and Holger Militz. 2004. "Modification of Wood with Silicon Compounds. Treatment Systems Based on Organic Silicon Compounds — a Review." *Wood Science and Technology* 37 (6): 453–461.
- Maldhure, Atul V., J. D. Ekhe, and E. Deenadayalan. 2012. "Mechanical Properties of Polypropylene Blended with Esterified and Alkylated Lignin." *Journal of Applied Polymer Science* 125 (3): 1701–1712.
- Matsuo, Masaru, Yuezhen Bin, Chunye Xu, Lin Ma, Takahiko Nakaoki, and Takenori Suzuki. 2003. "Relaxation Mechanism in Several Kinds of Polyethylene Estimated by Dynamic Mechanical Measurements, Positron Annihilation, X-Ray and 13C Solid-State NMR." *Polymer* 44 (15): 4325–4340.
- Matturro, Giacomo, Paolo Danesi, Andrea Festuccia, and Carlo Mustacchi deceased. 2006. Process and plant to extract and concentrate tannins from wood and from other natural products. US7145031 B1, filed October 27, 1998, and issued December 5, 2006.
- McCrum, N. G., C. P. Buckley, and C. B. Bucknall. 1997. *Principles of Polymer Engineering*. Oxford University Press.

- Morschbacker, Antonio. 2009. "Bio-Ethanol Based Ethylene." *Polymer Reviews* 49 (2): 79–84.
- Moses, J. E., and A. D. Moorhouse. 2007. "The Growing Applications of Click Chemistry." *Chemical Society Reviews* 36 (8): 1249–1262.
- Munaro, Marilda, and Leni Akcelrud. 2007. "Correlations between Composition and Crystallinity of LDPE/HDPE Blends." *Journal of Polymer Research* 15 (1): 83–88.
- Nadji, H., P. N. Diouf, A. Benaboura, Y. Bedard, B. Riedl, and T. Stevanovic. 2009. "Comparative Study of Lignins Isolated from Alfa Grass (*Stipa Tenacissima* L.)." *Bioresource Technology* 100 (14): 3585–3592.
- Nagabhushana, K. S., and B. Ravindranath. 1995. "Efficient Medium-Scale Chromatographic Group Separation of Anacardic Acids from Solvent-Extracted Cashew Nut (*Anacardium Occidentale*) Shell Liquid." *Journal of Agricultural and Food Chemistry* 43 (9): 2381–2383.
- Nair, Devatha P., Maciej Podgórski, Shunsuke Chatani, Tao Gong, Weixian Xi, Christopher R. Fenoli, and Christopher N. Bowman. 2014a. "The Thiol-Michael Addition Click Reaction: A Powerful and Widely Used Tool in Materials Chemistry." *Chemistry of Materials* 26 (1): 724–744.
- Naveau, H. P. 1975. "Methacrylic Derivatives of Lignin." *Cellulose Chemistry and Technology* 18 (1): 71-77.
- Nawrat, Christopher C., and Christopher J. Moody. 2014. "Quinones as Dienophiles in the Diels–Alder Reaction: History and Applications in Total Synthesis." *Angewandte Chemie International Edition* 53 (8): 2056–2077.
- Nitta, K. -h, and A Tanaka. 2001. "Dynamic Mechanical Properties of Metallocene Catalyzed Linear Polyethylenes." *Polymer* 42 (3): 1219–1226.
- Noreen, Aqdas, Khalid Mahmood Zia, Mohammad Zuber, Shazia Tabasum, and Ameer Fawad Zahoor. 2016. "Bio-Based Polyurethane: An Efficient and Environment Friendly Coating Systems: A Review." *Progress in Organic Coatings* 91 (February): 25–32.
- Notley, Shannon M., and Magnus Norgren. 2010. "Surface Energy and Wettability of Spin-Coated Thin Films of Lignin Isolated from Wood." *Langmuir* 26 (8): 5484–5490.

- Oehlenschlaeger, Kim K., Jan O. Mueller, Josef Brandt, Stefan Hilf, Alben Lederer, Manfred Wilhelm, Robert Graf, Michelle L. Coote, Friedrich G. Schmidt, and Christopher Barner-Kowollik. 2014. "Adaptable Hetero Diels–Alder Networks for Fast Self-Healing under Mild Conditions." *Advanced Materials* 26 (21): 3561–3566.
- Over, Lena C., and Michael A. R. Meier. 2015. "Sustainable Allylation of Organosolv Lignin with Diallyl Carbonate and Detailed Structural Characterization of Modified Lignin." *Green Chemistry* 18 (1): 197–207.
- Pan, Xuejun, John F. Kadla, Katsunobu Ehara, Neil Gilkes, and Jack N. Saddler. 2006. "Organosolv Ethanol Lignin from Hybrid Poplar as a Radical Scavenger: Relationship between Lignin Structure, Extraction Conditions, and Antioxidant Activity." *Journal of Agricultural and Food Chemistry* 54 (16): 5806–5813.
- Park, Saerom, Sung Hee Kim, Keehoon Won, Joon Weon Choi, Yong Hwan Kim, Hyung Joo Kim, Yung-Hun Yang, and Sang Hyun Lee. 2015. "Wood Mimetic Hydrogel Beads for Enzyme Immobilization." *Carbohydrate Polymers* 115 (January): 223–229.
- Park, Shin Ae, Choong Hwan Lim, and Kyoo-Hyun Chung. 2007. "Epoxide Opening with Tetrabutylammonium Fluoride (TBAF)." *Bulletin of the Korean Chemical Society* 28 (10): 1834–1836.
- Patschinski, Pascal, Cong Zhang, and Hendrik Zipse. 2014. "The Lewis Base-Catalyzed Silylation of Alcohols—A Mechanistic Analysis." *The Journal of Organic Chemistry* 79 (17): 8348–8357.
- Pearl, Irwin A. 1942. "Vanillin from Lignin Materials." *Journal of the American Chemical Society* 64 (6): 1429–1431.
- Petzold, Katrin, Andreas Koschella, Dieter Klemm, and Brigitte Heublein. 2003. "Silylation of Cellulose and Starch – Selectivity, Structure Analysis, and Subsequent Reactions." *Cellulose* 10 (3): 251–269.
- Philip, S., T. Keshavarz, and I. Roy. 2007. "Polyhydroxyalkanoates: Biodegradable Polymers with a Range of Applications." *Journal of Chemical Technology & Biotechnology* 82 (3): 233–247.

- Pizzi, A. 2013. "Bioadhesives for Wood and Fibres." *Reviews of Adhesion and Adhesives* 1 (1): 88–113.
- Plaisted, Thomas A., and Sia Nemat-Nasser. 2007. "Quantitative Evaluation of Fracture, Healing and Re-Healing of a Reversibly Cross-Linked Polymer." *Acta Materialia* 55 (17): 5684–5696.
- "PlasticsEurope - Plastics - the Facts 2016." 2017.
- Podkościelna, Beata, Magdalena Sobiesiak, Yadong Zhao, Barbara Gawdzik, and Olena Sevastyanova. 2015. "Preparation of Lignin-Containing Porous Microspheres through the Copolymerization of Lignin Acrylate Derivatives with Styrene and Divinylbenzene." *Holzforschung* 69 (6): 769–776.
- Podschun, Jacob, Alexander Stücker, Bodo Saake, and Ralph Lehnen. 2015. "Structure–Function Relationships in the Phenolation of Lignins from Different Sources." *ACS Sustainable Chemistry & Engineering* 3 (10): 2526–2532.
- Posner, Theodor. 1905. "Beiträge Zur Kenntniss Der Ungesättigten Verbindungen. II. Ueber Die Addition von Mercaptanen an Ungesättigte Kohlenwasserstoffe." *Berichte Der Deutschen Chemischen Gesellschaft* 38 (1): 646–657.
- Pounder, Ryan J., Matthew J. Stanford, Paul Brooks, Stephen P. Richards, and Andrew P. Dove. 2008. "Metal Free Thiol–maleimide 'Click' Reaction as a Mild Functionalisation Strategy for Degradable Polymers." *Chemical Communications* 41: 5158–5160.
- Pouteau, C., P. Dole, B. Cathala, L. Averous, and N. Boquillon. 2003. "Antioxidant Properties of Lignin in Polypropylene." *Polymer Degradation and Stability* 81 (1): 9–18.
- Pouteau, Charlyse, Stéphanie Baumberger, Bernard Cathala, and Patrice Dole. 2004. "Lignin–polymer Blends: Evaluation of Compatibility by Image Analysis." *Comptes Rendus Biologies* 327 (9–10): 935–943.
- Pucciariello, R., V. Villani, C. Bonini, M. D'Auria, and T. Vetere. 2004. "Physical Properties of Straw Lignin-Based Polymer Blends." *Polymer* 45 (12): 4159–4169.

- Qin, Anjun, Jacky W. Y. Lam, and Ben Zhong Tang. 2010a. "Click Polymerization." *Chemical Society Reviews* 39 (7): 2522–2544.
- Ragauskas, Arthur J., Gregg T. Beckham, Mary J. Biddy, Richard Chandra, Fang Chen, Mark F. Davis, Brian H. Davison, et al. 2014. "Lignin Valorization: Improving Lignin Processing in the Biorefinery." *Science* 344 (6185): 1246843-1246847.
- Ralph, John, Knut Lundquist, Gösta Brunow, Fachuang Lu, Hoon Kim, Paul F. Schatz, Jane M. Marita, et al. 2004a. "Lignins: Natural Polymers from Oxidative Coupling of 4-Hydroxyphenyl-Propanoids." *Phytochemistry Reviews* 3 (1–2): 29–60.
- "Rethinking the Future of Plastics." 2017. *New Plastics Economy*.
<http://newplasticseconomy.org/report-2016>.
- Rinaldi, Roberto, Robin Jastrzebski, Matthew T. Clough, John Ralph, Marco Kennema, Pieter C. A. Bruijninx, and Bert M. Weckhuysen. 2016. "Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis." *Angewandte Chemie International Edition* 55 (29): 8164–8215.
- Robert, Danielle R., and Gösta Brunow. 2009. "Quantitative Estimation of Hydroxyl Groups in Milled Wood Lignin from Spruce and in a Dehydrogenation Polymer from Coniferyl Alcohol Using ¹³C NMR Spectroscopy." *Holzforschung - International Journal of the Biology, Chemistry, Physics and Technology of Wood* 38 (2): 85–90.
- Roberts, M. J., M. D. Bentley, and J. M. Harris. 2002. "Chemistry for Peptide and Protein PEGylation." *Advanced Drug Delivery Reviews, Peptide and Protein Pegylation*, 54 (4): 459–476.
- Roper, T. M., T. Kwee, T. Y. Lee, C. A. Guymon, and C. E. Hoyle. 2004. "Photopolymerization of Pigmented Thiol–ene Systems." *Polymer* 45 (9): 2921–2929.
- Rostovtsev, Vsevolod V., Luke G. Green, Valery V. Fokin, and K. Barry Sharpless. 2002. "A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective 'Ligation' of Azides and Terminal Alkynes." *Angewandte Chemie* 114 (14): 2708–2711.

- Rúnarsson, Ögmundur Vidar, Clemens Malainer, Jukka Holappa, Snorri Th. Sigurdsson, and Már Másson. 2008. "Tert-Butyldimethylsilyl O-Protected Chitosan and Chitooligosaccharides: Useful Precursors for N-Modifications in Common Organic Solvents." *Carbohydrate Research* 343 (15): 2576–2582.
- Sadeghifar, Hasan, Chengzhong Cui, and Dimitris S. Argyropoulos. 2012. "Toward Thermoplastic Lignin Polymers. Part 1. Selective Masking of Phenolic Hydroxyl Groups in Kraft Lignins via Methylation and Oxypropylation Chemistries." *Industrial & Engineering Chemistry Research* 51 (51): 16713–16720.
- Sadeghifar, Hasan, Richard Venditti, Jesse Jur, Russell E. Gorga, and Joel J. Pawlak. 2016. "Cellulose-Lignin Biodegradable and Flexible UV Protection Film." *ACS Sustainable Chemistry & Engineering* 5 (1): 625–631.
- Sailaja, R. R. N., and M. V. Deepthi. 2010. "Mechanical and Thermal Properties of Compatibilized Composites of Polyethylene and Esterified Lignin." *Materials & Design* 31 (9): 4369–4379.
- Salanti, Anika, Luca Zoia, and Marco Orlandi. 2016. "Chemical Modifications of Lignin for the Preparation of Macromers Containing Cyclic Carbonates." *Green Chemistry* 18 (14): 4063–4072.
- Scheltjens, G., M. M. Diaz, J. Brancart, G. Van Assche, and B. Van Mele. 2013. "A Self-Healing Polymer Network Based on Reversible Covalent Bonding." *Reactive and Functional Polymers, Network Polymers towards High Performance Materials*, 73 (2): 413–420.
- Sen, Sanghamitra, Hasan Sadeghifar, and Dimitris S. Argyropoulos. 2013. "Kraft Lignin Chain Extension Chemistry via Propargylation, Oxidative Coupling, and Claisen Rearrangement." *Biomacromolecules* 14 (10): 3399–3408.
- Sen, Sanghamitra, Hasan Sadeghifar, and Dimitris S. Argyropoulos. 2013. "Kraft Lignin Chain Extension Chemistry via Propargylation, Oxidative Coupling, and Claisen Rearrangement." *Biomacromolecules* 14 (10): 3399–3408.

- Sevastyanova, Olena, Mikaela Helander, Sudip Chowdhury, Heiko Lange, Helena Wedin, Liming Zhang, Monica Ek, John F. Kadla, Claudia Crestini, and Mikael E. Lindström. 2014. "Tailoring the Molecular and Thermo–mechanical Properties of Kraft Lignin by Ultrafiltration." *Journal of Applied Polymer Science* 131 (18): 9505–9515.
- Stirn, Z., A. Rucigaj, and M. Krajnc. 2016. "Characterization and Kinetic Study of Diels-Alder Reaction: Detailed Study on N-Phenylmaleimide and Furan Based Benzoxazine with Potential Self-Healing Application." *Express Polymer Letters* 10 (7): 537–547.
- Strassberger, Zea, Stefania Tanase, and Gadi Rothenberg. 2014. "The Pros and Cons of Lignin Valorisation in an Integrated Biorefinery." *RSC Advances* 4 (48): 25310–25318.
- Suarez, H., J. W. Barlow, and D. R. Paul. 1984. "Mechanical Properties of ABS/Polycarbonate Blends." *Journal of Applied Polymer Science* 29 (11): 3253–3259.
- Sultania, Minakshi, J. S. P. Rai, and Deepak Srivastava. 2010. "Studies on the Synthesis and Curing of Epoxidized Novolac Vinyl Ester Resin from Renewable Resource Material." *European Polymer Journal* 46 (10): 2019–2032.
- Suwanprasop, Somsaluay, Thumnoon Nhujak, Sophon Roengsumran, and Amorn Petsom. 2004. "Petroleum Marker Dyes Synthesized from Cardanol and Aniline Derivatives." *Industrial & Engineering Chemistry Research* 43 (17): 4973–4978.
- Symes, W. F., and C. R. Dawson. 1953. "Separation and Structural Determination of the Olefinic Components of Poison Ivy Urushiol, Cardanol and Cardol." *Nature* 171 (4358): 841–842.
- Syrett, Jay A., C. Remzi Becer, and David M. Haddleton. 2010. "Self-Healing and Self-Mendable Polymers" 1 (7): 978–987.
- Teramoto, Yoshikuni, Seung-Hwan Lee, and Takashi Endo. 2009. "Phase Structure and Mechanical Property of Blends of Organosolv Lignin Alkyl Esters with Poly([epsilon]-Caprolactone)." *Polym. J* 41 (3): 219–227.
- Teramoto, Yoshikuni, Seung-Hwan Lee, and Takashi Endo. 2012. "Molecular Composite of Lignin: Miscibility and Complex Formation of Organosolv Lignin and Its Acetates with Synthetic

- Polymers Containing Vinyl Pyrrolidone And/Or Vinyl Acetate Units.” *Journal of Applied Polymer Science* 125 (3): 2063–2070.
- “The Cashew Export Promotion Council Of India|cashew Supplier in India|cashew Producer.” 2017. <http://www.cashewindia.org/index.php>.
- Thiebaud, S., and M. E. Borredon. 1995. “Solvent-Free Wood Esterification with Fatty Acid Chlorides.” *Bioresource Technology* 52 (2): 169–173.
- Thiebaud, S., M. E. Borredon, G. Baziard, and F. Senocq. 1997a. “Properties of Wood Esterified by Fatty-Acid Chlorides.” *Bioresource Technology* 59 (2): 103–107.
- Thielemans, Wim, and Richard P. Wool. 2005. “Lignin Esters for Use in Unsaturated Thermosets: Lignin Modification and Solubility Modeling.” *Biomacromolecules* 6 (4): 1895–1905.
- Tiainen, Eija, Torbjörn Drakenberg, Tarja Tamminen, Kirsi Kataja, and Anneli Hase. 2005. “Determination of Phenolic Hydroxyl Groups in Lignin by Combined Use of ¹H NMR and UV Spectroscopy.” *Holzforschung* 53 (5): 529–533.
- Tomani, Per. 2010. “The Lignoboost Process.” *Cellulose Chemistry and Technology* 44 (1–3): 53–58.
- Toriz, G., F. Denes, and R. A. Young. 2002. “Lignin-Polypropylene Composites. Part 1: Composites from Unmodified Lignin and Polypropylene.” *Polymer Composites* 23 (5): 806–813.
- Tornøe, Christian W., Caspar Christensen, and Morten Meldal. 2002. “Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides.” *The Journal of Organic Chemistry* 67 (9): 3057–3064.
- Trevisan, M. T. S., B. Pfundstein, R. Haubner, G. Würtele, B. Spiegelhalder, H. Bartsch, and R. W. Owen. 2006. “Characterization of Alkyl Phenols in Cashew (*Anacardium Occidentale*) Products and Assay of Their Antioxidant Capacity.” *Food and Chemical Toxicology* 44 (2): 188–197.
- Trimble, Henry. 1892. *The Tannins. A Monograph on the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents, with an Index to the Literature of the Subject*. Philadelphia, J.B. Lippincott Company.

- Tyman, J. H. P. 1975. "Long-Chain Phenols." *Journal of Chromatography A* 111 (2): 277–284.
- Tyman, J. H. P., and N. Jacobs. 1971. "The Composition of the Unsaturated Phenolic Components of Anacardic Acid." *Journal of Chromatography A* 54 (January): 83–90.
- Upton, Brianna M., and Andrea M. Kasko. 2016. "Strategies for the Conversion of Lignin to High-Value Polymeric Materials: Review and Perspective." *Chemical Reviews* 116 (4): 2275–2306.
- Vaca-Garcia, C, and M. E Borredon. 1999. "Solvent-Free Fatty Acylation of Cellulose and Lignocellulosic Wastes. Part 2: Reactions with Fatty acids¹." *Bioresource Technology* 70 (2): 135–142.
- Verge, Pierre, Thierry Fouquet, Caroline Barrère, Valérie Toniazzo, David Ruch, and João A. S. Bomfim. 2013. "Organomodification of Sepiolite Clay Using Bio-Sourced Surfactants: Compatibilization and Dispersion into Epoxy Thermosets for Properties Enhancement." *Composites Science and Technology* 79 (April): 126–132.
- Voirin, Coline, Sylvain Caillol, Nilakshi V. Sadavarte, Bhausahab V. Tawade, Bernard Boutevin, and Prakash P. Wadgaonkar. 2014. "Functionalization of Cardanol: Towards Biobased Polymers and Additives." *Polymer Chemistry* 5 (9): 3142–3162.
- Whetten, R, and R Sederoff. 1995. "Lignin Biosynthesis." *The Plant Cell* 7 (7): 1001–1013.
- Wozniak, John C., Donald R. Dimmel, and Earl W. Malcolm. 1989a. "Diels-Alder Reactions of Lignin-Derived Quinones." *Journal of Wood Chemistry and Technology* 9 (4): 513–534.
- Wozniak, John C., Donald R. Dimmel, and Earl W. Malcolm. 1989b. "The Generation of Quinones from Lignin and Lignin-Related Compounds." *Journal of Wood Chemistry and Technology* 9 (4): 491–511.
- Wu, Leo C.-F., and Wolfgang G. Glasser. 1984. "Engineering Plastics from Lignin. I. Synthesis of Hydroxypropyl Lignin." *Journal of Applied Polymer Science* 29 (4): 1111–1123.
- Xi, Weixian, Timothy F. Scott, Christopher J. Kloxin, and Christopher N. Bowman. 2014. "Click Chemistry in Materials Science." *Advanced Functional Materials* 24 (18): 2572–2590.

- Yang, Po, Jun Yan, Huazhen Sun, Haojun Fan, Yi Chen, Fang Wang, and Bi Shi. 2015. "Novel Environmentally Sustainable Cardanol-Based Plasticizer Covalently Bound to PVC via Click Chemistry: Synthesis and Properties." *RSC Advances* 5 (22): 16980–16985.
- Yao, Leilei, Qinhui Chen, Wenqin Xu, Zhibin Ye, Zhaodi Shen, and Meijin Chen. 2017. "Preparation of Cardanol Based Epoxy Plasticizer by Click Chemistry and Its Action on Poly(vinyl Chloride)." *Journal of Applied Polymer Science* 134 (23): 44890-44897.
- Yao, Zhen, Bo-en Dai, Yun-fei Yu, Hai-wei Ji, Li-zhong Zhou, and Kun Cao. 2017. "Kinetics Based on the Base-Catalyzed Mechanism of a Click Reaction between Glycol Dimercaptoacetate and Glycidyl Phenyl Ether" 7 (18): 10881–10884.
- Yu, Juan, Jifu Wang, Chunpeng Wang, Yupeng Liu, Yuzhi Xu, Chuanbing Tang, and Fuxiang Chu. 2015. "UV-Absorbent Lignin-Based Multi-Arm Star Thermoplastic Elastomers." *Macromolecular Rapid Communications* 36 (4): 398–404.
- Yu, Long, Katherine Dean, and Lin Li. 2006. "Polymer Blends and Composites from Renewable Resources." *Progress in Polymer Science* 31 (6): 576–602.
- Yue, Xiaopeng, Fangeng Chen, Xuesong Zhou, and Guangjian He. 2012. "Preparation and Characterization of Poly (Vinyl Chloride) Polyblends with Fractionated Lignin." *International Journal of Polymeric Materials* 61 (3): 214–228.
- Zhang, Chaoqun, and Michael R. Kessler. 2015. "Bio-Based Polyurethane Foam Made from Compatible Blends of Vegetable-Oil-Based Polyol and Petroleum-Based Polyol." *ACS Sustainable Chemistry & Engineering* 3 (4): 743–749.
- Zinn, Manfred, Bernard Witholt, and Thomas Egli. 2001. "Occurrence, Synthesis and Medical Application of Bacterial Polyhydroxyalkanoate." *Advanced Drug Delivery Reviews, Polymeric Materials for Advanced Drug Delivery*, 53 (1): 5–21.
- Zoia, Luca, Anika Salanti, Paola Frigerio, and Marco Orlandi. 2014. "Exploring Allylation and Claisen Rearrangement as a Novel Chemical Modification of Lignin." *BioResources* 9 (4): 6540–6561.



Pietro Buono



Modification chimie de lignine pour l'élaboration de nouveaux matériaux polymères et additifs aromatiques biosourcés

Résumé en français

Parmi les composants de la biomasse, la lignine est considérée comme l'un des plus prometteurs polymères naturels qui convient à la conversion de la biomasse en valables produits chimiques et matériaux. Malgré une grande quantité de lignine est générée dans l'industrie papetière, seule une petite quantité (2%) est exploitée dans l'industrie chimique, tandis la plupart est utilisée comme combustible à bas prix. La présence de soufre et la grande diversité moléculaire sont les principaux obstacles pour l'utilisation de la lignine comme composant de base pour la production de valables produits. La modification chimique a été reconnue comme un outil pour contourner ces limites, principalement pour l'amélioration de la réactivité chimique, la réduction de la fragilité des polymères, l'augmentation de la solubilité dans les solvants organiques et l'incorporation dans des matrices polymériques hydrophobes. Dans cette thèse, différentes stratégies de synthèse ont été appliquées pour introduire de nouveaux groupes chimiques sur une soude lignine qui présente une haute fonctionnalisation de groupes hydroxyles. Les dérivés correspondants de lignine ont été utilisés soit pour l'élaboration des matériaux par "click" polymérisations, soit pour augmenter l'hydrophobicité de la lignine afin de faciliter son traitement avec des matrices polymériques.

Mot-clef : lignine, biopolymères, matériaux polymères, chimie clique, additifs

Résumé en anglais

Among biomass components, lignin is considered one of the most promising natural polymers suitable for the conversion of biomass into renewable added-value chemicals and materials. However, large amount of lignin generated from wood pulping industry is burn as low cost energy source, and only a small amount (e.g. 2%), is exploited in the chemical industry. The presence of sulphur moieties and the large molecular diversity are the most reasons impeding the use of lignin as building blocks for the production of chemicals and materials. Chemical modifications have been acknowledged to be an important tool to circumvent these limitations, mainly by improving the chemical reactivity, reducing the brittleness of polymers, increasing the solubility in organic solvents and facilitating the ease of processing of lignin. In the current work, taking advantage of the high hydroxyl groups content of a sulphur free soda lignin (SL), different synthetic strategies have been applied to introduce new chemical groups and used either to produce lignin derivatives suitable for "click" polymerization either to increase lignin hydrophobicity, facilitating its processing in polymeric matrices.

Keywords: lignin, biopolymers, polymeric materials, click chemistry, additives