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# New generation of epoxy networks based on ionic liquids: From structuration to final properties

Thi Khanh Ly Nguyen

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**New generation of epoxy networks based on ionic liquids:**  
**From structuration to final properties**

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*“Man's dearest possession is life. It is given to him but once, and he must live it so as to feel no torturing regrets for wasted years, never know the burning shame of a mean and petty past”*

*\_Nikolai Ostrovsky\_*



*For my splendid days in France*



# Abstract

Having excellent intrinsic properties with an infinity cation/anion combination, ionic liquids (ILs) have become very attractive in the field of polymer science, especially in the epoxy networks. Thus, this research work presents the preparation, characterization and modification of epoxy/IL networks. The first part of this work is dedicated to study the effect of ILs as comonomers in the formation of epoxy networks. The reactivity of ILs towards epoxy prepolymer and their role either as initiators or as curing agents in the formation of epoxy/IL networks was investigated. Then, the effect of the chemical nature of ILs on the final properties of epoxy/IL networks was demonstrated including thermomechanical properties, thermal stability, surface properties and mechanical behaviors. In addition, the mechanism of curing reaction between epoxy prepolymer and ILs was revealed using different methods (FTIR and NMR). In the second part, modifiers (thermoplastics and core-shell particles) were incorporated into epoxy/IL networks in order to improve their mechanical performances. In the last section, the combination of ILs and bio-based epoxy networks was studied as partial or complete substitutions for petroleum based epoxy systems aiming for “green materials” coatings applications. Thus, the unique properties of ionic liquids led to remarkable changes in morphology and properties of epoxy systems. The relation between the chemical nature of ILs, the morphology and the properties of obtained epoxy networks was highlighted.

**Keywords:** Epoxy networks; ionic liquids; epoxy/ionic liquid networks; structure-properties relation; reactivity; networks properties; reaction mechanism; modifications; thermosetting/thermoplastic blends; core-shell particles; bio-based epoxy networks.

# Résumé

Les liquides ioniques (LIs), possédant d'excellentes propriétés intrinsèques et offrant une infinité de combinaisons possibles ouvrent de nouvelles perspectives dans le domaine des polymères, en particulier dans celui des réseaux époxyde. Ce travail de thèse présente la préparation, la caractérisation et la modification de réseaux époxy / liquides ioniques. Dans un premier temps, ce travail est dédié à étudier l'influence des LIs comme comonomères de prépolymère époxyde. Ainsi, la réactivité des LIs vers la DGEBA et leur rôle en tant qu'amorceurs et/ou durcisseurs de systèmes époxyde ont été étudiés. Ensuite, l'effet de la nature chimique des LIs sur les propriétés de réseaux époxy / LIs, y compris les propriétés thermomécaniques, la stabilité thermique, les propriétés de surface et les comportements mécaniques, a été démontré. En outre, le mécanisme de la réaction entre les prépolymères époxy et LIs a été révélé à l'aide de différentes méthodes (IRTF et RMN). Dans la deuxième partie, les agents modifiants (thermoplastiques et des particules cœur-coquille) ont été incorporés dans des réseaux époxy / LI en vue d'améliorer leurs performances mécaniques. Dans la dernière section, la combinaison des LIs et des réseaux époxyde biosourcés a été étudiée en tant que substituts partiels ou complets aux systèmes époxyde issus du pétrole afin de développer des matériaux à faible empreinte environnementale. Ainsi, l'utilisation des liquides ioniques a eu des effets bénéfiques sur la morphologie mais également sur les propriétés des réseaux. La relation entre la nature chimique des LIs, la morphologie et les propriétés obtenues a été soulignée.

**Mots clés** Réseaux époxydes ; liquides ioniques ; réseaux époxy / liquides ioniques ; relation structure propriétés ; réactivité ; propriétés des réseaux ; mécanisme de la réaction ; modifications ; mélange thermodurcissable / thermoplastique ; particules cœur-coquille ; réseaux époxydes biosourcés.

# Table of Contents

---

<b>Acknowledgements</b> .....	<b>iii</b>
<b>Abstract</b> .....	<b>x</b>
<b>Résumé</b> .....	<b>xi</b>
<b>Table of Contents</b> .....	<b>xii</b>
<b>List of Tables</b> .....	<b>xvi</b>
<b>Lists of Figures</b> .....	<b>xviii</b>
<b>Lists of Schemes</b> .....	<b>xxiv</b>
<b>List of abbreviations and symbols</b> .....	<b>xxv</b>
<b>General Introduction</b> .....	<b>1</b>
<b>Résumé Étendu</b> .....	<b>3</b>
<b>Chapter 1: Literature Review</b> .....	<b>28</b>
<b>1.1. Ionic liquids and Polymers</b> .....	<b>31</b>
1.1.1. Ionic liquids.....	31
1.1.2. Interaction between Ionic liquids and polymers.....	32
1.1.3. Ionic liquids applications in polymer systems .....	33
1.1.4. Conclusion .....	39
<b>1.2. Ionic liquids in epoxy networks</b> .....	<b>39</b>
1.2.1. Epoxy networks.....	39
1.2.2. Ionic Liquids in epoxy networks .....	42
1.2.3. Conclusion .....	58
<b>1.3. Modification of epoxy networks</b> .....	<b>58</b>
1.3.1. Introduction.....	58

1.3.2. Modification of epoxy networks by thermoplastics .....	58
1.3.3. Modification of epoxy networks by core-shell particles .....	66
1.3.4. Conclusion .....	73
<b>1.4. Bio-based epoxy networks .....</b>	<b>73</b>
1.4.1. Introduction .....	73
1.4.2. Preparation of epoxy and curing agent monomers based on cardanol.....	74
1.4.3. Preparation of epoxy networks using Cardanol based compounds .....	77
1.4.4. Conclusion .....	82
<b>1.5. Conclusion of chapter 1 .....</b>	<b>83</b>
<b>References of chapter 1 .....</b>	<b>84</b>
<b>Chapter 2: Ionic liquids: A new route for the design of epoxy networks .....</b>	<b>94</b>
<b>2.1. Introduction .....</b>	<b>97</b>
<b>2.2. Experimental.....</b>	<b>98</b>
2.2.1. Materials and methods .....	98
2.2.2. Preparation of samples .....	100
2.2.3. Characterization of epoxy/IL mixtures and networks.....	100
<b>2.3. Results and Discussions .....</b>	<b>103</b>
2.3.1. Ionic Liquids as reactive additives for the preparation and modification of Epoxy networks .....	103
2.3.2. Effect of ILs nature on the design of Epoxy networks .....	114
2.3.3. Conclusion .....	124
<b>2.4. Polymerization Mechanism between phosphonium ionic liquids and the epoxide functional group of epoxy prepolymer .....</b>	<b>125</b>
2.4.1. Introduction and materials.....	125
2.4.2. Preparation of samples.....	126
2.4.3. Characterization of epoxy/IL mixtures.....	126
2.4.4. Results and discussion.....	127

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2.4.5. Conclusion .....	137
<b>2.5. Conclusion of chapter 2 .....</b>	<b>137</b>
<b>References of chapter 2 .....</b>	<b>138</b>
<b>Supporting Information of chapter 2.....</b>	<b>143</b>
<b>Chapter 3: Modification of Epoxy/Ionic Liquid networks .....</b>	<b>145</b>
<b>3.1. Toughening of epoxy/ionic liquid networks with thermoplastics based on poly (2,6-dimethyl-1,4-phenylene ether) (PPE).....</b>	<b>148</b>
3.1.1. Introduction .....	148
3.1.2. Experimental.....	149
3.1.3. Results and discussion.....	152
3.1.4. Conclusion .....	164
<b>3.2. Dual functions of IL in the core-shell particle reinforced epoxy networks: curing agent vs dispersion aids.....</b>	<b>165</b>
3.2.1. Introduction .....	165
3.2.2. Experimental.....	165
3.2.3. Results and discussions .....	167
3.2.4. Conclusion .....	179
<b>3.3. Conclusion of chapter 3 .....</b>	<b>180</b>
<b>References of chapter 3 .....</b>	<b>181</b>
<b>Supporting Information of chapter 3.....</b>	<b>181</b>
<b>Chapter 4: Bio-based Epoxy/IL networks .....</b>	<b>192</b>
<b>4.1. Introduction .....</b>	<b>194</b>
<b>4.2. Experimental.....</b>	<b>195</b>
4.2.1. Materials.....	195
4.2.2. Samples preparation.....	196
<b>4.3. Results and discussions.....</b>	<b>196</b>

4.3.1. Bio based epoxy/IL (CA/IL) networks.....	196
4.3.2. Influence of Cardolite on the properties of DGEBA/ILs systems.....	204
<b>4.4. Conclusion of chapter 4 .....</b>	<b>215</b>
<b>References of chapter 4 .....</b>	<b>216</b>
<b>Chapter 5: Conclusions and Perspectives .....</b>	<b>219</b>

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# List of Tables

<b>Table 2-1</b> Principal properties of used materials: DGEBA, Jeffamine D230, Jeffamine D400, MCDEA, and phosphonium ionic liquids. ....	99
<b>Table 2-2</b> Curing conditions of epoxy/amine and epoxy/IL systems. ....	100
<b>Table 2-3</b> Decomposition temperatures Td of different DGEBA networks under inert atmosphere. ....	108
<b>Table 2-4</b> Determination of dispersive and non-dispersive components of the surface energy on epoxy/ amine and epoxy/ionic liquid network from contact angles with water and diiodomethane. ....	109
<b>Table 2-5</b> Variation of glass transition temperature $T_g$ of DGEBA systems. ....	110
<b>Table 2-6</b> DMA values of epoxy/ amine and epoxy/ionic liquid systems (measurement rate of 3 °C.min <sup>-1</sup> ). ....	110
<b>Table 2-7</b> DMA Modulus value of DGEBA system with 10 phr of phosphate ionic liquid. ....	112
<b>Table 2-8</b> Contact angles and surface energy of epoxy networks measured by sessile drop method. ....	118
<b>Table 2-9</b> Thermo-mechanical behavior of epoxy networks cured by different curing agents. .	121
<b>Table 2-10</b> Mechanical behavior (determined at room temperature) of epoxy networks cured by different curing agents. ....	122
<b>Table 2-11</b> TGA data of EPP, IL-TMP, IL-EPC, EPP/IL-TMP and EPP/IL-EPC network.	128
<b>Table 3-1</b> Chemical structure and some principal properties of DGEBA, MCDEA, phosphonium ILs and PPE thermoplastics. ....	150
<b>Table 3-2</b> Curing protocol for PPE-modified epoxy networks. ....	151
<b>Table 3-3</b> Thermal and viscoelastic properties of neat PPE, unmodified and PPE-modified epoxy networks. ....	156
<b>Table 3-4</b> Thermal stability of neat PPE, unmodified and PPE-modified epoxy networks.....	158
<b>Table 3-5</b> Surface energy of neat PPE, unmodified and PPE-modified epoxy/amine and epoxy/IL networks. ....	160

---

<b>Table 3-6</b> Mechanical properties of unmodified and PPE-modified epoxy/amine and epoxy/IL networks. ....	161
<b>Table 3-7</b> Curing protocol for CSR-modified epoxy networks. ....	167
<b>Table 3-8</b> Exothermal peak temperature of G52-modified epoxy networks measured by DSC.	168
<b>Table 3-9</b> Relaxation temperatures of unmodified and CSR-modified epoxy networks. ....	174
<b>Table 3-10</b> Degradation temperature of CSR, neat epoxy networks and CSR-modified epoxy networks from TGA. ....	175
<b>Table 3-11</b> Surface energy of neat epoxy networks and epoxy networks modified by CSR. ....	176
<b>Table 3-12</b> Mechanical behavior (Determined at room temperature) of epoxy networks modified by CSR. ....	177
<b>Table 4-1</b> Reaction enthalpy peak temperature (DSC, 10 K.min <sup>-1</sup> ) of different epoxy/IL reactive systems. ....	197
<b>Table 4-2</b> Contact angles and surface energy of epoxy networks measured by sessile drop method. ....	200
<b>Table 4-3</b> Degradation temperatures used epoxy prepolymers and formed epoxy/IL networks	202
<b>Table 4-4</b> Relaxation temperature $T_{\alpha}$ , storage modulus in the rubbery state ( $E'_R$ ) of epoxy/IL networks. ....	203
<b>Table 4-5</b> Exothermal peak temperature of CA-modified epoxy/IL networks measured by DSC. ....	204
<b>Table 4-6</b> Thermomechanical behavior of CA-modified epoxy/IL networks (IL-DCA or IL-TMP). ....	209
<b>Table 4-7</b> Thermal stability of neat CA, unmodified and CA-modified epoxy networks. ....	210
<b>Table 4-8</b> Surface energy of neat epoxy/IL networks and epoxy/IL networks modified by CA. ....	212
<b>Table 4-9</b> Fracture toughness ( $K_{Ic}$ ) of unmodified and CA-modified epoxy/IL networks. ....	213

# Lists of Figures

<b>Figure 1-1</b> Structure of commonly used ionic liquids .....	31
<b>Figure 1-2</b> Publications about “ionic liquids” and “ionic liquids and polymer” determined from ISI Web of Science in the last twenty years.....	33
<b>Figure 1-3</b> Ionic conductivity of ILs (○), PILs (□), PILs with equimolar amount of LiTFSI (Δ) compared to a model electrolyte salt (▲). .....	34
<b>Figure 1-4</b> TEM micrographs of neat PTFE (a) and blends of PTFE with imidazolium (b), pyridinium (c) and phosphonium (d) ILs.....	35
<b>Figure 1-5</b> Epoxy based networked polymer having ILs cation grafted on the backbone .....	43
<b>Figure 1-6</b> Epoxy based networked polymers having lithium salts with anionic groups grafted on the backbone .....	43
<b>Figure 1-7</b> Ionic-liquid-swollen epoxy based networked polymers.....	44
<b>Figure 1-8</b> Crosslinked triazolium based epoxy-amine networks .....	44
<b>Figure 1-9</b> DSC thermograms of DGEBA/MCDEA networks as a function of heating rate and IL content (a) 0, (b) 1, (c) 2.5 and (d) 5 phr of IL .....	46
<b>Figure 1-10</b> TEM images of epoxy networks containing 10 phr of (a) Phos-DCA, (b) Phos-DBS, (c) Phos-TFSI and (d) without IL .....	46
<b>Figure 1-11</b> Tensile stress-strain curves of hard thermoset (black curve) showing perfectly brittle fracture at 10 % IL, plastic thermosets showing ductile behavior at 30 % of IL (red curve) and S-shaped curves of elastomeric thermosets at 50 % IL (green curve).....	47
<b>Figure 1-12</b> Ionic conductivity of gel polymer electrolyte with different amounts of Phos-TMP with 0.2 M of lithium salt .....	49
<b>Figure 1-13</b> Surface topography and cross section profiles of epoxy/amine networks containing 12 wt% of IL showing the evolution of wear track as a function of time.....	50
<b>Figure 1-14</b> Surface topography of cross section showing porosity of epoxy/amine networks containing a) 9 wt% and b) 12 wt% .....	50

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<b>Figure 1-15</b> IL-modified clay dispersion in epoxy nanocomposite cured with a) imidazoles (intercalation) and b) anhydride (exfoliation).....	51
<b>Figure 1-16</b> Epoxy-silica hybrids: (a) without ILs and those formed in the presence of (b) methyl sulfonate based IL,(c) tetrafluoroborate based IL and (d) tetrafluoroborate based IL and hydrochloric acid .....	52
<b>Figure 1-17</b> TEM micrographs of the epoxy networks cured with (a) 5 phr, (b) 10 phr and (c) 30 phr of phosphonium dicyanamide ILs.....	56
<b>Figure 1-18</b> Samples of epoxy networks cured with dicyanamide anion ILs containing phosphonium (left) and imidazolium (right) cation.....	56
<b>Figure 1-19</b> Conversion vs composition transformation diagram type LCTS for a TS/TP blends in case of stepwise polymerization (M: TP phase) .....	59
<b>Figure 1-20</b> Ternary phase diagram of TS/TP blends formed by chainwise polymerization (Crit. = critical point).....	60
<b>Figure 1-21</b> Phase diagram of epoxy/PPE blends including (—) cloud point curve, (-·-) calculated $T_g$ lines and (—) $T_g$ due to thermoreversible gelation .....	61
<b>Figure 1-22</b> Morphology of epoxy/PPE blends with PPE molar mass of 10 and 30 $\text{kg}\cdot\text{mol}^{-1}$ and PPE content of 30-80 wt% after cooling from 200°C to room temperature observed by scanning electron microscopy .....	62
<b>Figure 1-23</b> Optical micrographs of PPE-modified epoxy blends (30phr) cured for different times at 180 °C showing the spinodal decomposition.....	63
<b>Figure 1-24</b> SEM micrographs of PPE modified epoxy networks cured by imidazole with different PPE content (10-60 wt%).....	65
<b>Figure 1-25</b> Shear yielding mechanism of rubber-modified epoxy networks indicated by the formation of furrows running almost parallel to the principal tensile .....	67
<b>Figure 1-26</b> Toughening mechanism of CSR-modified epoxy networks summarized by four steps: a) initial starter crack; b) formation of cavitation zone; c) formation of initial shear-yielded plastic zone and d) propagation of crack under shear yielding .....	68
<b>Figure 1-27</b> Different multi-layer CSR particles used by Day <i>et al.</i> to toughen epoxy networks. ....	73

<b>Figure 1-28</b> SEM micrographs of the fracture surface of DGEBA based epoxy networks cured with a) MBCBE showing the cavities and b) Phenalkamines with no phase separation.....	82
<b>Figure 2-1</b> Chemical structure of DGEBA, Jeffamine D230, Jeffamine D400, MCDEA, and phosphonium ionic liquids.....	99
<b>Figure 2-2</b> Compact Tension specimen configuration.....	102
<b>Figure 2-3</b> Samples of epoxy prepolymer containing different amount of IL-TMP of (a) 10 phr and (b) 20 phr (Exudation of IL on the surface of samples with color change due to the oxidation). .....	103
<b>Figure 2-4</b> DSC thermograms of epoxy/Jeffamine D400 (■), epoxy/ 10 phr IL-TMP (○) and epoxy/ 10 phr IL-DEP (★).....	104
<b>Figure 2-5</b> DSC thermograms of epoxy/ 10phr IL-DEP (■), epoxy/ 20phr IL-DEP (○) and epoxy/ 30phr IL-DEP (★).....	104
<b>Figure 2-6</b> Proposed curing mechanism for the polymerization of epoxy prepolymer initiated by phosphate ionic liquid.....	105
<b>Figure 2-7</b> Conversion of epoxide groups versus reaction time of (a) epoxy/different curing agents and (b) epoxy/different amounts of IL-DEP.....	106
<b>Figure 2-8</b> Evolution of weight loss as a function of temperature (TGA) of epoxy networks with different curing agents: Jeffamine D400 (■), 10 phr IL-TMP (○) and 10 phr IL-DEP (★).....	107
<b>Figure 2-9</b> Evolution of weight loss as a function of temperature (TGA, DTGA) of neat ionic liquid IL-DEP (■) and epoxy/IL-DEP networks: 10 phr (○), 20 phr (★) and 30 phr (Δ).....	108
<b>Figure 2-10</b> Storage Modulus $E'$ (a) and loss factor $\tan\delta$ (b) as a function of temperature of DGEBA systems with different types of curing agent: Jeffamine (■), 10 phr IL-TMP (○) and 10 phr IL-DEP (★) from DMA with measurement rate of $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .....	111
<b>Figure 2-11</b> Loss factor $\tan\delta$ as a function of temperature of epoxy/phosphate ionic liquid IL-DEP at different contents: 10 phr (■), 20 phr (○) and 30 phr (★).....	111
<b>Figure 2-12</b> Storage Modulus $E'$ (a) and loss factor $\tan\delta$ (b) as a function of temperature of epoxy/10 phr IL-DEP at different DMA measuring velocity: $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (■), $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (○) and $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (★).....	112
<b>Figure 2-13</b> Proposed mechanism for the polymerization of phosphate ionic liquid with epoxy prepolymer.....	113

<b>Figure 2-14</b> Reaction enthalpy peak temperature (DSC, 10 K.min <sup>-1</sup> ) of different epoxy reactive systems.....	114
<b>Figure 2-15</b> Epoxide group conversion as a function of curing time calculated from FT-IR spectra of different epoxy/IL systems during cure (see Table 2-2 for curing schedules which differ for each reactive system).....	116
<b>Figure 2-16</b> TEM micrographs of IL-EPC (a), IL-TMP (b), IL-DEP (c) and IL-EHP (d) networks.....	117
<b>Figure 2-17</b> Contact angle with water on surfaces of epoxy networks cured with different types of IL and different ILs amount.....	118
<b>Figure 2-18</b> Weight loss as a function of temperature (TGA, DTGA) of epoxy networks: MCDEA (■), Jeffamine D230 (○), IL-TMP (Δ), IL-EPC (◆), IL-DEP (☆) and IL-EHP (◄) (heating ramp 20 K.min <sup>-1</sup> , N <sub>2</sub> atmosphere).....	119
<b>Figure 2-19</b> Storage modulus E' and loss factor tan δ as a function of temperature of DGEBA-based networks cured with different types of curing agent: MCDEA (■), Jeffamine D230 (○), IL-TMP (Δ), IL-EPC (◆), IL-DEP (☆), and IL-EHP (◄) at 1Hz.....	120
<b>Figure 2-20</b> Fractured surfaces of epoxy networks cured with IL-EPC (a), IL-TMP (b), and MCDEA (c) at magnification of ×500 (up) and MCDEA (d), IL-DEP (e) and D230 (f) at magnification of ×50 (down).....	123
<b>Figure 2-21</b> Load-deflection curves of epoxy/different curing agents: MCDEA (○), Jeffamine D230 (■), IL-TMP (Δ), IL-EPC (◆) and IL-DEP (★) (2 mm.min <sup>-1</sup> ).....	124
<b>Figure 2-22</b> Chemical structures of phosphonium ILs (IL-EPC, IL-TMP) and mono-epoxy denoted 1,2-epoxy-3-phenoxypropane (EPP).....	125
<b>Figure 2-23</b> DSC thermogram of EPP/IL-TMP (■,□) and EPP/IL-EPC (●,○) systems: before (■,●) and after the curing procedure (□,○).....	127
<b>Figure 2-24</b> TGA (■,●,★) and DTGA (□,○,☆) curves of EPP (■,□), neat IL (●,○) and EPP/ILs (★,☆) for EPP/IL-TMP (left) and EPP/IL-EPC (right) systems.....	128
<b>Figure 2-25</b> SEC analysis for IL, EPP, EPP/ILs systems after curing for IL-TMP (left) and IL-EPC (right).....	129
<b>Figure 2-26</b> Epoxy conversion as a function of curing time of EPP/IL-TMP (■) and EPP/IL-EPC (○) systems.....	129

<b>Figure 2-27</b> $^1\text{H}$ NMR of EPP and EPP/IL-TMP system after 2h and 5h of curing. ....	131
<b>Figure 2-28</b> $^{13}\text{C}$ NMR of EPP and EPP/IL-TMP system after 2h and 5h of curing.....	131
<b>Figure 2-29</b> $^{31}\text{P}$ NMR of IL-TMP and EPP/IL-TMP system after 5 minutes, 15 minutes, 30 minutes and 1 hour at 80 °C.....	132
<b>Figure 2-30</b> $^{31}\text{P}$ NMR of IL-EPC and EPP/IL-EPC systems before the reaction and after 30 minutes and 5 h of curing process.....	133
<b>Figure 2-31</b> Predicted $^{13}\text{C}$ NMR of EPP/IL-EPC primary product by Chemdraw. ....	135
<b>Figure 2-32</b> $^{13}\text{C}$ NMR of IL-EPC, EPP and EPP/IL-EPC systems before the reaction and after 5, 15, 30 mins, 2 hours and 5 hours of curing (chemical shift from 44 to 74 ppm). ....	135
<b>Figure 2-33</b> $^{13}\text{C}$ NMR of IL-EPC and EPP/IL-EPC systems before the reaction and after 30 mins and 5 hours of curing (chemical shift from 173 to 184 ppm). ....	136
<b>Figure 3-1</b> Morphology of different PPE-1 (a, c, e) and PPE-2 (b, d, f) modified epoxy/amine (a, b), epoxy/IL-TMP (c, d) and epoxy/IL-DEP (e, f) networks.....	152
<b>Figure 3-2</b> DMA analysis of (■) unmodified, (●) PPE-1-modified and (☆) PPE-2-modified epoxy networked cured by a) MCDEA, b) IL-TMP and c) IL-DEP.....	155
<b>Figure 3-3</b> Weight loss as a function of temperature of neat PPE-1 (■), PPE-2 (○), unmodified epoxy networks (▷) and PPE-modified considering the addition of PPE-1 (◀) and PPE-2 (☆) cured by a) MCDEA, b) IL-TMP and c) IL-DEP.....	159
<b>Figure 3-4</b> Fracture surface of unmodified (a, d, g), modified by PPE-1 (b, e, h) and PPE-2 (c, f, i) modified epoxy/amine (a, b,c), epoxy/IL-TMP (d, e, f) and epoxy/IL-DEP (g, h,i) networks observed by SEM.....	163
<b>Figure 3-5</b> Epoxide group conversion as a function of curing time of epoxy/IL networks (□) modified by 10 phr (●) and 20 phr (Δ) CSR and cured with a) IL-TMP and b) IL-DEP.....	169
<b>Figure 3-6</b> TEM image of epoxy networks modified by 10 (a, c, e) and 20 phr (b, d, f) of CSR using MCDEA (a, b), IL-TMP (c, d) and IL-DEP (e, f).....	172
<b>Figure 3-7</b> DMA curves of epoxy networks modified by CSR using MCDEA (a), IL-TMP (b) and IL-DEP (c). ....	173
<b>Figure 4-1</b> Chemical structures of Cardolite® cardanol derived epoxy prepolymer and phosphonium ILs. ....	195

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<b>Figure 4-2</b> DSC curves (10 K.min <sup>-1</sup> , under nitrogen) of different epoxy/IL reactive systems containing IL-DCA (left) and IL-TMP (right).....	197
<b>Figure 4-3</b> Conversion of epoxide groups versus reaction time of different CA/ILs systems....	199
<b>Figure 4-4</b> Weight loss as a function of temperature (TGA, DTGA) of epoxy/IL networks cured with IL-DCA (up) and IL-TMP (down): at left, evolution of weight and at right, derivative of weight loss as a function of temperature.....	201
<b>Figure 4-5</b> DSC thermogram of CA-modified epoxy/IL networks.....	204
<b>Figure 4-6</b> Epoxide group conversion as a function of curing time of CA-modified epoxy/IL networks (IL-DCA or IL-TMP) with different amount of CA.....	206
<b>Figure 4-7</b> TEM micrographs of CA-modified epoxy/IL networks cured with IL-DCA (a,b,c) and IL-TMP (d,e) containing cardanol based epoxy prepolymer of 10 phr (a,d), 20 phr (b,e) and 30 phr (c).....	207
<b>Figure 4-8</b> DMA analysis of (■) unmodified, CA-modified epoxy networks containing 10 phr (○), 20 phr (▲), 30 phr of CA (☆) cured by IL-DCA (left) and IL-TMP (right). .....	208
<b>Figure 4-9</b> Weight loss as a function of temperature (TGA, DTGA) (■) unmodified and CA-modified epoxy networks containing 10 phr (○), 20 phr (▲), 30 phr of CA (☆) cured by IL-DCA (up) and IL-TMP (down). .....	211
<b>Figure 4-10</b> Flexibility test on CA-modified DGEBA/IL-DCA (a,b,c) and DGEBA/IL-TMP (d,e) networks containing 10 phr (a,d), 20 phr (b,e) and 30 phr (c) of CA.....	214
<b>Figure 4-11</b> Fracture surface of unmodified (a,d) and CA-modified epoxy/IL networks containing 10 phr (b,e) and 20 phr (c,f) of CA cured with IL-DCA (a,b,c)and IL-TMP (d,e,f).....	215
<b>Figure 5-1</b> Heat release rate curves for epoxy resins in cone calorimeter test (heat flux 35 kW/m <sup>2</sup> ). .....	221
<b>Figure 5-2</b> Residue after cone calorimetry test of epoxy/amine and epoxy/IL networks cured with 10, 20, 30 phr of IL-DEP. ....	221

# Lists of Schemes

<b>Scheme 1-1</b> Synthesis of DGEBA.....	39
<b>Scheme 1-2</b> Mechanism of addition reactions between epoxy and amine groups with reaction rate constant $k_1$ and $k_2$ .....	40
<b>Scheme 1-3</b> Etherification mechanism between epoxy and hydroxyl groups. ....	40
<b>Scheme 1-4</b> Chain homopolymerization of epoxy prepolymer initiated by imidazoles.....	41
<b>Scheme 1-5</b> Mechanism of anhydride epoxy copolymerization initiated by tertiary amines. ....	42
<b>Scheme 1-6</b> Proposed mechanism for curing reaction between imidazolium ILs and epoxy prepolymer.....	53
<b>Scheme 1-7</b> Curing mechanism for epoxy networks formation by 1-alkyl imidazolium ILs proposed by Szychaj <i>et al.</i> including (a) the decomposition of IL into 1-alkyl imidazoles; (b) the formation of imidazole epoxy adduct and the polymerization of epoxy resin and (c) the regeneration of alkyl imidazoles and the structurization of final epoxy networks).....	54
<b>Scheme 1-8</b> Mechanism for the homopolymerization of epoxy prepolymer initiated by the phosphonium phosphinate ionic liquid proposed by our groups.....	55
<b>Scheme 1-9</b> Possible thermal decomposition of 1-ethyl-3-methylimidazolium dicyanamide ionic liquid with the formation of isocyanurate rings.....	57
<b>Scheme 1-10</b> Natural compounds present or derived from cashew nutshell liquid.....	74
<b>Scheme 1-11</b> Synthesis of diepoxidized cardanol.....	75
<b>Scheme 1-12</b> Structure of commercial cardanol epoxy derivatives provided by Cardolite.....	76
<b>Scheme 1-13</b> Formation of Phenalkamine through Mannich condensation .....	77
<b>Scheme 1-14</b> Synthesis of amine-functionalized cardanol through thiolene reaction.....	77
<b>Scheme 1-15</b> Synthesis of cardanol based epoxy novolac resin.....	78
<b>Scheme 1-16</b> Chemical structure of cardanol NC-514 proposed by Caillol's group. ....	81
<b>Scheme 2-1</b> Possible mechanism of curing reaction between EPP and ionic liquid. ....	134
<b>Scheme 2-2</b> Proposed chemical structure of EPP/IL-EPC primary product based on proposed mechanism.....	134
<b>Scheme 2-3</b> Decomposition mechanism of EPP/IL-EPC primary product to form EPP and free IL. ....	137

# List of abbreviations and symbols

## Nomenclature

a/e	Amino hydrogen to epoxy ratio
AHEW	Amine Hydrogen Equivalent Weight
AN	Acrylonitrile
BASIL	Biphasic acid scavenging using ionic liquids
BF <sub>4</sub> <sup>-</sup>	Tetrafluoroborate
BPA	Bisphenol A
Br <sup>-</sup>	Bromide
CA	Cardolite NC-514
CNSL	Cashew nutshell liquid
CNT	Carbon nanotube
CSR	Core-shell rubbery nanoparticles
CTBN	Liquid rubber
DBS	Sulfonate
DCA	Dicyanamide
DDA	4,4-diaminodiphenylamine
DDM	4,4'-methylenedianiline
DEC	Diepoxidized cardanol
DGEBA	Diglycidyl ether of bisphenol A
DOP	Diethyl phthalate
ECP	Cardanol based epoxy prepolymer
EDA	Electron donor acceptor
EEW	Epoxide equivalent weight
EPP	1,2-epoxy-3-phenoxypropane
GMA	Glycidyl methacrylate
GNP	Graphite nanophletelets
GPE	Gel polymer electrolyte
HDPE	High density polyethylene
IL	Ionic liquid
IL-DCA	Trihexyl(tetradecyl)phosphonium dicyanamide
IL-DEP	Tributyl(ethyl)phosphonium diethylphosphate
IL-EHP	Trihexyl(tetradecyl) phosphonium bis(2-ethylhexyl)phosphate
IL-EPC	Trihexyl(tetradecyl) phosphonium 2-ethylhexanoate
IL-TMP	Trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate

IPDA	Isophorone diamine
LCTS	Lower critical temperature solution
LDH	Layer double hydroxide
LiTFSI	Lithium bis(trifluoromethane sulfonyl) imide
MBCBE	Mannich base of cardanol butyl ether
MCDEA	4,4'-Methylene bis(3-Chloro-2,6-Diethylaniline)
MMA	Methyl methacrylate
MMT	Montmorillonite
MS	Monomer styrene
PA6	Poly (amide 6)
PAN	Poly (acrylonitrile)
PBA	Poly (butyl acrylate)
PBAT	Poly (butylenes adipate- co-terephthalate)
PBD	Poly (butadiene)
PDMS	Poly (dimethyl siloxane)
PECGE	Poly (epoxide cardanol glycidyl ether)
PEEK	Poly (ether ether ketone)
PEI	Poly (ether imide)
PEO	Poly (ethylene oxide)
PES	Poly (ether sulfone)
PF <sub>6</sub> <sup>-</sup>	Hexafluorophosphate
Phos-DBS	Phosponium-sulfonat IL
Phos-DCA	Phosponium-dicyanamide IL
Phos-TFSI	Phosponium-bis(trifluoromethane sulfonyl) imide IL
Phos-TMP	Phosponium-phosphinate IL
Phr	Per hundred
PIL	Poly (ionic liquid)
PLA	Poly (lactic acid)
PMC	Polymer matrix composite
PMMA	Poly (methyl methacrylate)
PP	Polypropylene
PPE	Poly (phenylene ether)
PS	Polystyrene
PSF	Polysulfone
PTFE	Poly (tetrafluoroethylene)
PVA	Poly (vinyl alcohol)
PVC	Poly (vinyl chloride)
P(VDF-HFP)	Poly (vinylidene fluoride hexafluoro propylene)
P(VDF-CTFE)	Poly (vinylidene fluoride-co-chlorotrifluoroethylene)
RIPS	Reaction induced phase separation

RTILs	Room temperature ionic liquids
SBR	Poly (styrene butadiene rubber)
SWNT	Single wall carbon nanotubes
TFSI	Trifluoro methane sulfonyl imide
TGC	Triglycidyl cardanol resin
TMP	Phosphinate
TS/TP	Thermosetting/thermoplastic
UCTS	Upper critical temperature solution
UV	Ultraviolet
wt%	Weight percent

### **Characterization**

DMA	Dynamic mechanical analysis
DMS	Dynamic mechanical spectroscopy
DSC	Differential scanning calorimetry
DTG	Derivative Thermogravimetric Analysis
E'	Storage Modulus
E' <sub>R</sub>	Storage modulus at rubbery state
E <sub>f</sub>	Flexural Modulus
FTIR	Fourier transform infrared spectroscopy
G <sub>Ic</sub>	Fracture energy
K <sub>Ic</sub>	Fracture toughness
M <sub>n</sub>	Molar mass
v <sub>ε</sub>	Crosslink density
NMR	Nuclear magnetic resonance
SEC	Size exclusion chromatography
SEM	Scanning Electron Microscopy
T <sub>α</sub>	Relaxation temperature
tan	Loss factor
T <sub>d</sub>	Degradation temperature
TEM	Transmission electronic microscopy
T <sub>g</sub>	Glass transition temperature
TGA	Thermogravimetric Analysis
σ <sub>R</sub>	Flexural Strength



# General Introduction

Nowadays, the development of new high-performance materials has become crucial in order to meet industrial demand. Epoxy networks, one of the most important classes of thermosetting polymers, are one of the biggest targets. Thanks to their excellent mechanical, thermal and electrical properties, epoxy networks provide applications in several fields from adhesives, electrical insulation to polymer matrix composite (PMC) design in aerospace. However, the high crosslinking density of epoxy networks results in their low impact resistance, which requires the use of modifiers. Recently, ionic liquids have appeared as new reactive additives to epoxy networks with unprecedented properties. In fact, ionic liquids are organic salts with a melting temperature lower than 100 °C. The unique properties of ionic liquids such as nonflammability, great thermal stability, low saturated vapor pressure and a good ionic conductivity gained the attention of both research and industry. However, the application of ionic liquids in the polymer fields, particularly in the epoxy systems has not been widely investigated.

Thus, the objective of this research work aims to explore the potential of ionic liquids in the preparation, characterization, modification and applications of epoxy networks. Hence, this thesis will focus on: *i)* the effect of IL chemical nature on the formation and properties of epoxy/ionic liquids networks in which phosphonium ILs will be used to replace the conventional curing agents; *ii)* the modification of epoxy/IL networks by using thermoplastics and core-shell particles; and *iii)* the design of bio-based epoxy/IL networks.

In order to fulfill these objectives, this manuscript is divided into four chapters.

The first chapter dedicated to the state of the art will set the context of this research including four main literature sections. The first section presents a state of the art on ionic liquids and their application in the polymer fields as ionic conducting agents for polymer electrolytes, as structuration agents for polymer matrices, as processing aids and compatibilizers, as plasticizers and as surfactant in the preparation of functional polymers. The second section focuses on the use of ionic liquids in the epoxy networks *i.e.* on the synthesis and development of new functionalized ILs and the use of ILs as additives or comonomers to prepare epoxy systems. Then, the third section covers the different routes to modify conventional epoxy networks using thermoplastics and core-shell particles in order to improve their performance. The last section of this chapter gives an overview of the research on the bio-based epoxy networks, in particular those derived from cashew nut liquid shell (cardanol).

The second chapter is dedicated to discover the role of phosphonium ionic liquids in the formation of epoxy networks. Firstly, the effect of the chemical nature of ILs on the curing behavior of epoxy/IL blends as well as the morphology and final properties (thermal, thermomechanical, surface and mechanical properties) of epoxy/IL networks is highlighted in comparison with epoxy/amine networks. Therefore, several kinds of phosphonium ionic liquids containing different counter anions and/or cations with different functionalization were used as comonomers to conventional epoxy prepolymers, which are normally cured by aliphatic or aromatic amines. Secondly, the mechanism of the reaction between epoxy group and ionic liquids was studied with Fourier transform infrared spectroscopy and nuclear magnetic resonance using a “model” such as a monoepoxy compound with a similar structure of epoxy prepolymer.

The third chapter describes two methods to reinforce epoxy/IL networks and to improve their mechanical performance: *i)* Reaction induced phase separation using thermoplastic and *ii)* preformed core-shell particles. The first part will reveal the influence of the ionic liquids on the phase separation of thermoplastic in the epoxy matrix, which is the decisive factor of the final properties of the networks. The second part highlights the dual function of ionic liquids as curing agent for epoxy prepolymer and as dispersion aids of the core-shell nanoparticles in the epoxy networks. In both parts, the structure-property relationships of epoxy networks will be investigated.

The final chapter will discuss the application of epoxy/IL networks in the formation of biobased materials. The reactivity of IL towards a cardanol based epoxy prepolymer will be studied compared to conventional epoxy prepolymers. The chapter will also focus on the formation of partially or totally sustainable systems based on the combination of ionic liquids and bio-based epoxy prepolymers aiming for the design of environmentally friendly materials.

# Résumé Étendu

## Chapitre 1 : Étude bibliographique

- **Liquides ioniques et polymères**

Les liquides ioniques (LIs) sont des sels organiques fondus composés d'ions, généralement un cation organique et un anion organique / inorganique. Diverses combinaisons de cations et anions sont possibles.<sup>1</sup> Normalement, les liquides ioniques possèdent une faible température de fusion ainsi qu'une grande stabilité thermique supérieure à 300 °C. Ils sont également ininflammables et possèdent une faible pression de vapeur saturante.<sup>2</sup> Un autre avantage des LIs vient de leurs combinaisons infinies dû au couple cation / anion ainsi qu'à leur fonctionnalisations qui peuvent déterminer leurs propriétés physico-chimiques. Les LIs ont été largement utilisés en tant que solvant ou milieu réactionnel pour la polymérisation et dépolymérisation. Néanmoins, l'utilisation de LIs dans les polymères s'est développée rapidement au cours de ces dernières décennies menant à d'excellentes propriétés dans plusieurs domaines d'applications. Dans la littérature, les LIs sont utilisés dans les matrices polymères comme agents ioniques pour les électrolytes polymères, comme agents de structuration, comme adjuvants pour dissolution de la cellulose, comme agents de compatibilité pour les mélanges de polymères, comme plastifiants ou encore comme tensioactifs dans la préparation de nanocomposites polymères.

- **LIs dans les réseaux époxyde**

Récemment, les LIs ont reçu de l'intérêt en tant que nouveaux additifs pour les réseaux époxyde. Les réseaux époxyde font parmi des matériaux thermodurcissables et sont couramment utilisés comme adhésifs, revêtements ou dans les composites pour les applications aérospatiales et aéronautiques.<sup>3</sup> Afin de former un réseau époxyde réticulé, les prépolymères époxy doivent soit réagir avec des durcisseurs (amines, phénols, iso cyanates ou acides) ou être combiner avec des amorceurs (amines tertiaires, imidazoles ou sels d'ammonium).<sup>3</sup> Selon la littérature, deux méthodes principales ont été étudiées pour combiner les LIs aux réseaux époxyde: *i*) la synthèse et le développement de nouveaux LIs fonctionnalisés et *ii*) l'utilisation de LIs comme additifs réactifs ou non-réactifs aux systèmes époxyde classiques. Premièrement, plusieurs auteurs ont développé de nouveaux liquides ioniques fonctionnalisés afin de fournir une meilleure conductivité ionique pour le développement d'électrolytes polymères. Les LIs portant des groupements époxyde, soit

sur le cation ou l'anion ont été synthétisés par Matsumoto *et al.* afin de préparer les réseaux époxy / amine.<sup>4</sup> D'autres auteurs ont synthétisé de nouveaux prépolymères LIs pour préparer des poly(liquide ionique)s (PLIs) et les ionogels (PLI / LI) à base des réseaux époxy / amine.<sup>5,6</sup> Les ion-gels (PLI / LI) ont présenté une amélioration significative de la perméabilité et sélectivité au CO<sub>2</sub>.<sup>5</sup> Deuxièmement, les LIs peuvent également être utilisés comme des additifs non-réactifs pour modifier les propriétés des réseaux époxyde conventionnels. En effet, l'incorporation d'une petite quantité de liquides ioniques peut conduire à augmenter la cinétique de la réaction de polymérisation,<sup>7,8</sup> et à modifier les morphologies des réseaux époxyde classiques conduisant à une amélioration des propriétés des réseaux tels que le comportement thermomécanique,<sup>9</sup> la conductivité ionique<sup>10</sup> et la résistance à l'usure.<sup>11,12</sup> Par exemple, Sanes *et al.* ont trouvé une amélioration de la résistance à l'usure et aux rayures des réseaux époxy / amine en utilisant seulement 1,5 % en masse de LI imidazolium.<sup>11</sup> D'autre part, Saurin *et al.* ont montré que l'utilisation de 9-12 % en masse de LI dans un système époxy / amine conduit à un effet d'auto-cicatrisation sur la surface d'échantillons après des essais d'abrasion de plus de 90 %.<sup>12</sup> Récemment, les LIs ont également été introduits comme durcisseurs (comonomères) de prépolymères époxy. En fait, plusieurs auteurs ont montré que les LIs contenant des cations imidazolium ou pyridinium agissent comme des amorceurs ou des durcisseurs de la DGEBA (diglycidyl éther de bisphénol A) par polymérisation anionique afin de former des réseaux époxy / LI.<sup>13,14</sup> Plus récemment, d'autres auteurs, ainsi que notre groupe de recherche ont trouvé que les LIs phosphonium combinés avec différents anions étaient également de très bons candidats pour remplacer les amines.<sup>15-17</sup> En fait, la nature des anions phosphinate (IL-TMP) et dicyanamide (IL-DCA) permet la formation des réseaux époxyde /LIs via polymérisation anionique. Les auteurs ont également démontré que ces nouveaux réseaux époxy / LIs possèdent d'excellentes propriétés telles qu'une haute stabilité thermique (> 400 °C) et une température de transition vitreuse comprise entre 80 et 140 °C dépendant de la nature chimique de l'anion utilisé. L'apparition d'une nanostructuration a également été mise en évidence en raison de la limite de miscibilité entre le prépolymère époxyde et le liquide ionique.<sup>16</sup>

- **Modifications de réseaux époxyde**

Malgré leurs excellentes propriétés thermiques et mécaniques, la fragilité des réseaux époxyde limite leurs applications en particulier dans le domaine aérospatial. Des modifications doivent être considérées pour améliorer leur résistance à la rupture et pour cela, deux voies principales sont couramment utilisées : *i*) La séparation de phase induite par réaction (SPIR) concernant les thermoplastiques ; *ii*) l'utilisation d'élastomères préformés non-miscibles par exemple des particules de type cœur-coquille (CSR).

L'utilisation de thermoplastiques à haute performance est intéressante grâce à leur capacité d'améliorer la résistance à la rupture des réseaux époxyde sans avoir d'effet néfaste sur leurs comportements mécaniques. Parmi les thermoplastiques, le plus utilisé est le poly (phénylène éther) (PPE) qui a été largement appliqué dans les réseaux époxyde grâce à ses excellentes propriétés. La morphologie des réseaux époxy / PPE ne dépend que de la quantité de PPE introduit dans le système.<sup>18</sup> A basse concentration, le PPE est la phase dispersée qui forme des nodules dans le réseau époxyde. Lorsque la quantité de PPE est augmentée, une morphologie co-continue sera formée. Enfin, une inversion de phase va se produire à haute concentration de PPE avec des nodules de réseaux époxyde dispersés dans la phase PPE continue. Les propriétés des réseaux époxyde modifiés par le PPE sont déterminées par la morphologie des systèmes donc par la composition des mélanges au départ. La stabilité thermique et les propriétés mécaniques des réseaux époxyde modifiés par l'addition de PPE sont similaires aux réseaux non-modifiés.<sup>19</sup> De plus, l'existence de PPE a renforcé les réseaux époxyde avec une amélioration significative de la résistance à la rupture  $K_{Ic}$  et l'énergie de rupture  $G_{Ic}$  à partir de l'apparition de la morphologie co-continue.<sup>19,20</sup>

Ensuite, l'utilisation de particules de type cœur-coquille (CSR) avec un cœur souple et une coque dure permet de contrôler la taille et la composition de la phase dispersée dans la matrice époxyde. L'amélioration de la ténacité des réseaux époxyde dépend fortement de la dispersion des particules CSR. Normalement, le matériau utilisé pour la coque est le poly (méthacrylate de méthyle) (PMMA), qui est compatible avec le réseau époxyde. Afin d'améliorer la dispersion des particules de CSR dans les réseaux époxyde, plusieurs modifications ont été menées sur des particules de CSR telles que la réticulation ou la fonctionnalisation de la coque c'est-à-dire du PMMA.<sup>21</sup> Parmi les matériaux composant le cœur de CSR, le polysiloxane (PDMS) a récemment attiré l'attention grâce à sa résistance thermique. L'utilisation de PDMS peut également augmenter la résistance à la rupture des réseaux époxyde même à basse température à  $-100$  °C.<sup>22</sup>

### • Réseaux époxyde biosourcés

Au cours des dernières années, en raison de la raréfaction du pétrole, du réchauffement climatique et d'autres problèmes environnementaux, il y a eu une forte demande sur les polymères à base des ressources renouvelables afin de remplacer partiellement ou même totalement les matériaux à base du pétrole. Les matériaux thermodurcissables, en particulier les réseaux époxyde sont devenus l'un des objectifs principaux concernant leur large gamme d'applications et la toxicité de la DGEBA. Dans la littérature, les prépolymères époxyde biosourcés ont été dérivés à partir d'huiles végétales, le saccharose et le cardanol. Parmi eux, le cardanol dérivé de la coque de noix de cajou est devenu un excellent candidat pour remplacer la DGEBA. En fait, la structure chimique

du cardanol contenant des cycles aromatiques et de longues chaînes alkyles fournit une combinaison exceptionnelle de propriétés.<sup>23</sup> Les composées époxyde à base de cardanol peuvent être utilisés en tant qu'agents modifiants pour les réseaux époxyde conventionnels afin d'améliorer leur processabilité,<sup>24</sup> leur flexibilité (résistance aux chocs et résistance à la rupture),<sup>25</sup> ainsi que leur résistance à l'eau et aux produits chimiques.<sup>26</sup> Par ailleurs, les prépolymères époxyde<sup>27</sup> ainsi que les durcisseurs<sup>28</sup> peuvent également être développés à partir de cardanol. La combinaison des prépolymères époxyde et de durcisseurs dérivés du cardanol permet de préparer des réseaux époxyde entièrement biosourcés suggérant une nouvelle façon de développer des matériaux durables.<sup>28</sup>

## • Conclusion

Cette partie bibliographique vise à résumer la littérature concernant les LIs dans les réseaux époxyde. Au cours des dernières années, les liquides ioniques sont devenus de nouveaux additifs fonctionnels pour les polymères en général que ce soit des thermoplastiques ou des thermodurcissables en particulier en tant qu'agents modifiants ou comonomères des réseaux époxyde. Cependant, la recherche sur les LIs phosphonium est encore limitée. Donc, des études sont nécessaires pour obtenir une meilleure compréhension du rôle du LI phosphonium dans la formation de réseaux époxyde ainsi que l'influence de la nature chimique de LIs sur les propriétés finales des réseaux (Chapitre 2). De plus, la présence de LIs peut affecter également l'incorporation des agents modifiants dans la matrice époxy conduisant à nouvelles propriétés (Chapitre 3). Enfin, la combinaison de liquides ioniques avec des matériaux biosourcés peut être intéressante pour développer une nouvelle génération de matériaux durables. (Chapitre 4).

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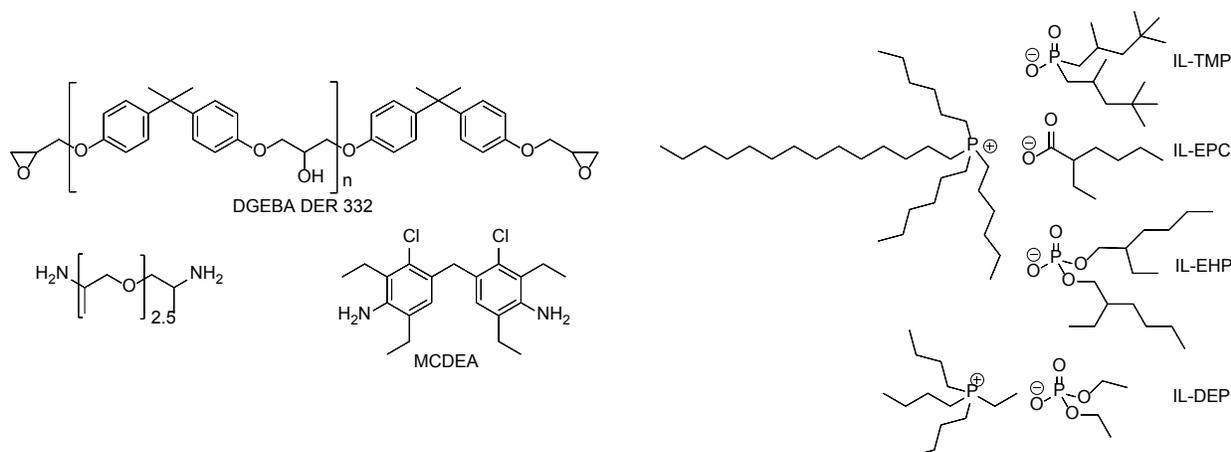
## Chapitre 2 : Les liquides ioniques: Une nouvelle route pour la conception de réseaux époxyde

### • Introduction

Récemment, les LIs phosphonium ont montré leur capacité à réagir en tant que co-monomère pour développer de nouveaux réseaux époxyde. Cependant, à notre connaissance, très peu de travaux mentionnent leur utilisation comme additifs réactifs de prépolymères époxyde. Ce deuxième chapitre est dédié à étudier l'effet de ces LIs phosphonium dans les systèmes époxyde, l'influence de la nature chimique des LIs sur les propriétés mécaniques des réseaux époxyde. De plus, le mécanisme de la réaction entre les groupements époxyde et les LIs a été étudié pendant le temps de cuisson.

### • Propriétés de systèmes époxy / LIs

Dans ce travail, différents liquides ioniques phosphonium combinés à des anions phosphinate (IL-TMP), carboxylate (IL-EPC), et phosphate (IL-DEP et IL-EHP) ont été utilisés comme durcisseurs pour les prépolymères époxyde (DGEBA). Deux diamines classiques, soit une diamine aromatique, MCDEA et une diamine aliphatique, Jeffamine D230 ont été utilisés comme références. Toutes les structures chimiques des produits utilisés sont représentées sur la Figure 1.

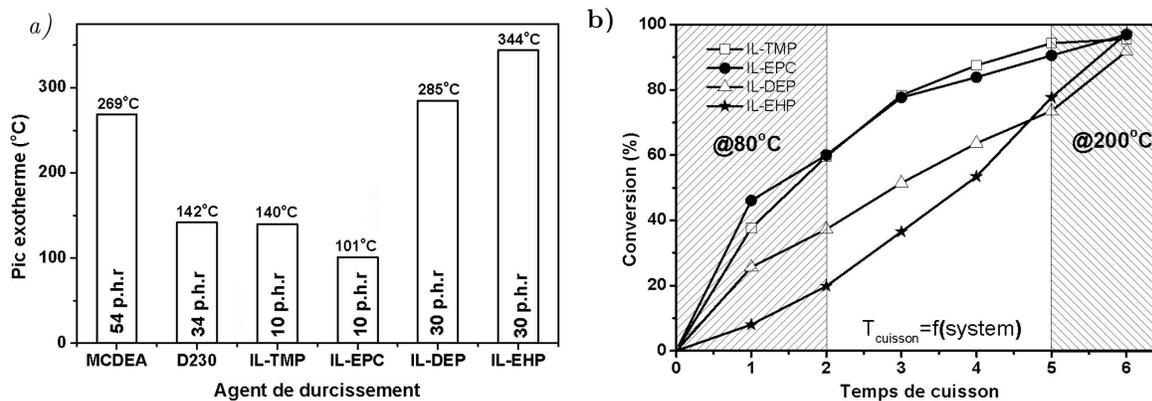


**Figure 1** Les structures chimiques de DGEBA, Jeffamine D230, MCDEA, et LIs phosphonium.

#### ○ La réactivité

Nous avons utilisé la DSC dynamique pour étudier la cinétique de la réaction entre le prépolymère époxyde et durcisseurs grâce à la position du pic exothermique correspondant à

l'enthalpie de la réaction tel qu'illustré sur la Figure 2a. De plus, la réaction a été suivie par IRTF afin de calculer la conversion des fonctions époxyde en fonction du temps de cuisson<sup>1</sup> présentée en Figure 2b.



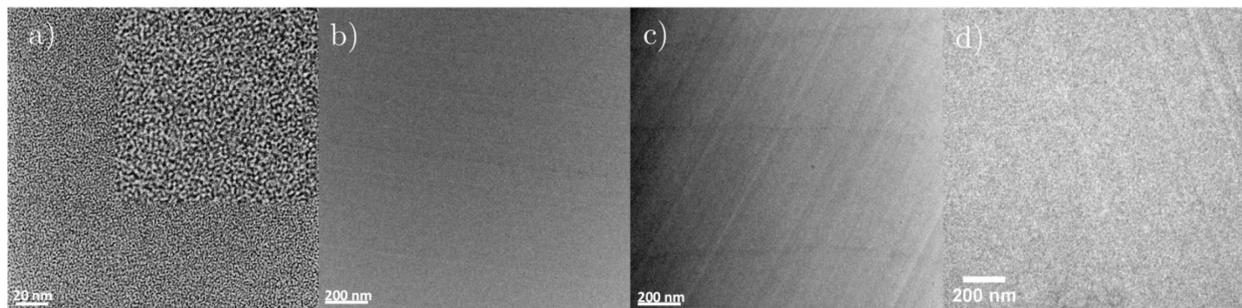
**Figure 2** Température du pic exotherme (DSC, 10 K.min<sup>-1</sup>) (a) et la conversion des groupements époxyde en fonction du temps de cuisson (IRTF) (b) de différents systèmes époxyde.

Dans tous les cas, les LIs phosphonium induisent un pic exotherme mettant en évidence la capacité des LIs à réagir comme amorceurs et/ou durcisseurs du prépolymère DGEBA. De plus, la réactivité des LIs dépend de la basicité des anions. Les LIs peuvent être classés en fonction de leur basicité dans l'ordre suivant : IL-EPC > IL-TMP > IL-DEP > IL-EHP. Ainsi, les LIs sont d'excellentes alternatives aux amines car des quantités plus faibles peuvent être utilisées pour une réactivité similaire, par exemple 10 phr pour IL-TMP et IL-EPC, 30 phr pour IL-DEP et IL-EHP par rapport à 34 phr pour la Jeffamine D230 et 54 phr pour la MCDEA. Nous observons sur la Figure 2b que la conversion des groupements époxyde des différents systèmes époxy / LI augmente progressivement avec le protocole de cuisson et atteint 90 % après 6 heures de cuisson. Les résultats IRTF confirment également l'ordre de grandeur de la réactivité de LIs sur le DSC.

#### o La morphologie

La microscopie électronique à transmission (MET) a révélé la structuration de LIs dans les réseaux époxyde (Figure 3).

Dans le cas des systèmes époxy contenant IL-TMP (10 phr), IL-DEP (30 phr), et IL-EHP (30 phr), nous n'avons pas observé de séparation de phases. Néanmoins, IL-EPC conduit à une (nano) séparation de phases caractérisée par l'apparition de petites inclusions de LIs générées par une limite de miscibilité entre le LI et le réseau époxyde. Ce phénomène est fréquemment rencontré dans les systèmes époxyde modifiés par les élastomères, thermoplastiques, ou copolymères à blocs.<sup>2,3</sup>



**Figure 3** Images MET des réseaux époxyde contenant IL-EPC (a), IL-TMP (b), IL-DEP (c) and IL-EHP (d).

○ Comportement thermomécanique et mécanique

Nous avons étudié l'influence de la nature chimique des LIs sur les propriétés thermomécaniques et mécaniques des réseaux époxyde. La température de relaxation ( $T_{\alpha}$ ), la densité de réticulation ( $\nu_e$ ) estimée en utilisant la théorie de l'élasticité,<sup>4</sup> le comportement en flexion ( $E_f$ ) et la ténacité ( $K_{Ic}$ ) des réseaux époxy / amine et époxy / LI sont représentés dans le Tableau 1.

**Tableau 1** Comportement thermomécanique (Température de relaxation  $T_{\alpha}$ , densité de réticulation  $\nu_e$ ) et mécanique (Module en flexion  $E_f$ , la ténacité  $K_{Ic}$ ) de réseaux époxyde utilisant des amines ou des liquides ioniques comme durcisseurs.

Système	$T_{\alpha}$ (°C)	$\nu_e$ (mol.m <sup>-3</sup> )	$E_f$ (GPa)	$K_{Ic}$ (MPa.m <sup>1/2</sup> )
MCDEA	160	1 385	2,30	0,56
D230	100	1 591	2,71	1,05
IL-TMP	150	9 201	1,61	0,39
IL-EPC	144	11 121	2,39	0,37
IL-DEP	117	1 527	2,22	0,64
IL-EHP	98	1 399	-	-

Pour les réseaux époxy / LI, deux comportements différents ont été observés. En effet, les  $T_{\alpha}$  des réseaux époxyde contenant les LIs phosphate (IL-DEP et IL-EHP) sont dans la même région de température que le système durcit avec la Jeffamine D230 (100-110 °C) tandis que celles des réseaux époxy contenant les LIs dénotés IL-TMP ou IL-EPC sont proches du réseau durcit avec la MCDEA (supérieure à 140 °C). En outre, les densités de réticulation des réseaux époxyde avec IL-EPC (11 121 mol.m<sup>-3</sup>) et IL-TMP (9 201 mol.m<sup>-3</sup>) sont significativement plus élevés par rapport

aux réseaux époxy / MCDEA et aux réseaux époxyde à base des LIs phosphate. Entre les deux LIs phosphate (IL-EHP et IL-DEP), les longues chaînes d'alkyles de l'IL-EHP augmentent la flexibilité de réseau époxy / LI conduisant à une baisse de  $T_g$  et de la densité de réticulation.

Ensuite, l'utilisation de LIs comme additifs réactifs conduit à la formation de réseaux époxyde fragiles. Les modules en flexion des réseaux époxyde avec IL-EPC et IL-DEP sont similaires à ceux des systèmes époxy / amine conventionnels. De plus, la ténacité des réseaux époxy / LI contenant IL-EPC et IL-TMP sont environ  $0,4 \text{ MPa}\cdot\text{m}^{1/2}$  tandis que le système époxyde avec IL-DEP a un  $K_{Ic}$  supérieur de  $0,64 \text{ MPa}\cdot\text{m}^{1/2}$ . Cette différence est liée à leurs densités de réticulation.<sup>5</sup> Cependant, la relation entre la densité de réticulation d'un réseau et la ténacité à la fracture reste ambiguë car plusieurs autres paramètres sont également impliqués tels que la flexibilité de la chaîne, le volume libre, et les interactions intermoléculaires.

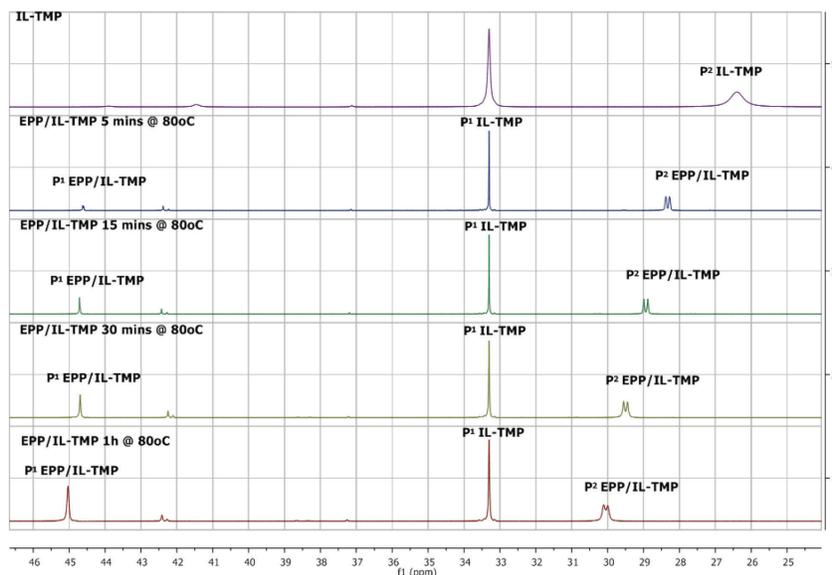
En conclusion, c'est possible de remplacer les diamines classiques par des liquides ioniques comme durcisseurs pour les prépolymères époxyde. La nature chimique des LIs contrôle les relations structure / propriété des réseaux préparés.

- **Mécanisme de réaction entre le liquide ionique et le prépolymère époxy**

Dans cette partie, nous avons utilisé un mono époxy dénoté 1,2-époxy 3-phénoxy propane (EPP) ayant une structure similaire à la DGEBA (Figure 4) et nous l'avons fait réagir avec différents LIs (IL-TMP et IL-EPC) afin d'étudier la polymérisation par Résonance magnétique nucléaire (RMN)  $^1\text{H}$ ,  $^{13}\text{C}$  et  $^{31}\text{P}$ .



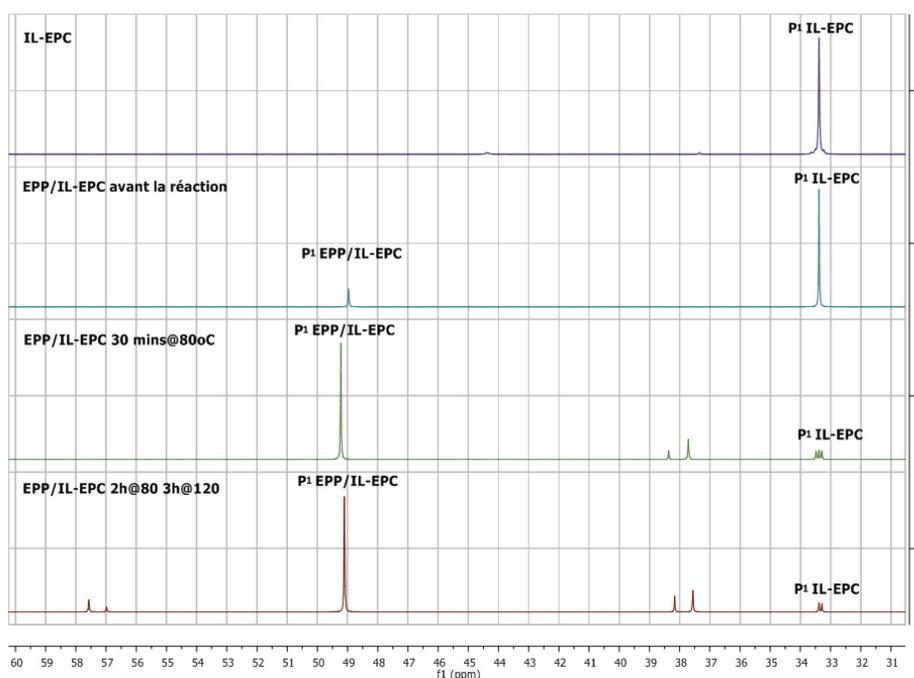
Après seulement 5 minutes, le pic correspondant au phosphore de l'anion phosphinate IL-TMP se déplace de 26,40 ppm<sup>6</sup> à 28,50 ppm et puis à 30 ppm après 1 heure de cuisson. Dans le même temps, le pic correspondant au phosphore du cation à 33,30 ppm ne se déplace pas au cours de la réaction. Ces résultats confirment le mécanisme de polymérisation anionique entre le LI et le prépolymère époxyde. Aussi, le spectre <sup>31</sup>P RMN sur les systèmes EPP/ IL-TMP montre l'apparition d'un nouveau pic à environ 45 ppm qui augmente en intensité pendant le temps de cuisson. Afin de définir ce pic, nous avons effectué de la RMN <sup>31</sup>P pour le système EPP / IL-EPC, plus simple à analyser.



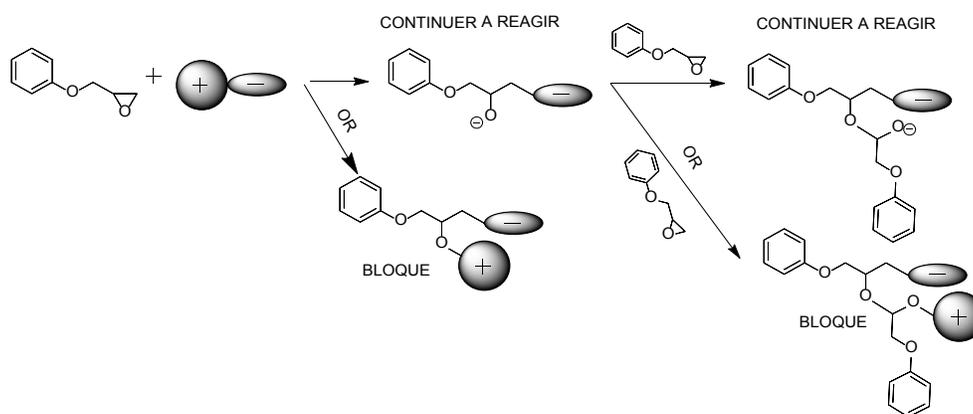
**Figure 5** Spectre <sup>31</sup>P NMR d'IL-TMP et du système EPP / IL-TMP après 5 minutes, 15 minutes, 30 minutes et 1 heure à 80 °C.

○ Système EPP/IL-EPC

En fait, la RMN <sup>31</sup>P effectuée sur les systèmes EPP / IL-EPC avant cuisson affiche un pic à 33,38 ppm correspondant au P du cation phosphonium (Figure 6). Au cours de la réaction, un pic secondaire apparaît à environ 49 ppm et continue à croître au cours du temps de cuisson. Cela signifie que le cation d'IL-EPC aussi interagit avec EPP entraînant le déplacement du pic. En outre, le déplacement chimique de ce pic est très proche du nouveau pic observé sur la RMN <sup>31</sup>P du EPP / IL-TMP indiquant qu'une partie du cation forme également une liaison ionique / covalente / réversible avec l'atome oxygène du groupement époxyde. Cette liaison bloque le groupement époxyde et arrête une partie de la réaction. Cependant, le reste des O<sup>-</sup> non-bloqué va continuer à réagir avec le groupement époxyde de l'EPP pour former plus d'oligomères. Le mécanisme de la réaction de cuisson entre l'EPP et le LI peut être résumé dans le schéma 1.



**Figure 6** Spectre  $^{31}\text{P}$  NMR d'IL-EPC et du système EPP/IL-EPC avant la réaction et après 30 minutes et 5 heures de cuisson.



**Schéma 1** Mécanisme proposé de réaction entre EPP et LI.

## • Conclusion

Ce chapitre fournit une étude comparative qui a démontré le potentiel de LIs comme additifs réactifs pour les prépolymères époxyde. Nous avons démontré que les LIs phosphonium combinés avec différents anions forment des réseaux époxyde ayant une température de transition vitreuse supérieure à  $90\text{ }^{\circ}\text{C}$  et une densité de réticulation élevée. La nature chimique de l'anion joue un rôle important dans la formation d'un réseau époxyde permettant de varier les propriétés des réseaux pour les différentes applications. Dans tous les cas, l'utilisation de LIs phosphonium conduit à une

hydrophobicité élevée et une stabilité thermique plus élevée ainsi que des propriétés mécaniques similaires par rapport aux réseaux époxy / amine. D'autre part, nous avons également démontré par RMN que la réaction entre le prépolymère époxyde et le LI se fait par polymérisation anionique.

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## Chapitre 3 : Modification des réseaux époxy / LI

### • Introduction

Malgré leurs excellentes propriétés thermiques et mécaniques, la fragilité des réseaux époxyde limite leurs applications et nécessite des modifications. Dans ce chapitre, deux types d'agents modifiants ont été utilisés dans les réseaux époxy / LI afin d'améliorer leurs performances :

- i)* Un thermoplastique : le poly (phénylène éther) (PPE)
- ii)* Des particules cœur-coquille préformés (Genioperl).

Dans ces systèmes, les LIs agissent non seulement comme un durcisseur mais également comme un agent interfacial fournissant la dispersion de ces polymères dans la matrice époxy.

### • Utilisation de PPE comme agent de renforcement pour les réseaux époxy / LI

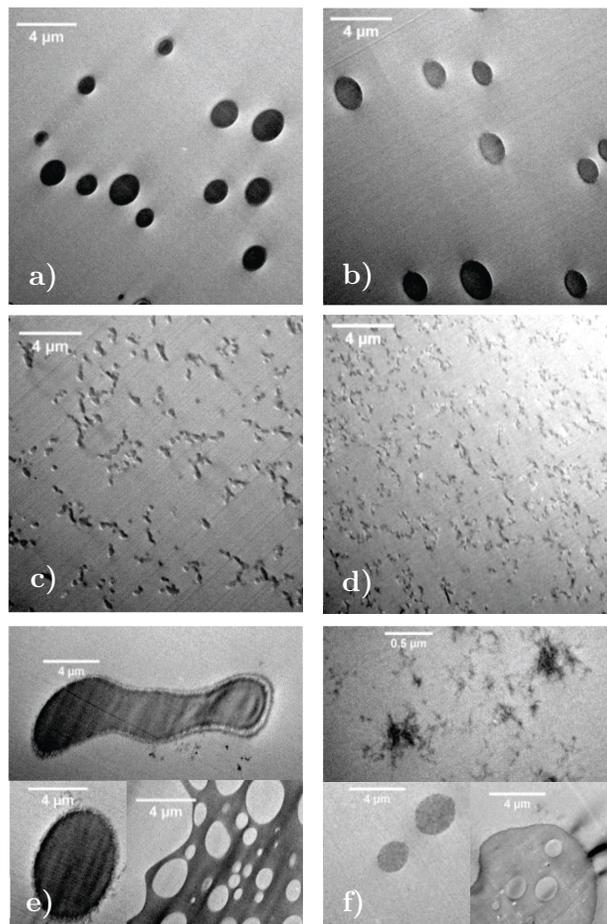
Une amine aromatique MCDEA (54 phr) et deux types de liquides ioniques IL-TMP et IL-DEP (10 phr) ont été utilisés comme durcisseurs du prépolymère époxyde DGEBA. De plus, deux types de poly (éther de 2,6-diméthyl-1,4-phénylène) (PPE-1 et PPE-2, 10 phr) de masses molaires différentes ( $M_n = 32\ 000$  et  $15\ 000\ \text{g}\cdot\text{mol}^{-1}$ ) ont été utilisés dans ce système.

#### ○ Morphologie

La MET a révélé les différentes morphologies des systèmes époxyde modifiés par la présence de PPE. Les images MET des réseaux époxy / PPE durcit avec la MCDEA ou avec les LIs (IL-TMP un IL-DEP) sont présentés sur la Figure 7.

Dans le chapitre précédent, nous n'avons pas observé de séparation de phase sur les réseaux époxy / LIs dénoté IL-DEP et IL-TMP (Figure 3). Puis, l'addition de PPE dans les réseaux époxyde conduit à la formation d'une seconde phase de PPE dans la matrice époxyde à cause de la séparation de phase induite par la réaction (Figure 7). La forme et la taille de cette phase de PPE dépendent fortement de la nature chimique des durcisseurs de type d'amine ou LIs et de la masse molaire du PPE. Dans le cas des systèmes époxy / amine, l'utilisation de 10 phr de PPE mène à la formation de particules sphériques ayant un diamètre compris entre 1 et 3  $\mu\text{m}$ . Cette morphologie est aussi observée par d'autres auteurs dans la littérature.<sup>1,2</sup> Pour le réseau époxy / IL-TMP, l'incorporation de PPE dans les réseaux époxyde induit une morphologie différente composée de particules PPE et d'une phase co-continue. En effet, cette morphologie compliquée peut être expliquée par le mécanisme de réaction entre l'époxy et les LIs (Chapitre 2) différente du cas du système époxy / amine.<sup>3</sup> De plus, la taille des particules PPE dans les réseaux DGEBA

/ IL-TMP est significativement plus faible par rapport à celles du système DGEBA / MCDEA. En fait, ces résultats peuvent être expliqués par l'utilisation de LIIs qui sont connus comme adjuvants de procédé ou comme agents compatibilisants de plusieurs polymères.<sup>4-6</sup> Dans la littérature, l'utilisation de seulement 1 % de masse d'IL-TMP dans le mélange PP / PA6 conduit à une réduction des domaines de PA de 27  $\mu\text{m}$  à 3  $\mu\text{m}$ .<sup>4</sup> Concernant le système époxy / IL-DEP, nous avons obtenu une morphologie plus complexe par rapport à IL-TMP avec un mélange de particules de PPE sphériques et non sphériques dans la matrice époxyde et une phase inversée composée de particules époxyde dans la matrice de PPE. La complexité de cette morphologie est due à la réactivité du prépolymère époxyde avec IL-DEP qui est inférieure à celle d'IL-TMP ou de la MCDEA. Dans les trois systèmes, l'utilisation de PPE de plus faible masse molaire conduit à une morphologie plus fine grâce à l'augmentation de la compatibilité entre le PPE et la matrice époxy.



**Figure 7** Morphologie du réseau époxy / amine (a, b), époxy / IL-TMP (c, d) et époxy / IL-DEP (e, f) contenant par PPE-1 (a, c, e) et PPE-2 (b, d, f).

○ Comportement thermomécanique et mécanique

Nous avons étudié l'influence de la nature chimique des durcisseurs (amine ou LIIs) sur les propriétés thermomécaniques et mécaniques des réseaux époxyde modifié par PPE et la température de relaxation ( $T_\alpha$ ), le comportement en flexion ( $E_f$ ) et la ténacité ( $K_{IC}$ ) de tous les systèmes sont représentés dans le Tableau 2.

**Tableau 2** Propriétés thermomécaniques et mécaniques du PPE pur et des réseaux époxyde non-modifié et modifié par le PPE.

Echantillons	DMA		$E_f$ (GPa)	$K_{IC}$ (MPa m <sup>1/2</sup> )
	$T_{\alpha 1}$ (°C)	$T_{\alpha 2}$ (°C)		
PPE-1	-	225	-	-
PPE-2	-	210	-	-
DGEBA / MCDEA	160	-	2,30	0,56
DGEBA / MCDEA/PPE-1	150	210	2,43	0,69
DGEBA / MCDEA/PPE-2	158	208	2,27	0,64
DGEBA / IL-TMP	150	-	1,61	0,39
DGEBA / IL-TMP / PPE-1	136	200	1,81	0,99
DGEBA / IL-TMP / PPE-2	149	-	2,45	0,46
DGEBA / IL-DEP	112	-	2,61	0,55
DGEBA / IL-DEP / PPE-1	133	195	2,42	1,67
DGEBA / IL-DEP / PPE-2	138	203	2,50	1,56

La séparation de phase dans les réseaux époxyde modifiés par le PPE est observée par DMS avec deux pics de relaxation correspondant à la matrice époxyde et au thermoplastique (Tableau 2). Les températures de relaxation de chaque phase diffèrent de celles des réseaux non modifiés à cause de l'effet d'interpénétration entre les deux phases.<sup>7</sup> En détail, l'incorporation du PPE dans le réseau époxy / amine et époxy / IL-TMP a entraîné une diminution des deux températures de relaxation correspondant à la phase riche en époxy et en PPE, respectivement. La diminution de la  $T_\alpha$  de la phase époxy riche peut être attribuée à la réduction de la conversion finale en raison de l'augmentation de la viscosité des mélanges avec l'existence de PPE.<sup>7</sup> Ainsi, la deuxième température de relaxation relative à la phase PPE dans les réseaux époxyde est inférieure à celle du thermoplastique pur en raison de l'incorporation des composé époxyde (monomères ou

oligomères) dans la phase PPE.<sup>8,9</sup> Concernant le système DGEBA / IL-DEP, les températures de relaxation correspondant à la phase PPE dans les réseaux modifiés sont inférieurs à celle du thermoplastique pur tandis que les pics de relaxation correspondant à la phase époxyde sont décalés à une température supérieure. En fait, l'existence de PPE à haute  $T_{\alpha}$  dans la phase de DGEBA / IL-DEP augmente la température de transition vitreuse de la phase époxyde.

Ensuite, l'addition de PPE a un faible effet sur les modules de flexion lorsque les réseaux époxy / amine ou époxy / LIs non modifiés ont des valeurs similaires de module en flexion du PPE. Cependant, la dispersion du PPE dans la matrice époxyde joue un rôle important sur la contrainte en flexion. En effet, dans le cas des réseaux époxy / IL-TMP, l'addition des thermoplastiques conduit à une augmentation significative de la contrainte en flexion de + 100 % pour les deux types de PPE. Ces résultats peuvent être expliqués par les morphologies co-continues représentés sur la Figure 7. En fait, cette bonne distribution des particules PPE contribue à la dissipation de la contrainte en flexion.<sup>10</sup>

Finalement, l'utilisation de thermoplastique dans les réseaux époxyde a une influence significative sur la ténacité. Les valeurs  $K_{Ic}$  sont dépendantes de plusieurs paramètres tels que la morphologie, la nature chimique de durcisseurs et la masse molaire du thermoplastique.<sup>11,12</sup> Dans le cas du système époxy / MCDEA, une légère augmentation de la ténacité de 20 % est obtenue dû à la morphologie nodulaire. Au contraire, l'incorporation de PPE dans les systèmes époxy / LI a une influence significative sur la ténacité, par exemple, de l'ordre de +150–200 % grâce à l'apparition de la morphologie co-continue ou de l'inversion de phase.

En conclusion, les propriétés des réseaux époxy / LI modifiés par PPE sont clairement dépendant de la morphologie des échantillons et donc de la nature chimique des liquides ioniques phosphonium et de la masse molaire de PPE.

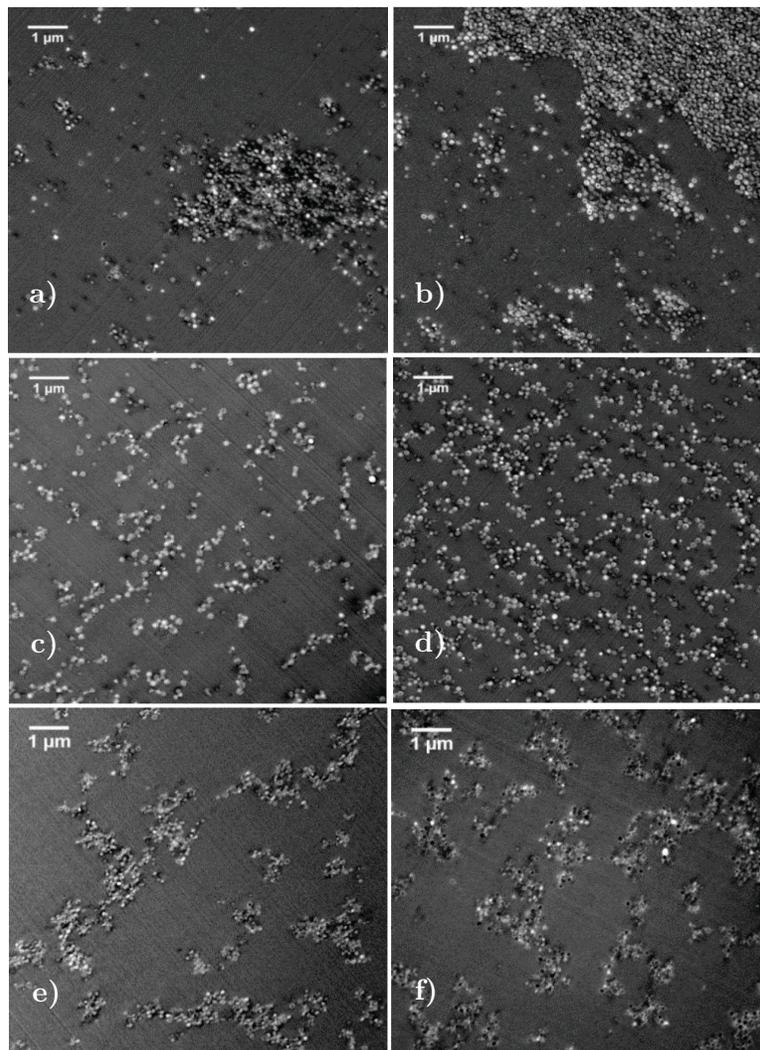
- **LIs comme durcisseurs et aide à la dispersion de particules cœur-coquille pour des réseaux époxy / LI**

Une amine aromatique MCDEA (54 phr) et deux types de liquides ioniques IL-TMP et IL-DEP (10 phr) sont utilisé comme durcisseurs pour le prépolymère époxyde DGEBA. Des particules cœur-coquille Genioperl P52 (CSR) (10 et 20 phr) avec le cœur de silicone et la coque de PMMA ont été utilisées et dispersés dans le réseau.

- Morphologie

Les images MET sur la Figure 8 ont montré l'effet du type de durcisseur sur la dispersion des particules de CSR dans les réseaux époxyde. Dans le cas du système époxy / amine, les particules CSR sont mal dispersées avec la présence de nombreux agrégats de 5 à 20  $\mu\text{m}$ . D'autre part, une

meilleure dispersion des particules CSR (10 et 20 phr) a été réalisée dans les réseaux époxy / LI. En fait, les LIs ont montré leur capacité en tant qu'agents plastifiants du PMMA.<sup>13</sup> Donc dans le cas des réseaux époxy / LI, l'interaction entre les deux LIs et les particules de CSR conduit à une morphologie plus fine et plus homogène que le système époxy / amine. D'ailleurs, la morphologie des réseaux époxy / LIs modifiés par les CSR dépend clairement de la nature chimique des LIs. Plusieurs agglomérats interconnectés de 1  $\mu\text{m}$  sont obtenus pour le réseau DGEBA / IL-DEP / CSR tandis que les particules de CSR sont dispersées individuellement ou interconnecté dans le réseau DGEBA / IL-TMP. Évidemment, la chaîne alkyle plus courte d'IL-DEP réduit l'interaction avec les particules CSR conduisant à un effet de dispersion moins importante.



**Figure 8** Images MET de réseaux époxyde modifiés avec 10 phr (a, c, e) et 20 phr (b, d, f) de CSR utilisant la MCDEA (a, b), et les LIs : IL-TMP (c, d) et IL-DEP (e, f) comme durcisseurs.

En conclusion, les LIs jouent un double rôle : *i*) de durcisseur et *ii*) comme aide à la dispersion des particules CSR dans les réseaux époxyde. De plus, la nature chimique des LIs a une influence importante sur la forme et la taille de la phase dispersée.

○ Propriétés mécaniques

Les propriétés mécaniques des réseaux époxyde modifié par les CSR y compris le comportement en flexion ( $E_f$ ,  $\sigma_R$ ) et la ténacité ( $K_{Ic}$ ) sont représentées dans le Tableau 3.

**Tableau 3** Comportement mécanique des réseaux époxyde modifiés par les particules CSR

Durcisseurs	CSR (phr)	$E_f$ (GPa)	$\sigma_R$ (MPa)	$K_{Ic}$ (MPa.m <sup>1/2</sup> )
MCDEA	0	2,30	77,1	0,56
	10	2,08	92,7	0,61
	20	1,93	79,5	0,71
IL-TMP	0	1,61	24,4	0,39
	10	2,07	54,5	0,40
	20	1,90	55,7	0,51
IL-DEP	0	2,61	72,7	0,55
	10	2,07	86,0	0,74
	20	1,92	60,9	0,85

L'addition des particules CSR dans les réseaux époxyde conduit à une légère baisse du module en flexion, ainsi qu'à une augmentation de la contrainte à la flexion ce qui est due à la ductilité de la particule CSR.<sup>14</sup> De plus, la dispersion des CSR contrôlée par la nature chimique du durcisseur joue un rôle important sur les propriétés en flexion des réseaux époxyde modifiés par les particules CSR.

En termes de résistance à la rupture, l'utilisation de CSR a amélioré la ténacité des réseaux époxyde. En fait, une augmentation proportionnelle du  $K_{Ic}$  avec la quantité de CSR a été découverte.<sup>15,16</sup> La grandeur de cette augmentation dépend de la nature des réseaux époxyde et de la quantité de CSR. Les valeurs de  $K_{Ic}$  augmentent de +27 %, 31 % et 55 % pour les systèmes à base de la MCDEA, et les LIs : IL-TMP et IL-DEP, respectivement. En fait, l'effet des particules cœur-coquille est plus important quand la dispersion particules des CSR est plus homogène.<sup>17,18</sup>

Par contre, la faible ténacité du système DGEBA / IL-TMP / CSR peut être expliquée par une pauvre interface entre les deux phases conduisant à un changement de mécanisme de renforcement (déliasion au lieu de cavitation).<sup>16,19</sup>

En conclusion, les propriétés des réseaux époxyde modifiés par les particules CSR sont clairement dépendantes de leur morphologie contrôlée par la nature chimique du durcisseur : amine ou liquides ioniques. Ainsi, l'utilisation de LIs a facilité la dispersion des particules de CSR dans les réseaux époxyde conduisant à des performances mécaniques améliorées.

## • Conclusion

Dans ce chapitre, les réseaux époxy / LIs ont été modifiés par deux méthodes différentes en utilisant des thermoplastiques et des particules élastomères. La morphologie et les propriétés des réseaux époxy / LIs modifiés sont caractérisés par rapport à un réseau époxy / amine classique. Dans la première partie, pour la même quantité de thermoplastique PPE, l'utilisation de LIs conduit à différentes morphologies allant de co-continue à l'inversion de phase au lieu de morphologie nodulaire dans le cas du réseau époxy / amine. La forme et la taille de la phase PPE dispersé dans les réseaux époxyde dépendent du type de LI et PPE. Une ténacité élevée est obtenue dans le cas des réseaux époxy / LI modifiés par l'ajout de PPE avec une amélioration de +154-200 % par rapport aux réseaux non-modifiés. Dans la deuxième partie, la dispersion des particules cœur-coquille est facilitée par la présence de LIs. En comparaison avec le réseau époxy / MCDEA, une morphologie plus uniforme est observée avec l'absence d'agglomération. Ainsi, une plus grande amélioration des propriétés des réseaux époxyde spécialement la ténacité a été mise en évidence dans le cas des LIs. Dans les deux cas, la morphologie et les propriétés des réseaux époxyde modifiés dépend de l'interaction entre l'agent modifiant et les LIs et donc de la nature chimique des liquides ioniques.

## Références

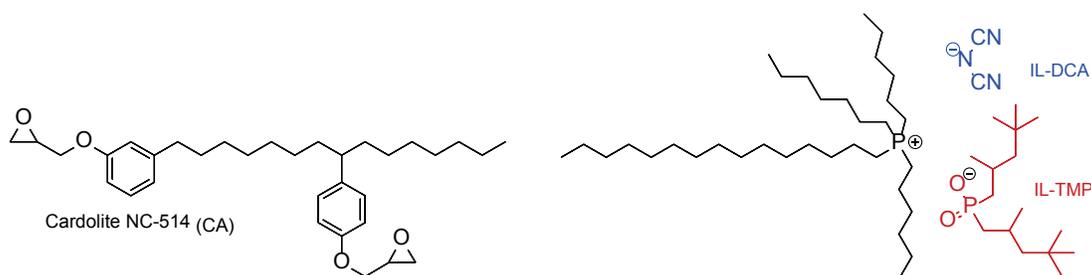
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## Chapitre 4 : En route vers les biosourcés

### • Introduction

Dans ce chapitre, les liquides ioniques phosphonium sont utilisés pour développer de nouveaux réseaux époxyde biosourcés. Le prépolymère biosourcé est dérivé de Cardanol sous la référence commerciale de Cardolite NC-514 (CA). Deux liquides ioniques : le trihexyl (tétradécyl) phosphonium dicyanamide - dénoté IL-DCA et le trihexyl (tétradécyl) phosphonium bis-2,4,4 (triméthyl pentyl) phosphinate - dénoté IL-TMP ont été utilisés. Les structures chimiques de la Cardolite et des liquides ioniques sont présentés sur la Figure 9.



**Figure 9** Les structures chimiques du prépolymère époxyde biosourcé et des LIs phosphonium.

### • Préparation de réseaux époxy / LIs biosourcés avec le prépolymère époxyde dérivé de cardanol

#### ○ Réactivité

Les courbes DSC de mélanges époxy / LI (IL-TMP ou IL-DCA) ont mis en évidence des pics exothermiques suggérant la capacité des LIs à réagir sur le prépolymère époxyde dérivé de Cardanol (CA). Ce pic exothermique est déplacé à une température plus élevée (210 °C) quand la CA est utilisé au lieu de la DGEBA à cause de l'existence des segments souples dans la structure chimique de CA ce qui ralentit la réactivité.<sup>1</sup> De plus, la composition complexe du prépolymère CA avec des oligomères a aussi conduit à un mécanisme compliqué de la réaction entre le CA et le LI.<sup>1</sup> Similaire aux systèmes à base de la DGEBA, la réactivité des systèmes CA / LI augmente avec la quantité de LIs.

Les spectres IRTF enregistrés pendant la réaction entre la CA et les LIs a confirmé la formation des réseaux CA / LIs avec une conversion des groupements époxyde supérieure à 95 %.

○ Propriétés thermomécaniques (DMA)

La température de relaxation de tous les systèmes CA / LIs est comprise entre 20-36 °C (Tableau 4). En fait, la longue chaîne aliphatique de prépolymère époxyde dérivé de cardanol adoucit les réseaux époxy / LI et génère des températures de relaxation inférieurs par rapport à ceux avec la DGEBA. De plus, la longue chaîne aliphatique entre deux groupements époxyde du CA diminue la densité de réticulation des réseaux époxyde.<sup>1,2</sup>

**Tableau 4** Températures de relaxation  $T_{\alpha}$  et les modules à l'état caoutchoutique ( $E'_R$ ) des réseaux époxy / LI biosourcés.

Echantillons	$T_{\alpha}$ (°C)	$E'_R$ (MPa)
DGEBA/IL-DCA-10	126	31,2
CA/IL-DCA-10	31	2,6
CA/IL-DCA-20	36	6,1
CA/IL-DCA-30	28	6,2
DGEBA/IL-TMP-10	150	104,0
CA/IL-TMP-10	20	1,1
CA/IL-TMP-20	25	3,8
CA/IL-TMP-30	22	5,7

○ La stabilité thermique

Les réseaux CA / LIs présentent un excellent comportement thermique avec une température maximale de dégradation à plus de 460 °C expliquée par la meilleure stabilité intrinsèque de prépolymère époxyde dérivé de cardanol. En effet, ces nouveaux réseaux époxy / LI fournissent une stabilité thermique supérieure à celle des systèmes époxy / amine biosourcés rapportés dans la littérature.<sup>2</sup>

○ Energie de surface des réseaux biosourcés

L'énergie de surface des réseaux époxy / LI (CA ou DGEBA) ont été déterminées par la méthode de la goutte sessile en utilisant la méthode Owens-Wendt à base des angles de contact avec l'eau et le diiodométhane. Le remplacement d'un prépolymère époxyde classique par celui dérivé de cardanol génère une réduction significative de l'énergie de surface pour tous les réseaux époxy / LI. En fait, la structure chimique du cardanol offre une excellente résistance à l'eau par

rapport à la DGEBA grâce à une longue chaîne aliphatique.<sup>3</sup> En général, la combinaison de deux composants hydrophobes : les liquides ioniques et le prépolymère époxyde à base de cardanol aboutit à des systèmes super-hydrophobes.

- **Modification de réseaux époxy / LI par l'ajout de cardolite**

- La réactivité des systèmes obtenus

L'utilisation du prépolymère époxyde dérivé de cardanol dans les mélanges DGEBA / LIs diminue la réactivité en raison de sa structure chimique qui possède plus de la flexibilité. Malgré tout, une conversion de groupement époxyde de plus de 90 % est obtenue pour tous les réseaux époxy / LI modifiés par la CA. L'augmentation de la teneur en CA diminue la réactivité du système DGEBA / LIs indiquée par la diminution de la conversion du groupement époxyde.

- Energie de surface des systèmes combinés

L'incorporation de CA dans les réseaux époxy / LI réduit leur énergie de surface suggérant la formation de systèmes hautement hydrophobes. En fait, tous les réseaux époxy / LI modifiés par CA présentent une énergie de surface inférieure à 17 mJ.m<sup>-2</sup>. Apparemment, la résistance à l'eau du prépolymère époxyde dérivé de cardanol est la raison principale de cette augmentation de l'hydrophobicité du système.

- Comportement propriétés thermomécaniques et mécaniques

Les propriétés thermomécaniques des réseaux époxy / LI modifiés par CA ont été évaluées par DMA avec les températures de relaxation ( $T_\alpha$ ) listées dans le Tableau 5. L'utilisation du prépolymère époxyde dérivé de cardanol dans la matrice époxy / LI a une influence sur leurs propriétés thermomécaniques, notamment la température de relaxation (Tableau 5). Dans tous les cas, les courbes DMA présentent deux pics de relaxation qui se déplacent à plus basse température avec l'ajout de CA. La diminution de  $T_\alpha$  peut être expliquée par la baisse de la densité de réticulation en raison de l'existence de la CA agissant en tant qu'agent plastifiant.<sup>4</sup>

La ténacité à la rupture des réseaux époxy / LI modifiés par CA a été étudiée et les valeurs de  $K_{Ic}$  des réseaux époxy / LI non modifiés et modifiés par CA sont présentées dans le Tableau 5. En fait, les réseaux époxy / LI avec IL-DCA ou IL-TMP ont une faible résistance à la rupture d'environ 0,4 MPa.m<sup>1/2</sup> en raison de sa densité de réticulation élevée (Chapitre 2). Ensuite, l'incorporation du CA avec les chaînes flexibles va améliorer la flexibilité de ces réseaux époxyde. En outre, la ténacité à la rupture des systèmes modifiés CA dans le Tableau 5 dépend du type de durcisseur et la quantité de CA. Pour les systèmes à base d'IL-DCA, aucune amélioration de la ténacité à la rupture est obtenue lorsque CA est introduit dans des réseaux époxy / LI expliqué

par le manque de la séparation de phases.<sup>5,6</sup> A l'inverse, nous avons obtenu une augmentation significative du  $K_{Ic}$  quand 10 phr de CA est incorporé dans le réseau DGEBA / IL-TMP (+ 180 %) avec une séparation de phase est observée.<sup>7</sup> Néanmoins, une valeur critique de la quantité de CA est également découvert par une baisse de la ténacité quand 20 phr de CA est utilisé pour le réseau DGEBA / IL-TMP.

**Tableau 5** Comportement thermomécanique et mécanique de réseaux époxy / LI modifiés par l'ajout de CA.

Echantillons	1 <sup>er</sup> $T_{\alpha}$ (°C)	2 <sup>e</sup> $T_{\alpha}$ (°C)	$K_{Ic}$ (MPa.m <sup>1/2</sup> )
DGEBA/IL-DCA	126	150	0.41 ± 0.02
DGEBA/IL-DCA/CA-10	107	147	0.33 ± 0.03
DGEBA/IL-DCA/CA-20	82	132	0.38 ± 0.03
DGEBA/IL-DCA/CA-30	55	71	0.41 ± 0.03
DGEBA/IL-TMP	--	150	0.39 ± 0.02
DGEBA/IL-TMP/CA-10	104	140	1.08 ± 0.06
DGEBA/IL-TMP/CA-20	62	118	0.39 ± 0.02

En général, les propriétés des réseaux époxy / LI modifiés par l'addition de CA ont été clairement dépendant de la nature chimique des liquides ioniques (dicyanamide ou phosphinate).

## • Conclusion

En conclusion, les liquides ioniques phosphonium ont été utilisés comme durcisseurs pour développer des systèmes époxy / LIs biosourcés. Les réseaux époxy / LI dérivés de cardanol ont été préparées possédant d'excellentes propriétés thermiques combinées à une hydrophobicité élevée grâce à la structure unique de prépolymère époxyde à base de cardanol avec le cycle aromatique et ces longues chaînes d'alkyle. Ensuite, ce composé époxyde biosourcé a été utilisé dans les réseaux époxy / LI pour améliorer la ténacité à la rupture. En outre, la combinaison d'un prépolymère époxyde avec des longues chaînes d'alkyle et des LIs hydrophobes conduit à une faible énergie superficielle. Dans l'ensemble, ce travail ouvre une nouvelle façon de développer des matériaux durables aux propriétés améliorées.

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**Chapter 1:**

# **Literature Review**

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## Table of contents

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<b>1.1. Ionic liquids and Polymers .....</b>	<b>31</b>
1.1.1. Ionic liquids.....	31
1.1.1.1. Introduction of Ionic liquids.....	31
1.1.1.2. Properties of Ionic liquids .....	32
1.1.2. Interaction between Ionic liquids and polymers.....	32
1.1.3. Ionic liquids applications in polymer systems.....	33
1.1.3.1. As Ionic conducting agents for polymer electrolytes.....	33
1.1.3.2. As structuration agents for polymer matrices.....	34
1.1.3.3. As processing aids for cellulose.....	36
1.1.3.4. As compatibilizers for polymer blends.....	36
1.1.3.5. As plasticizers for polymers.....	37
1.1.3.6. As surfactant in the preparation of functional polymers.....	37
1.1.4. Conclusion .....	39
<b>1.2. Ionic liquids in epoxy networks .....</b>	<b>39</b>
1.2.1. Epoxy networks.....	39
1.2.1.1. Introduction.....	39
1.2.1.2. Formation of epoxy networks - Reaction mechanism .....	39
1.2.2. Ionic Liquids in epoxy networks .....	42
1.2.2.1. Synthesis and development of new epoxide functionalized ILs.....	42
1.2.2.2. ILs as reactive and non-reactive additives for commercial epoxy prepolymer or epoxy-amine systems.....	45
1.2.3. Conclusion .....	58
<b>1.3. Modification of epoxy networks.....</b>	<b>58</b>
1.3.1. Introduction.....	58
1.3.2. Modification of epoxy networks by thermoplastics .....	58

---

1.3.2.1. Reaction-induced phase separation (RIPS) .....	58
1.3.2.2. PPE-modified epoxy networks .....	60
1.3.3. Modification of epoxy networks by core-shell particles .....	66
1.3.3.1. Toughening mechanism of CSR-modified epoxy networks.....	66
1.3.3.2. Different rubber core-shell particles used to modified epoxy networks.....	68
1.3.4. Conclusion .....	73
<b>1.4. Bio-based epoxy networks .....</b>	<b>73</b>
1.4.1. Introduction.....	73
1.4.2. Preparation of epoxy and curing agent monomers based on cardanol.....	74
1.4.2.1. Extraction of cardanol from cashew nut shell liquid.....	74
1.4.2.2. Synthesis of epoxy monomers based on cardanol.....	74
1.4.2.3. Synthesis of curing agent based on cardanol .....	76
1.4.3. Preparation of epoxy networks using Cardanol based compounds .....	77
1.4.3.1. Cardanol based novolac epoxy polymer.....	77
1.4.3.2. Cardanol based compounds as modifiers for conventional epoxy networks .....	78
1.4.3.3. Epoxy networks with Cardanol based prepolymer and/or curing agent.....	80
1.4.4. Conclusion .....	82
<b>1.5. Conclusion of chapter 1 .....</b>	<b>83</b>
<b>References of chapter 1 .....</b>	<b>84</b>

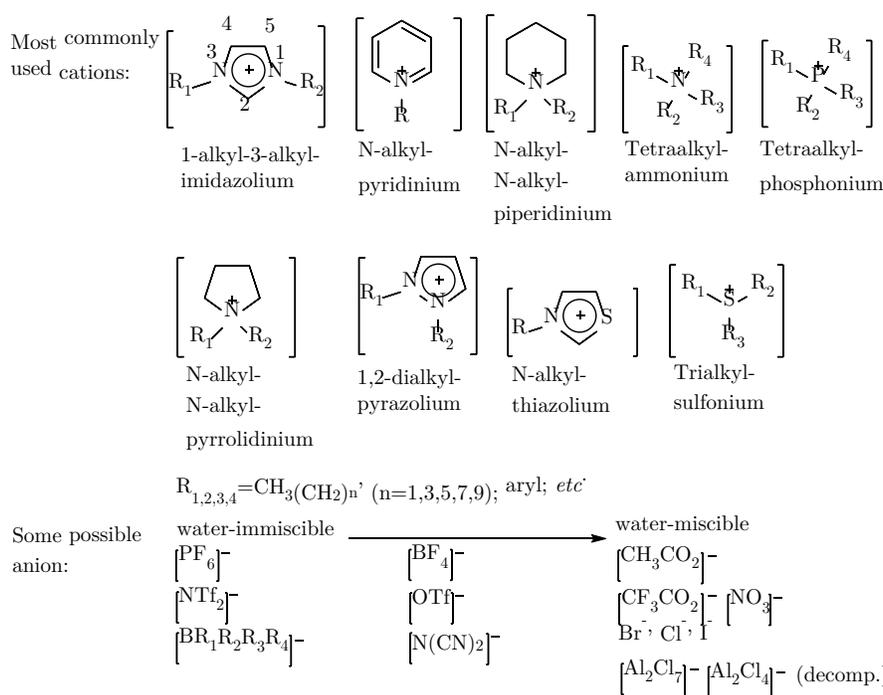
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## 1.1. Ionic liquids and Polymers

### 1.1.1. Ionic liquids

#### 1.1.1.1. Introduction of Ionic liquids

Ionic liquids (ILs) are organic salts and are composed of ions *i.e.* an organic cation and an organic/inorganic anion with low melting temperature. Various combinations of cations and anions are possible.<sup>1</sup> Different chemical structures of ILs used in the literature are presented in Figure 1-1.



**Figure 1-1** Structure of commonly used ionic liquids.<sup>1</sup>

While ionic liquids have recently gained worldwide academic and industrial attention, their history has started in the early 20<sup>th</sup> century with the first ionic liquid—ethyl ammonium nitrate—discovered in 1914 by Walden.<sup>2</sup> After that, ionic liquids have stayed in silence for two decades until a patent in 1934 revealed the use of “liquefied quaternary ammonium salts” as cellulose dissolution solvent.<sup>3</sup> This patent opened the ways of using ionic liquids for cellulose processing. Then, one of first striking discoveries of ionic liquids was the mixture of aluminum (III) chloride and 2-ethylpyridinium bromide discovered in the 1940s for electroplating of aluminium.<sup>4</sup> However, the instability of pyridinium cation limited the use of this system. Not until 1982 when Wilkes and Hussey developed new ILs with more stable cation – chloroaluminates of dialkyl imidazolium – the

great interest of ionic liquids has emerged in both academic and industrial field. This first kind of room temperature ionic liquids (RTILs) has also opened a new way for electrochemistry. Since then, new range of ionic liquids based on dialkyl imidazolium but alternative anions (*i.e.* Hexafluorophosphate  $\text{PF}_6^-$  or tetrafluoroborate  $\text{BF}_4^-$ ) have been synthesized to eliminate the moisture sensitivity of chloro aluminate based ionic liquids.<sup>5</sup> Following that, ionic liquids based on other cations (phosphonium and pyrrolidinium) have also been reported in the literature<sup>1</sup> with a large number of commercially available phosphonium based ionic liquids.<sup>6</sup> Nevertheless, the most commonly used ionic liquids are still based on imidazolium and pyridinium, very few researches on phosphonium based ionic liquids were carried out.

### 1.1.1.2. Properties of Ionic liquids

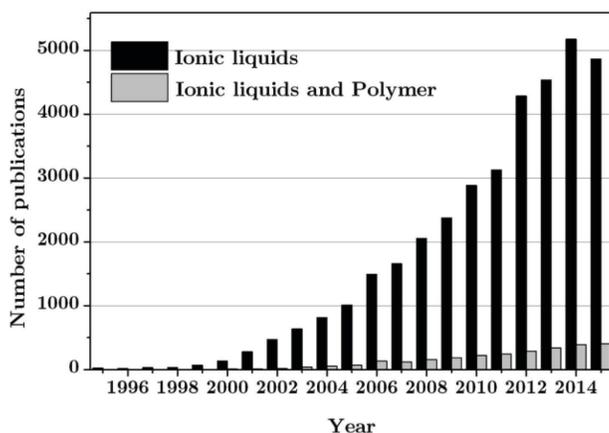
Normally, ionic liquids possess low melting temperature with high thermal stability higher than 300 °C<sup>6-8</sup> as well as non-flammability and low volatility.<sup>9</sup> In addition, their good ionic conductivity and large electrochemical window allow for their applications as electrolytes in electrochemistry.<sup>1</sup> Ionic liquids are also considered as “green solvent” due to their capacity to dissolve many substances and their ability to be reused and recycled.<sup>10</sup> Another advantage of ionic liquids comes from their versatile structure *i.e.* anion and cation type or alkyl chain length which determines their physico-chemical properties. In details, melting point of ionic liquids depends on the length of alkyl chain and the symmetry of IL cation. Lower melting points were obtained for asymmetric cation based ILs.<sup>7,11-13</sup> In addition, a higher alkyl chain length increases the force Van der Waals leading to a higher viscosity of ionic liquids.<sup>14</sup> Also, the nature of the counter anion plays a significant role on the IL properties.<sup>8</sup> The change of IL anion can vary the water solubility of ILs from water-immiscible to water-miscible (Figure 1-1).<sup>1</sup> The thermal stability of ILs also decreases dramatically due to the change of anion, *i.e.* from tetra fluoroborate ( $\text{BF}_4^-$ ) to bromide ( $\text{Br}^-$ ).<sup>7</sup> Likewise, for the same cation, ILs viscosity is also affected by the nature of anion.<sup>14</sup>

### 1.1.2. Interaction between Ionic liquids and polymers

Although the interest on ionic liquids has grown since the 1990s, the first publications on ionic liquids applications in the polymers have only been published from 2002. In fact, ionic liquids are mostly used as solvents,<sup>10,15</sup> and catalysis,<sup>16,17</sup> analytical chemistry,<sup>18,19</sup> physical chemistry,<sup>20</sup> to electrochemistry,<sup>12,21</sup> engineering,<sup>22,23</sup> and biological uses<sup>24</sup> with a large scale industrial application of ionic liquids – BASIL (biphasic acid scavenging using ionic liquids) process – announced in 2003.<sup>25</sup> Until now, the number of publications on the combination of ILs and polymers still stays as a minority part compared to those on ionic liquids (Figure 1-2). Despite the lack of research,

unprecedented properties have been received from the combination of ILs and polymers suggesting promising applications.

In fact, thanks to their recyclability, ionic liquids have been widely used as the solvent media for the polymerization,<sup>26</sup> and polycondensation reaction.<sup>27</sup> For example, the use of ionic liquids was reported to increase the polymerization degree in the radical polymerization.<sup>28</sup> Nevertheless, ILs were also applied as a component of polymer matrix. The versatility of ionic liquids with tunable structure and properties allows achieving desirable interactions towards polymer. In the following part, the use of ILs in the polymer matrix as ionic conducting agents for polymer electrolytes, as structuration agents for polymer matrices, as processing aids for cellulose, as compatibilizers for polymer blends, as plasticizers and as surfactants in the preparation of functional polymers will be discussed.



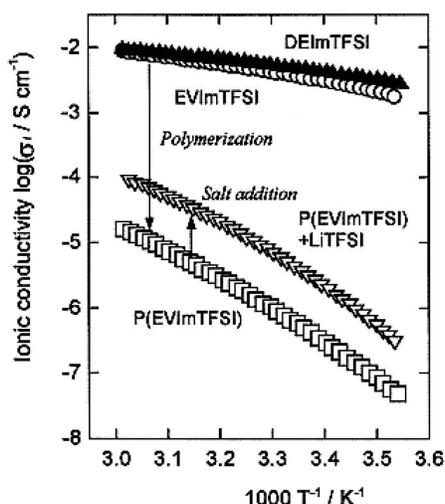
**Figure 1-2** Publications about “ionic liquids” and “ionic liquids and polymer” determined from ISI Web of Science in the last twenty years.

### 1.1.3. Ionic liquids applications in polymer systems

#### 1.1.3.1. As Ionic conducting agents for polymer electrolytes

Thanks to their excellent thermal stability, non-flammability, non-volatility, and very high ionic conductivity, ionic liquids are great candidates to replace conventional organic solvent for the development of polymer electrolytes.<sup>29,30</sup> In the literature, imidazolium based ionic liquids are most commonly used with several polymers<sup>31,32</sup> such as poly(methyl methacrylate) PMMA,<sup>33,34</sup> poly(acrylonitrile) PAN,<sup>35</sup> poly(ethylene oxide) PEO,<sup>35</sup> poly(vinyl alcohol) PVA,<sup>35</sup> and poly(vinylidene fluoride hexafluoro propylene) P(VDF-HFP).<sup>36-38</sup> Polymer electrolytes containing ionic liquids were developed by different methods including the polymerization of ionic liquids,<sup>39</sup> and the development of polymers in RTILs<sup>33,34</sup> and impregnation of polymer electrolytes in

RTILs.<sup>35-38</sup> In fact, Ohno has synthesized poly ionic liquids (PILs) from the polymerization of *N*-vinyl-3-ethylimidazolium trifluoromethane sulfonylimide through the vinyl functionality to form the polymer electrolytes.<sup>39</sup> However, the polymerization of ILs led to a significant drop of ionic conductivity from  $1.0 \times 10^{-2} \text{ S.cm}^{-1}$  at 60 °C for neat ILs to  $1.0 \times 10^{-5} \text{ S.cm}^{-1}$  at 50 °C for PILs due to the increase of viscosity and the limited number of mobile ions. The ionic conductivity of PILs can be improved by the incorporation of equimolar amount of Lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) to the polymer (Figure 1-3).<sup>39</sup> In the opposite, the other methods were proven to provide transparent and flexible polymer gels with excellent ionic conductivity combined with high thermal stability and good mechanical strength required for polymer electrolytes.<sup>33-38</sup> In fact, Susan *et al.* have polymerized MMA monomer in imidazolium ILs with the existence of small amount of crosslinker and have obtained the polymer gel with the ionic conductivity close to  $1.0 \times 10^{-2} \text{ S.cm}^{-1}$  at room temperature.<sup>33</sup> Moreover, Fuller *et al.* have prepared IL-polymer gel electrolytes from both hydrophobic and hydrophilic IL in P(VDF-HFP) matrix with ionic conductivity of over  $1.0 \times 10^{-3} \text{ S.cm}^{-1}$  at room temperature and of over  $1.0 \times 10^{-2} \text{ S.cm}^{-1}$  at 100 °C.<sup>37</sup> In general, ILs have shown their importance in the field of polymer electrolytes.

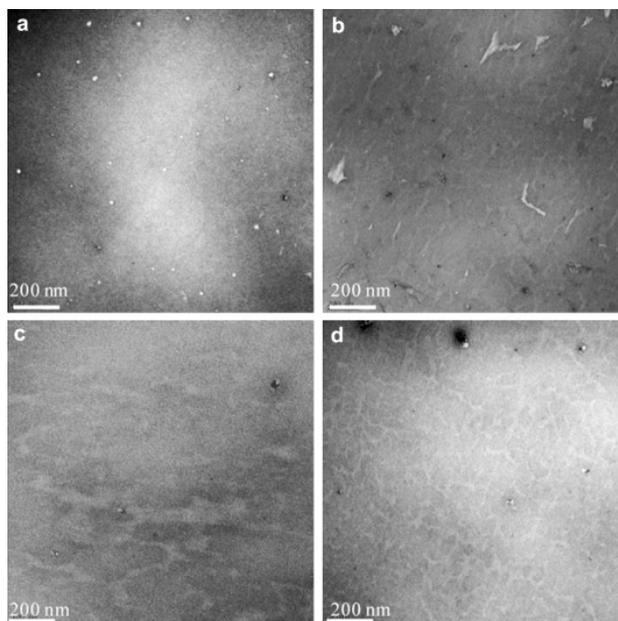


**Figure 1-3** Ionic conductivity of ILs (○), PILs (□), PILs with equimolar amount of LiTFSI (△) compared to a model electrolyte salt (▲).<sup>39</sup>

### 1.1.3.2. As structuration agents for polymer matrices

Recently, ionic liquids have gained interest as building blocks to design nanostructured polymers. Several polymeric materials containing ILs were prepared from various types of polymer matrix such as fluorinated matrix (poly (tetrafluoro ethylene) PTFE),<sup>40,41</sup> copolymer (poly (vinylidene fluoride-co-chloro trifluoro ethylene) P(VDF-CTFE))<sup>42</sup> and biopolymer matrix (poly (butylene adipate-co-terephthalate) PBAT).<sup>43</sup> The effect of ILs chemical nature – both cations and

anions – on the morphology and consequently on the final properties of these materials was also investigated. Indeed, the dispersion of ILs in PTFE matrix varied from ILs clusters and co-continuation for imidazolium and pyridinium based ILs to a “spider-web” nanostructuring for those using phosphonium based ILs (Figure 1-4) leading to unprecedented flexibility and stiffness.<sup>40,41</sup> Recently, phosphonium ILs was reported by Yang *et al.* to change the crystallization of P(VDF-CTFE).<sup>42</sup> The properties of nanostructured polymeric materials were found to depend on interactions between ILs and polymer resulting from the structure of IL cations and anions and their combinations. In fact, due to the diffusion and regular assembly of ILs in the rigid amorphous fraction of P(VDF-CTFE), the existence of small amount of ILs (2 wt%) resulted in a complete transition of nonpolar  $\alpha$ -phase to polar- and/or  $\beta$ -phase and a decrease of melting temperature, crystallization temperature, crystallinity and crystallite size of polymer.<sup>42</sup> Similarly, the introduction of small amount of ILs (2 wt%) in biopolymer matrix PBAT induced the nanostructuring and increased the water barrier properties due to the hydrophobicity of phosphonium based ILs.<sup>43</sup> In fact, significant reductions in water permeability coefficients up to -70% are observed using a small amount of phosphonium ionic liquids (2 wt%) without reducing the mechanical behavior of biodegradable matrix.<sup>43</sup> Overall, the versatility of ILs leading to various improvements of polymeric materials properties suggests their potential for advanced applications.



**Figure 1-4** TEM micrographs of neat PTFE (a) and blends of PTFE with imidazolium (b), pyridinium (c) and phosphonium (d) ILs.<sup>40,41</sup>

### 1.1.3.3. As processing aids for cellulose

Being well known as green solvents, ILs have become an alternative for conventional solvent as processing aids for cellulose. In fact, the use of ILs for cellulose dissolution has begun in 1934 with the research of Graenacher using N-ethyl pyridinium halide.<sup>3</sup> However, not until 2002, cellulose dissolution using ILs has been extensively recognized after Roger group's work based on imidazolium IL. The effect of IL anions and cations on the ability to dissolve cellulose was discussed.<sup>44</sup> In fact, cellulose is more soluble in IL with stronger hydrogen bond acceptors such as chloride. Concerning the effect of IL cation, the increase of alkyl length reduces the dissolving effectiveness.<sup>44</sup> Moreover, the modification of ILs structure helped to decrease the cellulose dissolving temperature from over 110 °C to 35–45 °C and even to room temperature, which is suitable for bio-refinery applications.<sup>45</sup> Noted that cellulose can be precipitated from the solution with ILs in adding water, acetone or ethanol,<sup>44</sup> it is possible to extract cellulose from lignocellulose using ILs.<sup>46</sup> Nevertheless, cellulose modifications can be executed in IL media. The preparation of new green fibers, blends, ion gels and composites based on cellulose combined with ILs was also investigated.<sup>47–50</sup>

### 1.1.3.4. As compatibilizers for polymer blends

Recently, phosphonium ILs were also applied in thermoplastic blends such as polypropylene/polyamide 6 (PP/PA6),<sup>51</sup> or biopolymer blends composed of poly(butylene-adipate-co-terephthalate)/poly(lactic acid) (PBAT/PLA).<sup>52</sup> In PP/PA6 blends, ILs were believed to stay at the interface of two polymers and act as interfacial agents.<sup>51</sup> The addition of only 1 wt% of ILs decreased the PA dispersion size in PP from 27 to 2–3 μm. Moreover, the mechanical properties of polymer blends were highly improved by the presence of ILs with the same Young's modulus but +1400 % higher of deformation compared to neat PP/PA6 blends.<sup>51</sup> In addition to this, the same improvements in morphology and properties were obtained for PBAT/PLA blends containing ILs using only 1 wt% of phosphonium ILs.<sup>52</sup> Indeed, ILs was found to locate in the interfacial region around the dispersed PLA phase and to improve the dispersion of PLA in the PBAT matrix. IL-modified PBAT/PLA blends exhibited an excellent compromise in mechanical behaviors *i.e.* the same deformation with higher Young's modulus compared to the neat ones. The morphology form and properties improvements of polymer/IL blends depend on the intermolecular interaction of polymer and ILs determined by the IL structure.<sup>52</sup> Then, in a recent work, 1 wt% of phosphonium ILs was used as new compatibilizing agents for the nanocomposite of PBAT/PLA reinforced with lignin.<sup>53</sup> The combination of ILs and lignin leads to significant improvements in the mechanical behavior and water vapor permeability of biopolymer blends. The chemical nature of ILs has great effect on the dispersion of lignin and PLA resulting in different morphologies and

final properties of polymeric materials.<sup>53</sup> Overall, the results reported in the literature highlight the beneficial effect of ionic liquids as new compatibilizers of polymers blends to replace the block copolymers, the nanoparticles and the ionomers.

#### **1.1.3.5. As plasticizers for polymers**

ILs have appeared as a great alternative to conventional plasticizers in several polymers, *i.e.* poly(methyl methacrylate) PMMA,<sup>54,55</sup> poly(vinyl chloride) PVC,<sup>56</sup> and poly(lactic acid) PLA.<sup>57</sup> In details, Scott *et al.* reported the use of imidazolium ILs as plasticizers for PMMA to replace conventional plasticizers based on dioctyl phthalate (DOP), which concerns various health and environmental aspects.<sup>54,55</sup> ILs showed higher compatibility in PMMA up to 50 wt% than DOP (40 wt%). Moreover, the existence of ILs in PMMA matrix led to an important decrease of glass transition temperature ( $T_g$ ) combining with a higher thermal stability than DOP.<sup>54,55</sup> The use of ILs also provides the ability to control the plasticizing extent ( $T_g$ ) over a wide range of temperature and to reduce volatility for high temperature applications.<sup>55</sup> Concerning PVC matrix, a large range of ILs based on phosphonium, ammonium and imidazolium cation up to 20 wt% were used as plasticizers. ILs with distinct charged species forming secondary bonds with the polar ends of PVC and the aliphatic hydrocarbon are expected to provide similar performance to conventional plasticizers in terms of integration with polymer chains. In fact, a higher flexibility was observed for ILs-plasticized PVC such as a decrease of glass transition temperature and elastic moduli combined with a better leaching and migration resistance compared to conventional plasticizers.<sup>56</sup> Besides, the plasticizing effect of ILs on PLA was investigated by Park *et al.* using two phosphonium ILs (5 and 10 wt%).<sup>57</sup> Both types of ILs are partly miscible with PLA leading to the decrease of flexural modulus (up to -57 %) and glass transition temperature of polymer blends. However, the extent of plasticization can also be related to the decrease of PLA molar mass during melting process due to the existence of ILs.

#### **1.1.3.6. As surfactant in the preparation of functional polymers**

Montmorillonite (MMT) and layered double hydroxide (LDH) are commonly used layered silicates for the preparation of nanocomposites. The chemical modifications of these clays by ionic liquids have been considered to obtain better compatibility between inorganic fillers and polymers. Livi *et al.* have synthesized imidazolium, phosphonium, pyridinium and quinolinium ILs to use as new surfactants for cationic exchange of layered silicates.<sup>58,59</sup> Higher thermal stability and better intercalation between the layers of montmorillonite were obtained compared to original  $\text{Na}^{\oplus}$  MMT. Then, numerous papers have been published on IL-modified-MMT polymeric nanocomposites based on different types of polymers and different structures of ILs. In all the

cases, nanocomposites properties were enhanced by good dispersion of IL-modified-MMT in the polymer matrix. In details, high degree of exfoliation of MMT modified by imidazolium ILs in polystyrene (PS) matrix was obtained by Bottino *et al.*, leading to high thermal properties and low ultraviolet (UV) photo-oxidative degradation of nanocomposites.<sup>60,61</sup> In addition, Pucci *et al.* observed an increase of degradation temperature of 60 °C when IL-modified MMT was applied into PS matrix.<sup>62</sup>

The influence of ILs modification on MMT was also investigated for nanocomposites based on polyolefines. Similar improvements in dispersion and thermal stability were achieved for these nanocomposites combining with excellent gas barrier and mechanical properties.<sup>63,64</sup> Indeed, the introduction of 4 vol% of MMT modified with Imidazolium IL into polypropylene matrix induced an increase of thermal stability of 90 °C and an improvement of Young's modulus of +35 %.<sup>64</sup> Concerning nanocomposites based on high-density polyethylene (HDPE), Livi *et al.* have demonstrated that better dispersion of clay layers was obtained when imidazolium and phosphonium ILs were used as surfactant agents.<sup>65,66</sup> The use of only 2 wt% of ILs-modified MMT can increase Young's modulus of polymer materials up to +50 % without reducing its fracture behavior. The authors also proposed a mechanism of the modification of ILs on MMTs in which ILs formed both chemical and physical bonding to MMTs. The existence of physical bonded ILs into MMTs then acting as compatibilizers was the main reason for the good stiffness-toughness compromise in HDPE/MMTs nanocomposites.<sup>65</sup> On the other hand, IL-treated layered silicates acted as plasticizers for fluorinated matrix (PVDF) leading to an increase of strain at break.<sup>67,68</sup> In fact, Livi *et al.* have discovered a significant improvement of +630 % achieved with only 1 wt% MMT treated by an imidazolium IL in the PVDF matrix with only -10 % decrease of stiffness.<sup>68</sup>

IL-treated layered silicates (MMT or LDH) were also considered for bio-nanocomposites based on PBAT or PLA. Thus, with only 2 wt% and 5 wt% of imidazolium and phosphonium treated MMT, a slight increase in the Young's modulus (15-25 %) is observed for PBAT nanocomposite coupled with significant decreases in water barrier properties of 60-80 %.<sup>69</sup> Moreover, ILs were used to modify LDH for PLA/LDH nanocomposites in order to enhance water barrier properties for food packaging applications. Despite a decrease of thermal stability of PLA matrix, an excellent stiffness-toughness compromise has been obtained.<sup>70</sup> Also, the presence of ILs-modified-LDH increased the surface hydrophobicity of the neat PLA resulting in a decrease in water permeability by +35 % for nanocomposites.<sup>71</sup>

#### 1.1.4. Conclusion

This part summarized the literature about ionic liquids and polymers. Thanks to their outstanding properties, the use of ILs in the polymers field has developed quickly in the last few decades spreading from polymerization solvents to functional additives for polymeric materials. Nevertheless, ionic liquids have gained the interests as new additives for epoxy networks, which will be described in the next part.

### 1.2. Ionic liquids in epoxy networks

#### 1.2.1. Epoxy networks

##### 1.2.1.1. Introduction

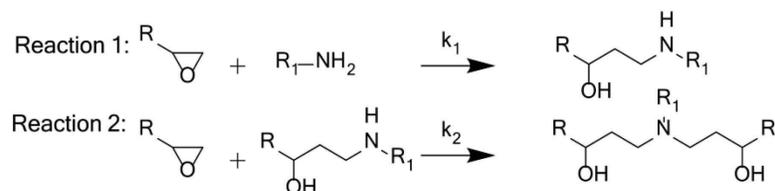
Epoxy networks are important thermosetting materials exhibiting outstanding properties which make them available for various fields such as adhesives, paints and coatings, electrical and electronic applications as well as composite matrix to combine with carbon fibers for aerospace applications.<sup>72</sup> Epoxy networks are derived from epoxy prepolymers, which consist of a minimum of two epoxide groups (oxirane rings). The high reactivity of this functional group allows epoxy prepolymers to form stable epoxy thermosetting networks. Nowadays, the most commonly used epoxy prepolymer is diglycidyl ether of bisphenol A (DGEBA) produced from the reaction between Bisphenol A (BPA) and epichlorohydrin in the presence of sodium hydroxide (Scheme 1-1).

+

controlled by changing the reactive compositions. Also, low contraction was observed for final products since the reactions are based on the opening of epoxy rings. The structure of epoxy networks depends on prepolymer functionality, the molar ratio between prepolymer and curing agent/initiator as well as the curing temperature (curing protocol).<sup>72</sup>

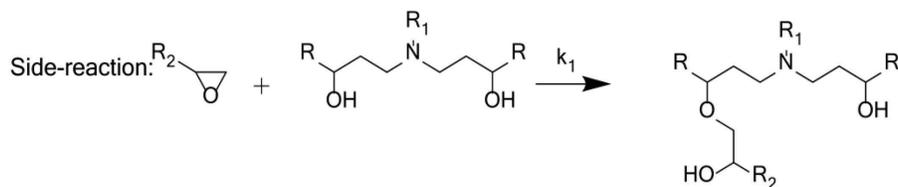
#### 1.2.1.2.1. Step-growth polymerization

Among several curing agents for epoxy prepolymers, amines are the most commonly used and the most representative for the case of step-growth polymerization. Reactions between epoxide groups and amines are summarized in Scheme 1-2. In fact, primary and secondary amine will react with epoxide groups to form secondary and tertiary amine, respectively. The stoichiometric ratio between epoxide groups and active hydrogen of amine groups plays an important role in the formation and properties of epoxy/amine networks.<sup>75,76</sup> As the attack of amino group can be facilitated by hydroxyl groups generated during the reaction, epoxy/amine reaction is an autocatalytic process.<sup>72</sup>



**Scheme 1-2** Mechanism of addition reactions between epoxy and amine groups with reaction rate constant  $k_1$  and  $k_2$ .<sup>72,77</sup>

A side-reaction between epoxy and hydroxyl groups of tertiary amine denoted etherification can also compete with the two major reactions (Scheme 1-3). However, this reaction is often negligible due to the requirement to work at high temperature and is only favored in case of excess of epoxide groups.<sup>78</sup>



**Scheme 1-3** Etherification mechanism between epoxy and hydroxyl groups.<sup>72</sup>

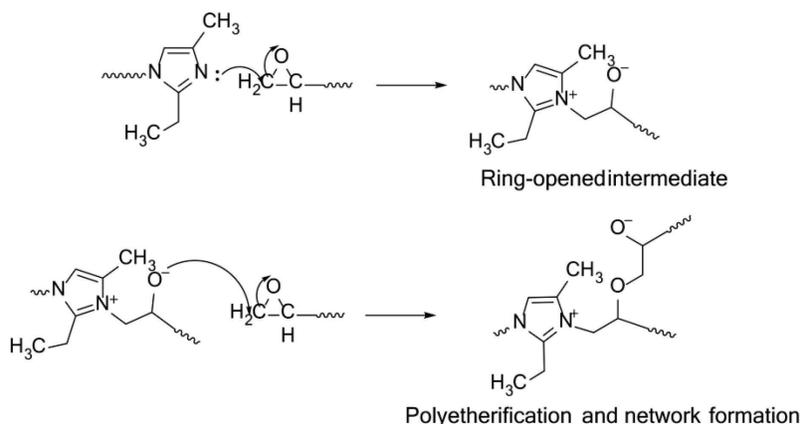
The reactivity of amines which decides kinetics of curing reactions varies by the chemical structure.<sup>79</sup> Normally, primary amines are more reactive than secondary one.<sup>80</sup> Aliphatic amines

are more likely to react than aromatic amines explaining the fact that aliphatic amines are widely used for low curing temperature applications.<sup>72</sup>

#### 1.2.1.2.2. Chain homopolymerization of epoxy prepolymer

Both nucleophilic and electrophilic compounds can react with epoxide groups, so anionic and cationic mechanisms are of great importance in epoxy polymer chemistry. The chain homopolymerization of epoxy prepolymer can be initiated by tertiary amines,<sup>81</sup> imidazoles,<sup>82</sup> or ammonium salts for anionic mechanism, and by latent cationic catalysts<sup>83</sup> such as iodonium, ammonium, pyrazinium and quinoxalinium salts for cationic homopolymerization. The anionic reaction mechanism of imidazoles initiation on epoxy prepolymer was proposed by Barton *et al.* (Scheme 1-4).<sup>82</sup>

Overall, the initiators do not have significant effect on the final properties of epoxy polymers which are determined by the nature of epoxy prepolymers.<sup>74</sup> Complex chain transfer and termination steps lead to low polymerization degree. The chain polymerization of multifunctional epoxy prepolymers can result in the formation of epoxy networks.<sup>72</sup>

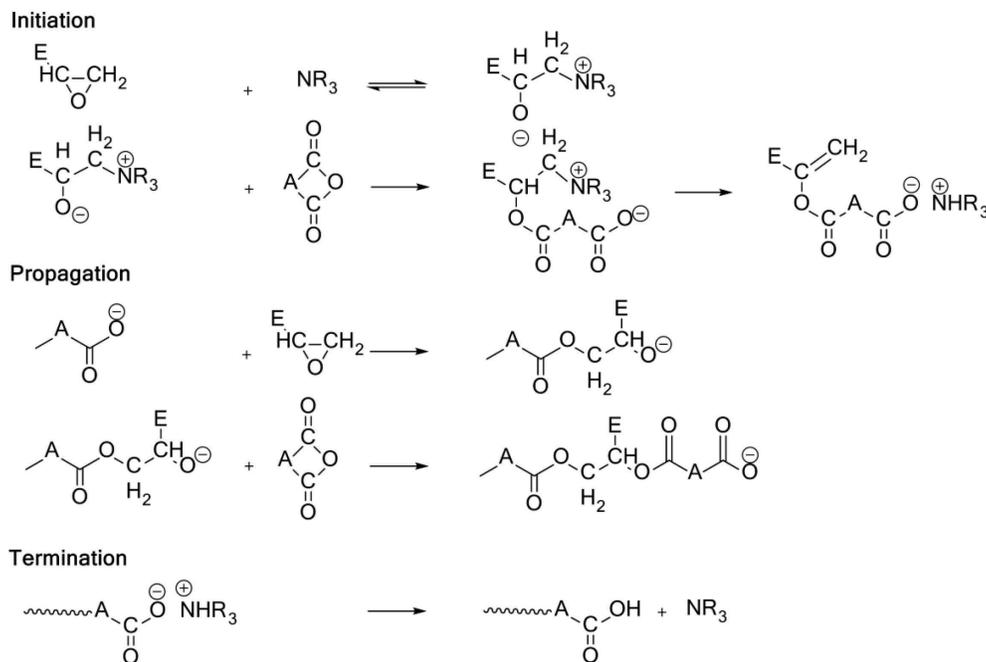


**Scheme 1-4** Chain homopolymerization of epoxy prepolymer initiated by imidazoles.<sup>82</sup>

#### 1.2.1.2.3. Chain copolymerization

The curing reaction of epoxy prepolymer by anhydride occurs at high temperature through a chain copolymerization including initiation, propagation, termination and chain transfer.<sup>72,84-86</sup> Concerning initiation, Lewis bases such as tertiary amines react with epoxide groups to form a zwitterion containing an alkoxide anion. Then reactive alkoxide groups attack anhydride groups to create an active center as a carboxylate anion. In propagation step, carboxylate anion reacts with epoxide group to regenerate the alkoxide, which in turn reacts with anhydride to regenerate

carboxylate anion. Then, termination of curing reaction involves the liberation of initiator Lewis bases. An example for mechanism of epoxy anhydride curing reaction initiated by tertiary amines is summarized in Scheme 1-5.



**Scheme 1-5** Mechanism of anhydride epoxy copolymerization initiated by tertiary amines.<sup>84</sup>

## 1.2.2. Ionic Liquids in epoxy networks

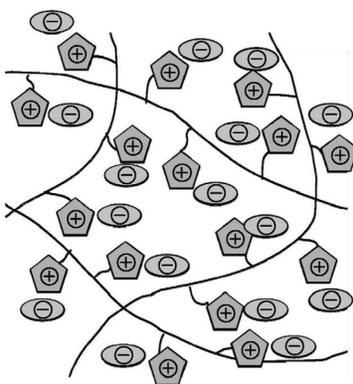
In the last few years, the ability of ILs in designing the structure of polymer has also gained the interest for epoxy thermosetting materials. Very recently, ILs were applied into epoxy networks to develop new polymer electrolytes, anti-corrosive coatings or for composite applications.<sup>87,88</sup> According to the literature, the combination between ILs and epoxy networks can follow two major paths: *i*) the synthesis and development of new functionalized ILs and *ii*) the combinations of ILs as additives or comonomers to conventional epoxy systems.

### 1.2.2.1. Synthesis and development of new epoxide functionalized ILs

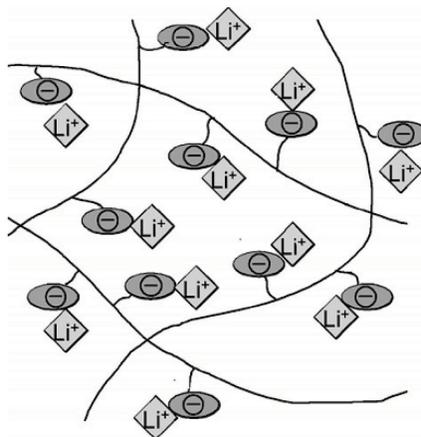
In fact, several ionic liquids containing epoxy functional group on either cation or anion structure were synthesized to form epoxy networks.

Matsumoto *et al.* have developed a variety of ionic-conductive film electrolytes based on the copolymerization of epoxy/amine networks combined with ILs bearing epoxide groups.<sup>89</sup> Different mono epoxide ILs were synthesized in order to covalently bond to the epoxy main structure including quaternary ammonium salts,<sup>90</sup> lithium sulfonate,<sup>91</sup> and lithium sulfonylimide ILs.<sup>92</sup> First

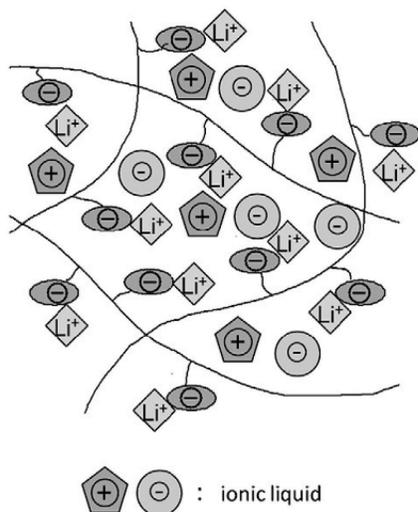
of all, quaternary ammonium ILs have been reported to form IL/amines adducts which in turn react with diepoxy monomers to form epoxy/amine networks. Thus, the obtained networked polymers having cationic groups on the networks backbone provide high ionic conductivity of  $2.8 \times 10^{-3} \text{ S} \cdot \text{m}^{-1}$  due to anions movements (Figure 1-5).<sup>90</sup> Considering the applications in Li-ion batteries with lithium cations as conducting agent, lithium sulfonate and lithium sulfonylimide ionic liquids were designed with mono epoxide groups on the anion structure (Figure 1-6). Hence, lithium single ionic conductive polymers in the form of flexible and self-standing films were prepared with high thermal stability in both cases (Temperature at 5 % of weight loss of over 270 °C). Networks containing lithium sulfonylimide ionic liquid have higher ionic conductivity ( $1 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ ) in dry condition than that containing lithium sulfonate ( $\sim 10^{-5} \text{ S} \cdot \text{m}^{-1}$ ) thanks to higher dissociative ILs structure.<sup>91,93</sup> These two networked polymers were then swollen in ILs in order to increase the ionic conductivity (Figure 1-7). Then, ionic-liquid-swollen networked polymers were discovered to have excellent non-flammability compared to conventional organo-gels.<sup>93</sup>



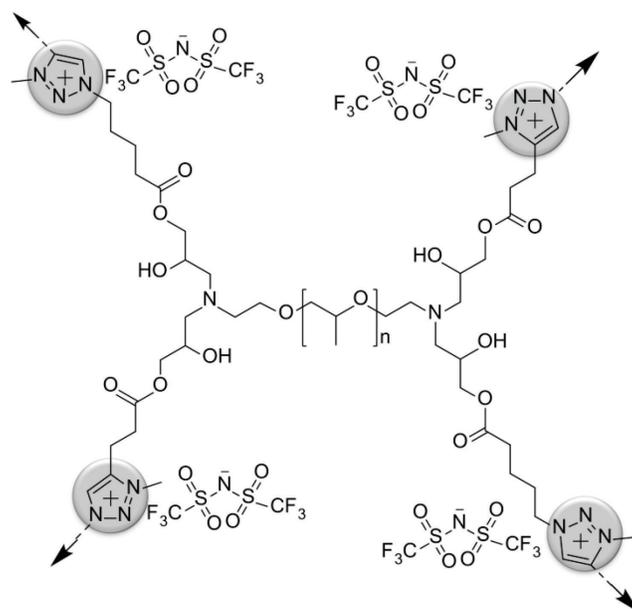
**Figure 1-5** Epoxy based networked polymer having ILs cation grafted on the backbone.<sup>89</sup>



**Figure 1-6** Epoxy based networked polymers having lithium salts with anionic groups grafted on the backbone.<sup>89</sup>



**Figure 1-7** Ionic-liquid-swollen epoxy based networked polymers<sup>89</sup>



**Figure 1-8** Crosslinked triazolium based epoxy-amine networks.<sup>94</sup>

Other authors synthesized ionic liquid monomers functionalized with two epoxide groups in order to prepare polymeric ionic liquids (PILs) and PIL/IL ion-gels based on epoxy amine reactions. Mcdanel *et al.* developed crosslinked epoxy amine PILs based on a synthesized bis-epoxide functionalized imidazolium ionic liquids. A free IL was also incorporated into the PILs up to 75 wt% to form PIL/IL gel membranes. The addition of IL increases the gas permeability while keeping the same selectivity.<sup>95</sup> Following this research, a variety of imidazolium and pyrrolidinium based ILs was also synthesized varying the cation structure *i.e.* the chain length and chemical

nature (alkyl or ether) between imidazolium and epoxide group. ILs molar mass was found to strongly affect the CO<sub>2</sub> uptake. The CO<sub>2</sub> solubility and permeability of PIL and PIL/IL gels membranes are tunable by the IL structure.<sup>96</sup> Very recently, our group has reported the formation of 1,2,3 triazolium based epoxy/amine networks from a diepoxy functionalized 1,2,3-triazolium ionic liquids (Figure 1-8). This epoxide-functionalized-IL/amine system has similar curing behavior and properties to a conventional DGBEA/amine system with low glass transition temperature of -42 °C and moderate value of ionic conductivity of  $2 \times 10^{-7}$  S.m<sup>-1</sup> discovered at 30 °C.<sup>94</sup>

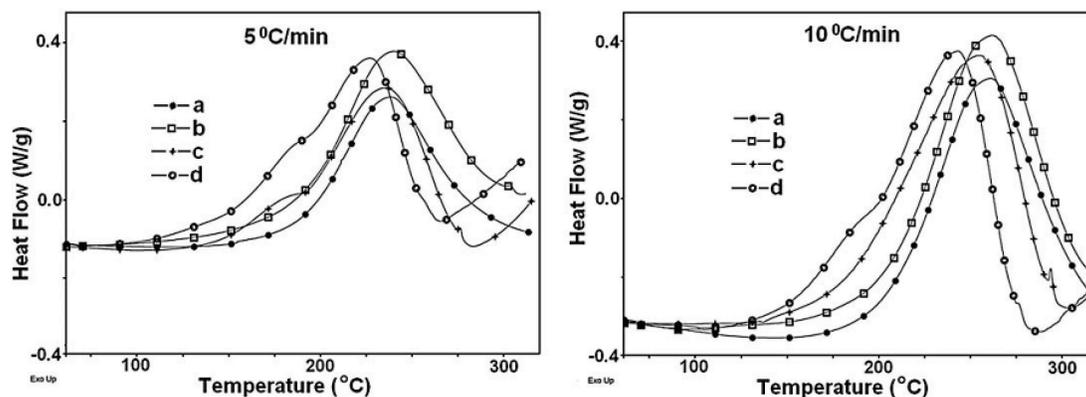
### ***1.2.2.2. ILs as reactive and non-reactive additives for commercial epoxy prepolymer or epoxy-amine systems***

#### ***1.2.2.2.1. As non-reactive additives***

Recently, ILs have been used as modifiers for epoxy/amine networks to improve their properties such as the curing behavior,<sup>97-100</sup> thermomechanical properties,<sup>97,98,101</sup> mechanical properties,<sup>99,102</sup> surface energy,<sup>100</sup> ionic conductivity,<sup>99,100,103-105</sup> and wear and scratch resistance.<sup>106-110</sup>

- ***Curing behavior – Catalytic effect of IL***

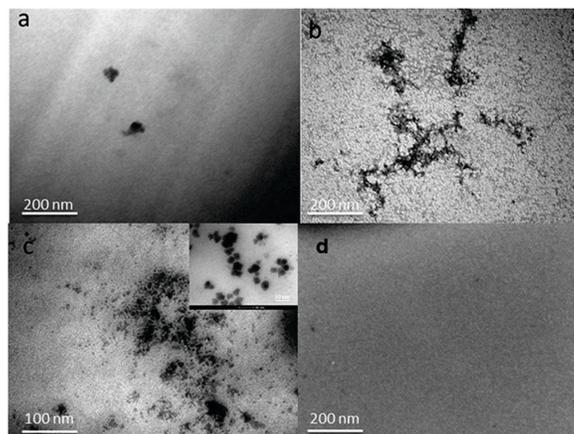
Firstly, the curing behavior of epoxy networks was modified by the presence of ILs. Imidazolium ILs combined with different counter anions have been used as alternatives to tertiary amines as the initiator for epoxy-anhydride curing reactions. ILs may also have a catalytic role on the formation of epoxy networks neglecting the chemical nature of hardener leading to glassy or rubbery networks. In fact, several studies in which ILs were incorporated into epoxy/amine networks was conducted by our research group.<sup>97-100</sup> The curing reaction of epoxy/MCDEA networks was catalyzed by the existence of a small amount of imidazolium based ILs (1–5 phr) with a decrease in temperature of the exothermal peak corresponding to curing reaction from 260 °C without ILs to 243 °C with 5 phr of IL (Figure 1-9). Likewise, a following study of our group revealed the effect of ILs structure on the catalytic effect on the epoxy/MCDEA systems using a series of imidazolium, pyridinium and phosphonium based ILs.<sup>98</sup> The presence of pyridinium and imidazolium based ILs has catalyzed the curing kinetic of epoxy/amine networks while no considerable effects were observed in the case of using ILs containing phosphonium cation. Recently, the effect of ILs on epoxy/Jeffamine systems was studied in which ILs also present the acceleration effect on the epoxy/amine reactions indicated by the decrease of exothermal peak temperature.<sup>99,100</sup>



**Figure 1-9** DSC thermograms of DGEBA/MCDEA networks as a function of heating rate and IL content (a) 0, (b) 1, (c) 2.5 and (d) 5 phr of IL.<sup>97</sup>

- Thermomechanical properties

Thermomechanical properties of epoxy/amine networks were modified by the presence of ILs due to the interactions between ILs and epoxy networks depending on the chemical nature of ILs.



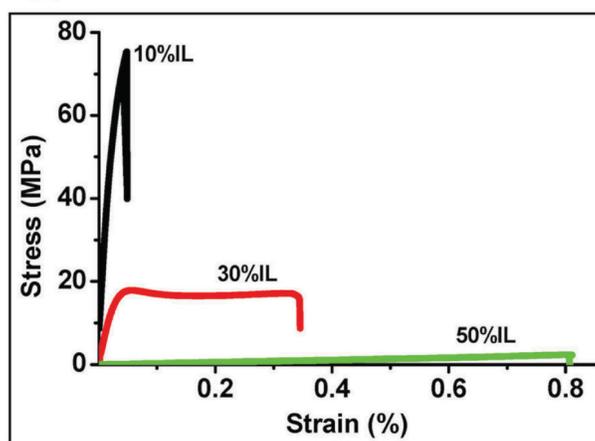
**Figure 1-10** TEM images of epoxy networks containing 10 phr of (a) Phos-DCA, (b) Phos-DBS, (c) Phos-TFSI and (d) without IL.<sup>100</sup>

Thus, the viscosity of epoxy/amine systems was significantly affected by imidazolium based ILs suggesting interactions between ILs and epoxy networks.<sup>99</sup> Moreover, the decrease in  $T_g$  values of epoxy/amine networks suggesting the plasticizing effect of ILs.<sup>99,100</sup> The plasticizing effect of ILs is less pronounced in the case of phosphonium based ILs than those based on pyridium and imidazolium cation.<sup>97</sup> IL anions also play a role on the plasticization.<sup>99,100</sup> For example, phosphonium ILs containing dicyanamide (Phos-DCA) and sulfonate (Phos-DBS) anions have a clear plasticizing effect on the glass transition temperature of epoxy/Jeffamine D230 networks whereas the presence of ILs containing trifluoro methane sulfonyl imide anion (Phos-TFSI) does

not affect  $T_g$  values even at high IL amount of 20 phr.<sup>100</sup> Thus, these results are explained by the confinement of ILs in epoxy/amine networks observed by transmission electron microscopy (TEM) which revealed different morphologies depending on IL structure. The change of IL counter anion in case of phosphonium based ILs varies the shape and size of IL aggregates (Figure 1-10). Thus, the lower miscibility of Phos-TFSI towards epoxy networks presented by an exudation at high IL content explains the unchanged glass transition temperature.<sup>100</sup> Overall, the dispersion of ILs is the decisive factor for the variation of epoxy networks properties.

- Mechanical properties

Afterwards, according to structure-properties dependence, the mechanical properties of epoxy networks are also modified by the addition of ILs. A significant stretchability improvement was achieved for epoxy/Jeffamine D400 networks modified by ILs, *i.e.* 196 % of elongation at break combined with a slight decrease of tensile strength (10–15 %) with only 5 phr of phosphonium iodide ILs.<sup>99</sup> Moreover, Young's Modulus of epoxy/amine networks containing imidazolium ILs was reported to be strongly dependent on the confinement of ILs into epoxy networks. IL confinement decreases dramatically as soon as IL content goes over 40 wt%, which in turn results in an abrupt decrease of Young's Modulus.<sup>99</sup> Likewise, Hameed *et al.* have reported the design of epoxy networks with varied mechanical properties using the incorporation of imidazolium ionic liquids.<sup>102</sup> In fact, flexibility of epoxy networks can be tuned from brittle at low ILs content (10-20 wt%) to ductile materials (30-40 wt% of IL) and even to elastomers at high incorporation of ILs (50-60 wt%) (Figure 1-11).



**Figure 1-11** Tensile stress-strain curves of hard thermoset (black curve) showing perfectly brittle fracture at 10 % IL, plastic thermosets showing ductile behavior at 30 % of IL (red curve) and S-shaped curves of elastomeric thermosets at 50 % IL (green curve).<sup>102</sup>

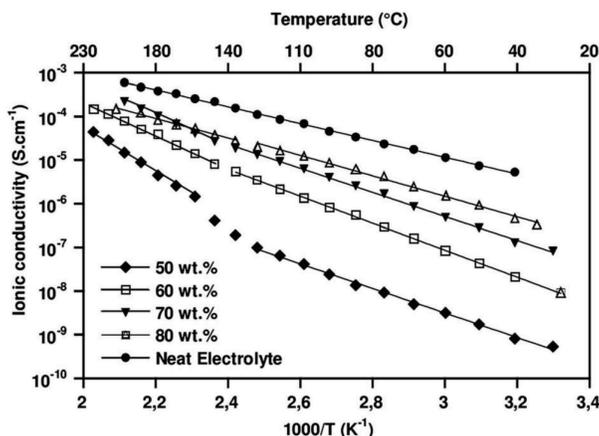
- Surface energy

By choosing a relevant functionalization of IL, the surface properties of epoxy networks can be tuned easily. Thus, the presence of hydrophobic phosphonium ILs in epoxy/Jeffamine D230 networks results in a decrease of their surface energy particularly the polar components.<sup>100</sup> Thus, the polar component of the DGEBA/Jeffamine D230 decreases from 13 mJ.m<sup>-2</sup> to less than 8 mJ.m<sup>-2</sup> when 2.5 wt% of phosphonium ILs are introduced into the epoxy networks. The impact of ILs on the surface properties highlights the migration of ILs at the surface of epoxy networks.

- Ionic conductivity

Furthermore, being well known as high conductive additives, in some cases, ILs are used as agents to increase the ionic conductivity of epoxy networks aiming to prepare polymer electrolytes.<sup>99,100,103-105</sup>

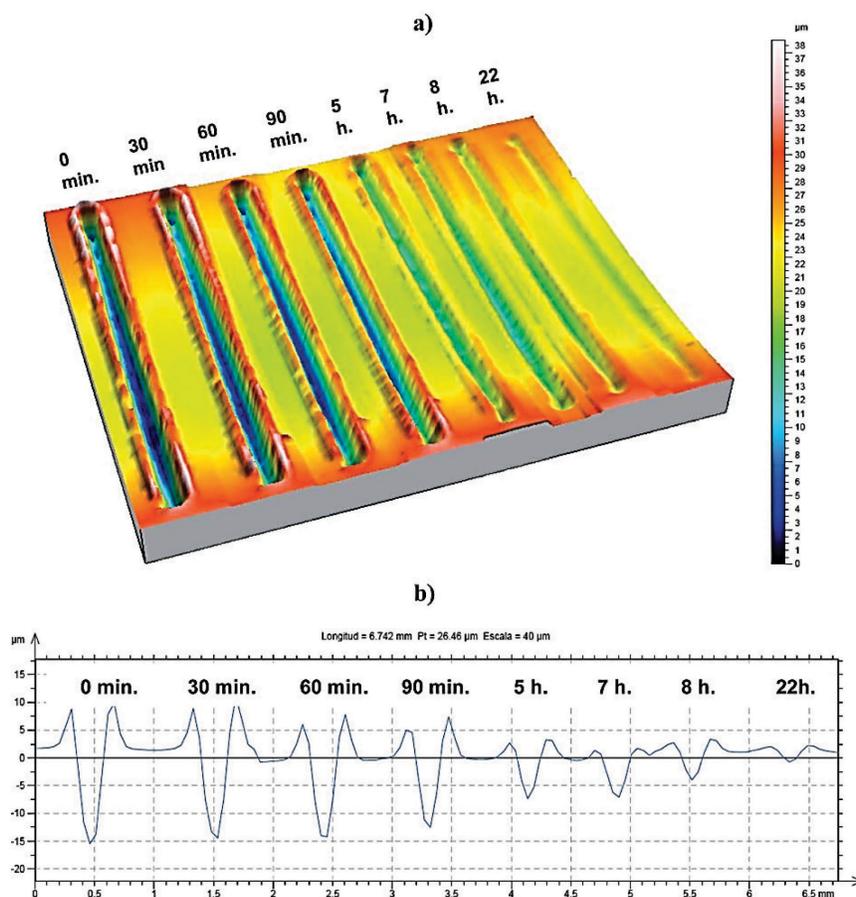
According to studies of our research group, ionic conductivity of epoxy networks was improved by the addition of ILs but these values are not high enough for polymer electrolytes.<sup>99</sup> This can be explained by the low amount of ILs and the stiffness of epoxy networks, which prevents the mobility of free ions. In fact, ionic conductivity of epoxy networks containing ILs increases when the measurement is conducted at high temperature *i.e.* higher than T<sub>g</sub> values. An ionic conductivity around 10<sup>-6</sup> S.m<sup>-1</sup> was obtained for DGEBA/Jeffamine networks containing 20 phr Phos-DCA ILs at 110 °C.<sup>100</sup> Thus, higher ILs confinement is still necessary to increase the ionic conductivity. Imidazolium ILs (up to 50 wt%) were confined into epoxy/amine networks in a study of Matsumoto *et al.* in 2008 which discovered the direct dependency of ionic conductivity to IL content. At low IL contents (< 40 wt%), IL confined materials were insulating whereas the ionic conductivity considerably increased with ILs content of above 40 wt%. Ionic conductivity of epoxy networks containing 50 wt% of ILs was 0.10-0.12 S.m<sup>-1</sup> (1/8 of bulk ILs) in the frequency range from 1 to 100 KHz.<sup>103</sup> Very recently, polymer electrolytes were prepared by Leclere *et al.* using phosphonium ILs dispersions in epoxy/amine networks for applications in Li<sup>+</sup> battery.<sup>104,105</sup> The incorporation of ILs in epoxy networks was up to 80 wt% depending on the chemical structure of IL anions. The highest compatibility of ILs in the epoxy/amine networks was achieved for phosphonium-phosphinate based IL (Phos-TMP). Thus, Gel Polymer Electrolyte (GPE) was prepared with high content of Phos-TMP of 80 wt% leading to an interesting conductivity of 1.4×10<sup>-4</sup> S.m<sup>-1</sup> at 60 °C (Figure 1-12).<sup>104,105</sup> However, the minimum temperature of utilization is 140 °C in order to ensure the mobility of lithium ions, which limits their applications.<sup>105</sup> Overall, ILs confined epoxy networks are promising materials for polymer electrolytes applications.



**Figure 1-12** Ionic conductivity of gel polymer electrolyte with different amounts of Phos-TMP with 0.2 M of lithium salt.<sup>105</sup>

- *Lubricating effect*

In addition, lubricating effect of ILs in epoxy networks is also reported by Sanes *et al.*<sup>106–109</sup> A friction reduction of 70 % was obtained for epoxy/steel contact when neat imidazolium ILs were used as external lubricants.<sup>106</sup> ILs are also used as internal lubricant for epoxy networks. The addition of small amount of ILs (0.5 to 3.3 wt%) led to significant decrease of friction coefficient and wear assistance particularly at the critical concentration of 2.7 wt% explained by the surface modification by the dispersion of ILs.<sup>106</sup> The effect of alkyl chain length of ILs was also investigated. Better miscibility of ILs with longer alkyl chains allowed to reduce the ILs amount to reach similar tribological performance (1.5 wt% compared to 2.7 wt%).<sup>107</sup> In the case of higher IL content (9 wt%), epoxy networks are self-healing. In details, the surface damage after sliding test against steel ball of epoxy networks was improved by the addition of 1.5 wt% ILs with obtained surface roughness of only from 0.06 to 0.26  $\mu\text{m}$  compared to severe surface damage in the case of neat epoxy networks.<sup>108</sup> The recovery process from abrasion test by effect of ILs (12 wt%) led to 90.9 % reduction in surface damage in respect to 22.1 % of unmodified epoxy samples after 22h at room temperature (Figure 1-13).<sup>109,110</sup> The effect of IL amount on the recovery process was also investigated and the authors have found an increase of self-repairing of the surface damage with the IL content.<sup>110</sup> Also, self-healing effect of IL depends on the porosity level of the modified epoxy networks. Indeed, despite the homogeneous dispersion of ILs in both cases, epoxy/amine network containing 9 wt% of IL has higher porosity than those with 12 wt% of ILs (Figure 1-14) explaining its higher self-healing percentage of 96.2 %.<sup>110</sup> In general, these results confirm the active participation of ILs in the self-healing behavior of the scratch abrasive grooves of epoxy/amine networks.



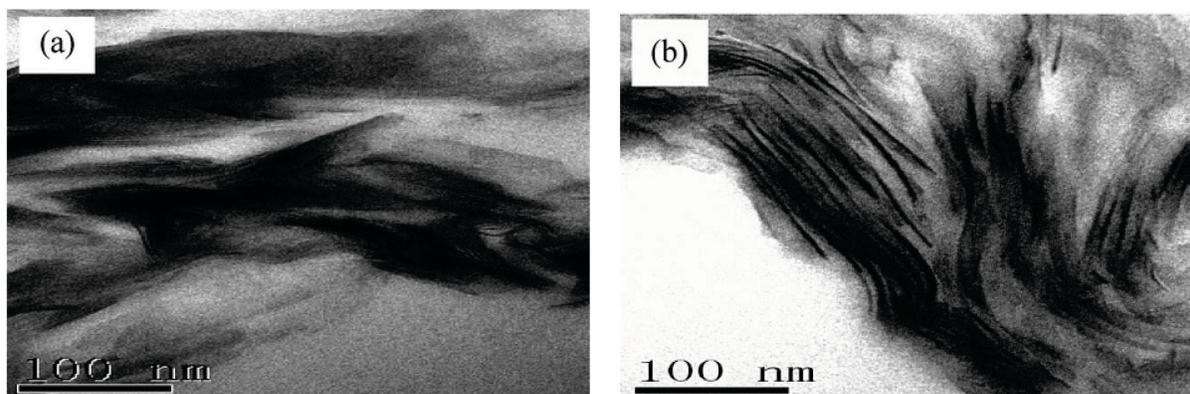
**Figure 1-13** Surface topography and cross section profiles of epoxy/amine networks containing 12 wt% of IL showing the evolution of wear track as a function of time.<sup>110</sup>



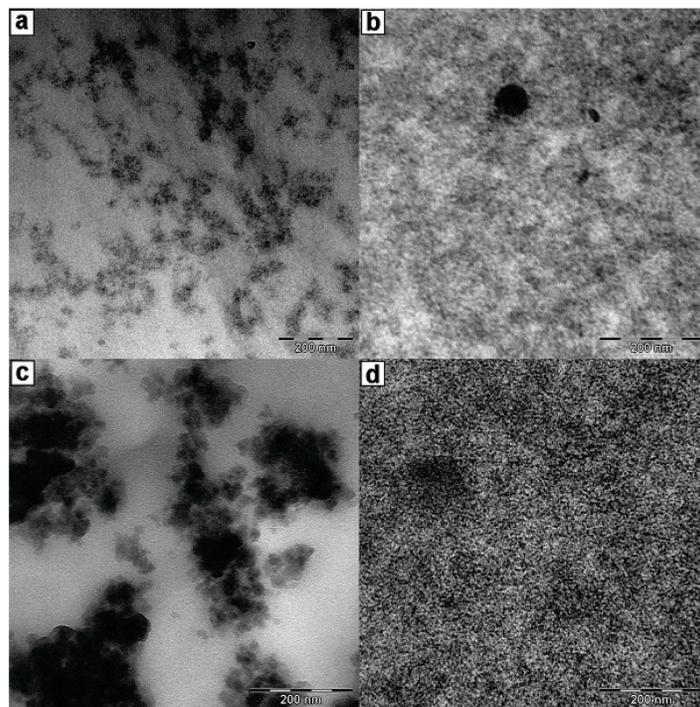
**Figure 1-14** Surface topography of cross section showing porosity of epoxy/amine networks containing a) 9 wt% and b) 12 wt%.<sup>110</sup>

- Dispersion aids for epoxy composites/nanocomposites

Finally, as efficient solvents, ILs were considered as dispersion agents in conventional epoxy composites/nanocomposites. Using the dissolution of cellulose in imidazolium based IL, Hameed *et al.* have prepared the partially miscible epoxy/cellulose blends in which IL acts as coupling agent by forming electron donor acceptor (EDA) complexes with two polymers.<sup>111</sup> Concerning the dispersion of fillers in the epoxy networks, Guo *et al.* have observed the separation of expanded graphite from stacked sheets to thinner sheets in DGEBA/Jeffamine D230 with the addition of 1-butyl-3-methyl-imidazolium hexafluorophosphate ILs.<sup>112</sup> Likewise, the rectorite treated with alkyl-imidazolium bromide ILs was well-dispersed into epoxy matrix with a resulting morphology going from intercalation to exfoliation depending on the curing agent types (Figure 1-15).<sup>113,114</sup> In addition, the influence of imidazolium based ILs chemical nature on the morphology of epoxy/amine silica nanocomposites has been revealed in the studies of Donato *et al.*<sup>115,116</sup> in which the silica dispersion changed from clusters of 200 nm without ILs to finer dispersion with divided particles of 10 nm using only 0.6 wt% of ILs (Figure 1-16).<sup>115</sup> Moreover, the addition of ILs improved the mechanical moduli of nanocomposites. The use of ILs cooperating with a coupling agent led to a remarkable compromise between toughness and stiffness of epoxy silica nanocomposites *i.e.* six times higher in modulus and 10 times higher for energy at break.<sup>116</sup> Very recently, Gholami *et al.* have discovered that the use of 15 wt% of choline chloride IL facilitated the dispersion of carbon nanotubes (CNTs) in the epoxy networks resulting in a remarkable increase of electrical conductivity of CNT-epoxy nanocomposite of 50 times higher than the nanocomposites without ILs.<sup>117</sup>



**Figure 1-15** IL-modified clay dispersion in epoxy nanocomposite cured with a) imidazoles (intercalation) and b) anhydride (exfoliation).<sup>113</sup>



**Figure 1-16** Epoxy-silica hybrids: (a) without ILs and those formed in the presence of (b) methyl sulfonate based IL, (c) tetrafluoroborate based IL and (d) tetrafluoroborate based IL and hydrochloric acid.<sup>115</sup>

#### 1.2.2.2.2. As reactive additives

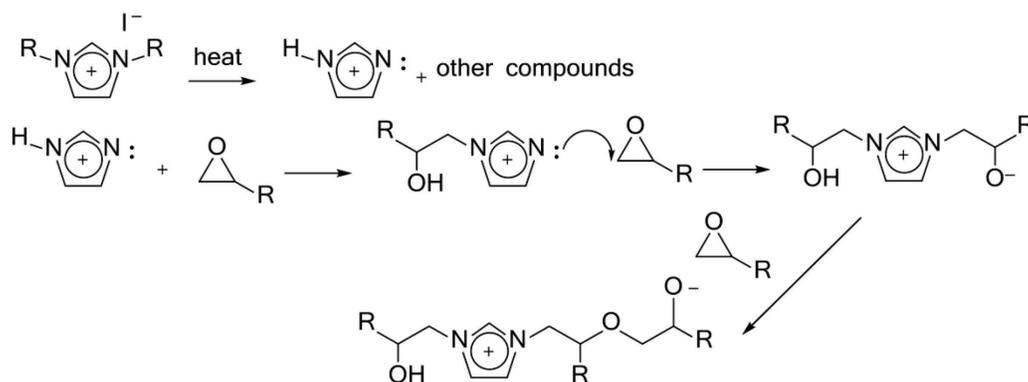
In recent years, ILs have been reported as reactive additives for epoxy prepolymer to replace conventional curing agents such as amines or anhydrides. In fact, the acceleration of curing reaction between epoxy prepolymer and amine networks by ILs<sup>97</sup> has proven their ability to form epoxy/IL networks with epoxy prepolymers.

- Imidazolium ionic liquids

In the literature, many papers presented the formation of epoxy networks cured by imidazolium ILs. The first study was conducted by Szychaj's group in 2003 concerning the use of 1-butyl 3-methyl imidazolium tetrafluoro borate as hardeners for epoxy prepolymer.<sup>118</sup> The capacity of this IL to induce ionic polymerization of epoxide groups has been discovered in using small ratio of ILs (0.5 to 5 phr). Also,  $T_g$  values of cured networks depend on the curing time and IL content. The highest  $T_g$  of 150 °C was reached by using 5 phr of IL with a curing time of 7h at 190 °C. Not until 2009, the second communication was published by Palmese's group on an imidazolium ILs coupled with dicyanamide anion as latent initiator of epoxy prepolymer.<sup>119</sup> The epoxy/IL mixtures remained stable at room temperature even after 60 days and the reaction was

initiated at high temperature leading to the formation of crosslinked networks with final epoxide group conversion of nearly 100 % and high thermal stability (413 °C). The curing behavior and properties of epoxy networks depends on the IL concentration and also IL cation/anion combinations. The reactivity of epoxy/IL systems was increased with increasing concentrations of ILs. On the other hand, a high IL content provides networks with lower  $T_g$  and lower crosslinking density due to the plasticizing effect.<sup>119</sup>

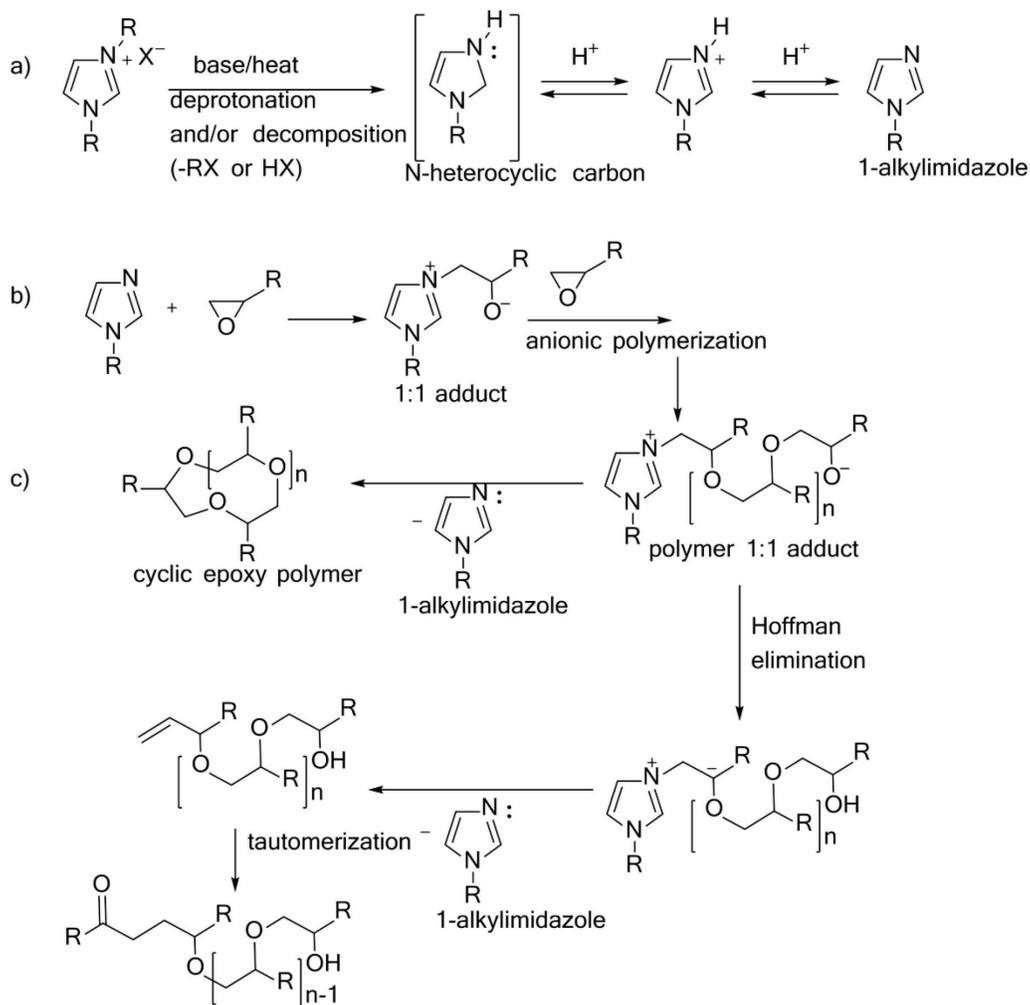
Afterwards, our research group characterized the binary blends of epoxy prepolymer and imidazolium ILs.<sup>97</sup> They have discovered the ability of ILs to promote the reaction with epoxy prepolymer using Differential Scanning Calorimetry (DSC) measurements. All the epoxy/IL blends displayed an exothermic peak on DSC curves corresponding to the curing reaction. From imidazolium based ILs coupled with inert iodide anion, a curing mechanism was proposed by attributing the formation of imidazole through the decomposition of imidazolium cations (Scheme 1-6). FTIR analyses confirmed the reaction between ILs and epoxide groups with the epoxide groups conversion of over 99 % after the curing process. In addition, the increase of double peak at 2350–2360  $\text{cm}^{-1}$  corresponding to  $\text{N}^+\text{H}$  ion supported the proposed mechanism.<sup>97</sup>



**Scheme 1-6** Proposed mechanism for curing reaction between imidazolium ILs and epoxy prepolymer.<sup>97</sup>

Later, this mechanism was verified and more clearly developed by Spychaj's group in investigating a series of ILs differing in cation/anion combinations.<sup>120–122</sup> They have found that various imidazolium based ILs are able to react with epoxy prepolymers including those combined with chloride,<sup>120,121</sup> dicyanamide,<sup>121</sup> tetrafluoro borate,<sup>121</sup> and thiocyanate.<sup>122</sup> The proposed mechanism for epoxy networks formation by 1,3-alkyl imidazolium ILs presented in Scheme 1-7 consists of 3 main steps: *i*) the decomposition of IL into 1-alkyl imidazoles; *ii*) the formation of imidazole epoxy adduct and the polymerization of epoxy polymer and *iii*) the regeneration of alkyl imidazoles and the structurization of final epoxy networks.<sup>121</sup> The curing behavior of epoxy/IL

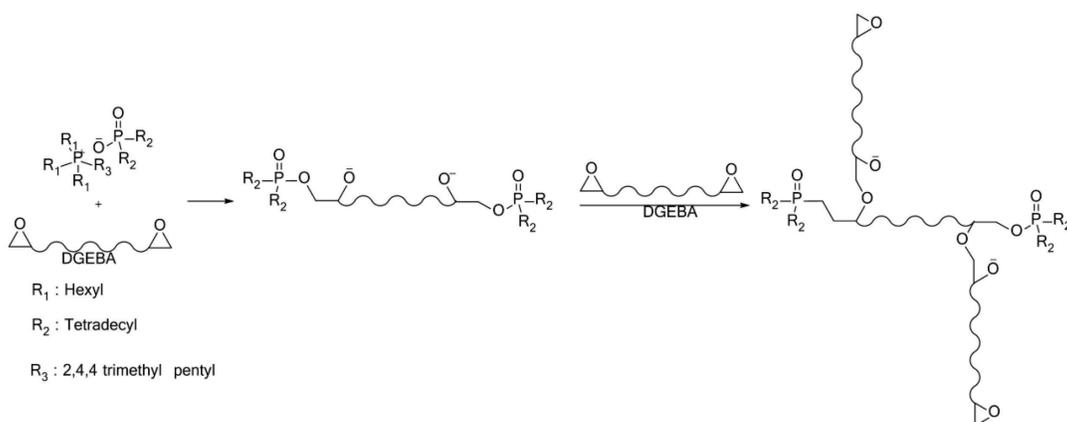
blends, *i.e.* the reactivity and properties of cured networks depend strongly on the nature and the concentration of ILs. Thus, dicyanamide based ILs are more reactive than those bearing with  $\text{BF}_4^-$ . The length of alkyl chain connecting to imidazolium center has a slight influence on the curing process. Also, curing mechanism through imidazolium cation decomposition differs by the basicity of IL counter anions. In fact, imidazolium ILs are unstable under basic condition, which explains the higher reactivity of ILs containing more basic counter anions such as dicyanamide compared to those based on  $\text{BF}_4^-$ . Concerning the properties of cured epoxy/IL networks, there is a critical value for IL content in order to provide the highest  $T_g$  for epoxy networks. Above this value, a plasticizing effect of ILs decreases the glass transition temperature of epoxy systems.



**Scheme 1-7** Curing mechanism for epoxy networks formation by 1-alkyl imidazolium ILs proposed by Szychaj *et al.*<sup>121</sup> including (a) the decomposition of IL into 1-alkyl imidazoles; (b) the formation of imidazole epoxy adduct and the polymerization of epoxy polymer and (c) the regeneration of alkyl imidazoles and the structuring of final epoxy networks).

- Phosphonium based ILs

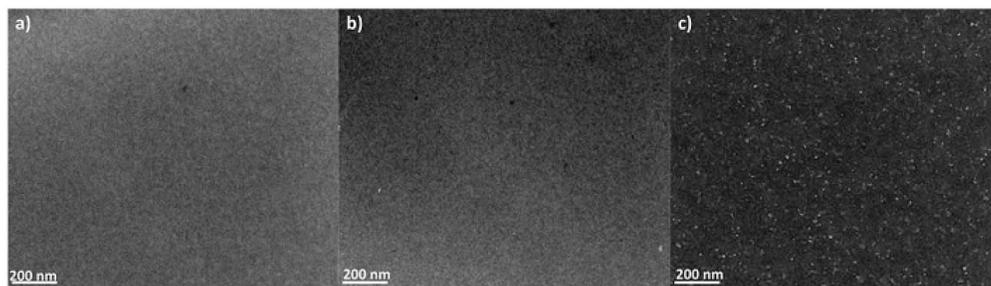
Phosphonium based ILs, thanks to their high thermal stability, have recently gained the attention as curing agents for epoxy prepolymers. The use of a commercial phosphonium-phosphinate IL to replace conventional amine in epoxy networks was reported by our group. The use of phosphonium ILs at different concentration (5 to 20 phr) allowed the formation of epoxy network with an epoxide group conversion of over 90 % without external conventional curing agent.<sup>87</sup> The curing reaction of epoxy/IL blends was able to occur at lower temperature, *i.e.* curing protocol of 2 hours at 80 °C and 3 hours at 125 °C, than the systems using imidazolium based ILs (> 150 °C). Moreover, unlike imidazolium based ILs, phosphonium based ILs are not latent hardeners for epoxy prepolymer as the gelation of epoxy/IL blends containing 10 phr of IL appeared only after 4 days at room temperature. Thus, another mechanism was proposed for phosphonium ILs in which the counter anion is the reactive agent to open epoxy ring (Scheme 1-8).



**Scheme 1-8** Mechanism for the homopolymerization of epoxy prepolymer initiated by the phosphonium phosphinate ionic liquid proposed by our group.<sup>87</sup>

In terms of thermomechanical properties, epoxy/Phosphonium based IL networks have high  $T_g$  (140–150 °C) and high crosslinking density expressed by high storage modulus at rubbery state. The thermal stability of epoxy networks was enhanced by the presence of phosphonium ILs which induces a degradation temperature of around 450 °C, much higher than epoxy networks cured by an aliphatic amine (387 °C).<sup>87</sup> The incorporation of phosphonium-phosphinate IL in the epoxy networks also resulted in improvements of limiting oxygen index *i.e.* 22.7 % compared to 20 % of epoxy/amine networks.<sup>123</sup> Very recently, a communication of our group has also revealed the ability to form epoxy networks with a new phosphonium based ILs coupled with dicyanamide anion<sup>124</sup>. The fully cured epoxy/Phosphonium based IL networks have excellent thermomechanical

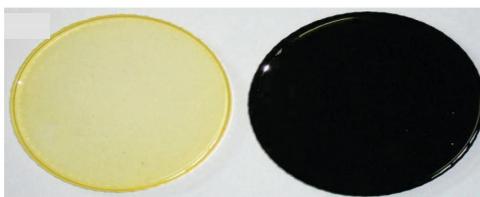
properties as well as high thermal stability of over 400 °C. A critical concentration of ILs (10 phr) was discovered for which the properties of ILs networks are optimized. In fact, over this concentration, the excess ILs plasticized the epoxy networks leading to the decrease of crosslinking density. For the first time, the dispersion of ILs domains into epoxy networks was observed by transmission electronic microscopy (TEM) in the form of ILs inclusions with sizes included between 20–30 nm (Figure 1-17).<sup>124</sup>



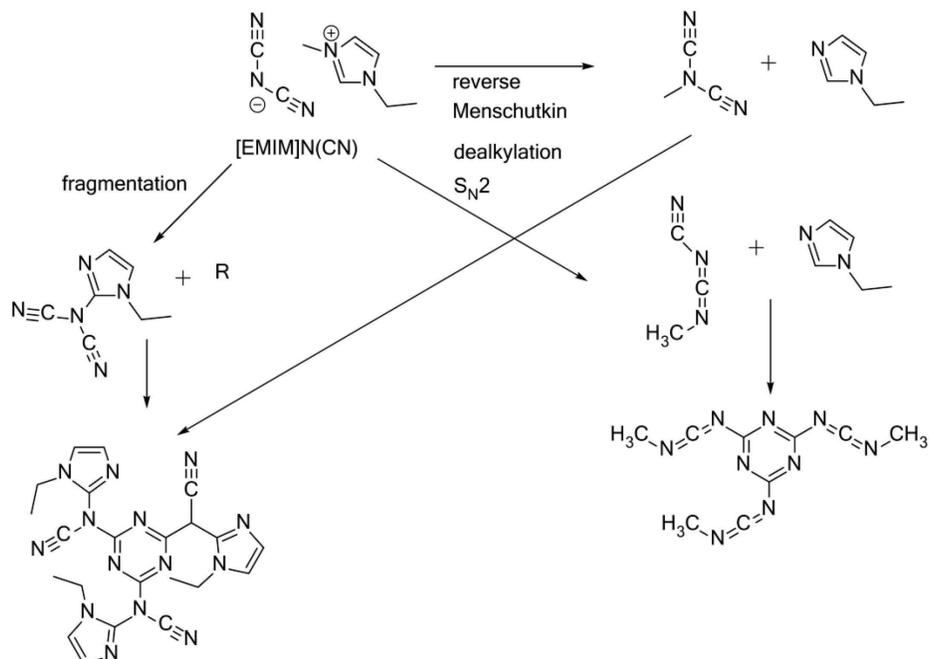
**Figure 1-17** TEM micrographs of the epoxy networks cured with (a) 5 phr, (b) 10 phr and (c) 30 phr of phosphonium dicyanamide ILs.<sup>124</sup>

- Comparison between imidazolium and phosphonium ILs

Very recently, a comparative study between imidazolium and phosphonium based ILs containing the same dicyanamide anion was carried out by Maka *et al.*<sup>88</sup> Different behaviors as a function of cation types were discovered including the pot life and the transparency of cured sample. Figure 1-18 presents samples cured by phosphonium ILs (left) with high transparency of over 85 % in contrast to a black opaque material obtained from imidazolium cured epoxy networks. However, better thermomechanical properties and thermal stability were obtained for epoxy materials cured with imidazolium dicyanamide, which was possible to explain by the formation of isocyanurate rings from 1-ethyl-3-methylimidazolium dicyanamide decomposition products (Scheme 1-9).<sup>88</sup> Overall, neglecting the nature of ILs, all epoxy/IL networks have high  $T_g$  of over 190 °C and excellent thermal stability *i.e.* degradation temperature at 5 wt% loss of 386 to 395 °C.<sup>88</sup>



**Figure 1-18** Samples of epoxy networks cured with dicyanamide anion ILs containing phosphonium (left) and imidazolium (right) cation.<sup>88</sup>



**Scheme 1-9** Possible thermal decomposition of 1-ethyl-3-methylimidazolium dicyanamide ionic liquid with the formation of isocyanurate rings.<sup>88</sup>

- Epoxy/IL composites/nanocomposites

Furthermore, epoxy/IL networks have also attracted interest as matrices for composites and nanocomposites. ILs allowed a viable process to produce epoxy nanocomposites with single-phase dispersion and curing.<sup>125</sup> Throckmorton *et al.* reported a good dispersion of epoxy/imidazolium IL/silica nanocomposites with simultaneous increase of mechanical properties. For single wall carbon nanotubes (SWNT) and graphite nanoplatelets (GNP), the use of ILs led to low percolation threshold at low fillers loading of  $8.6 \times 10^{-5}$  and  $1.7 \times 10^{-2}$  volume fraction for SWNT and GNP, respectively which approaches the theory model suggesting uniform dispersion<sup>125</sup>. In the recent studies of Maka *et al.*, both imidazolium and phosphonium based ILs coupled with different anions were used as dispersion agents for carbon nanofillers and the curing agents of epoxy prepolymers in order to prepare high performance nanocomposites. An improvement in electrical volume resistivity and flame retardancy was found for these nanocomposites at low loading of both fillers and ILs.<sup>88,122</sup>

Overall, ILs are excellent alternatives for conventional curing agents in epoxy networks. Epoxy/IL based systems with tunable properties enable the design for various engineering purposes.

### 1.2.3. Conclusion

In this part, the literature about epoxy networks including the formation, reaction mechanism and properties was summarized. The role of ionic liquids in the epoxy networks has been emphasized through the synthesis of ILs containing epoxide group, the use of ILs as modifiers for the conventional epoxy networks and the formation of epoxy/IL networks. Obviously, ILs were proven to be attractive for epoxy thermosetting materials. In addition, ILs can be served as both curing agents and dispersion aids for nanocomposites.

## 1.3. Modification of epoxy networks

### 1.3.1. Introduction

Despite the excellent thermal and mechanical properties, the brittleness of epoxy networks limits their range of applications particularly in the aerospace applications. Modifications must be considered to improve their fracture toughness using several external modifiers including rubbers,<sup>126</sup> inorganic fillers,<sup>127</sup> and thermoplastics.<sup>128</sup> In fact, modified epoxy networks can be classified in two main groups concerning the miscibility of modifiers towards epoxy prepolymer: *i*) the use of polymers that are initially miscible within epoxy prepolymer and the phase separation occurs during the curing process. This method is denoted as reaction induced phase separation (RIPS) and involves mostly thermoplastics as modifiers; *ii*) the use of non-miscible preformed rubbery particles.

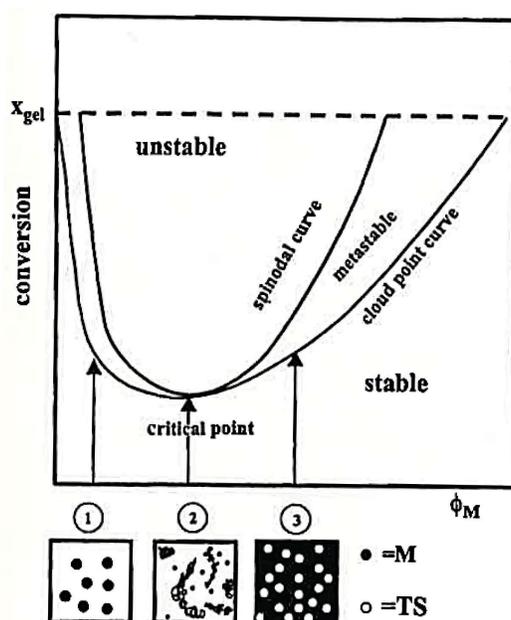
### 1.3.2. Modification of epoxy networks by thermoplastics

#### 1.3.2.1. Reaction-induced phase separation (RIPS)

Reaction induced phase separation (RIPS) occurs due to the increase of molar mass in the pre-gel step and of the crosslink density in the post-gel step of thermosetting polymers. RIPS induces different morphologies of thermosetting/thermoplastic (TS/TP) mixtures aiming to increase fracture toughness, to generate optical response and to produce porous material.<sup>72</sup>

Various factors can influence the morphology of TS/TP blends. Firstly, phase separation of TS/TP blends depends on the curing mechanism of TS networks. For stepwise polymerization *i.e.* epoxy/amine networks, diagram of temperature–transformation of TS/TP mixture is normally under form of upper critical temperature solution (UCTS) or lower critical temperature solution (LCTS) depending on the miscibility of TP in the TS matrix.<sup>129</sup> In addition, conversion–

composition diagram can be used to describe the morphology of TS/TP blends at a constant temperature. The conversion–composition diagram in Figure 1-19 illustrates the dependence of morphology of TS/TP blends on the location of trajectory *i.e.* TP nodules morphology for trajectory 1, co-continuous for trajectory 2 and inversed nodules morphology for trajectory 3.<sup>129</sup> On the other hand, miscibility of TS/TP blends formed by chainwise polymerization can be described by a triangular diagram in Figure 1-20.<sup>129</sup> Moreover, other factors can influence the morphology of TS/TP blends including the initial miscibility of blends, the polymerization rate, the adhesion of TS and TP and the existence of emulsifiers.<sup>129</sup> Then the properties of TS/TP blends particularly the toughening effect depend on the final morphology which is consequently turned to the size and particle distribution, the inter-particle distance, the volume fraction of dispersed phase, the nature and composition of dispersed phase and matrix and the interphase adhesion.<sup>130</sup>

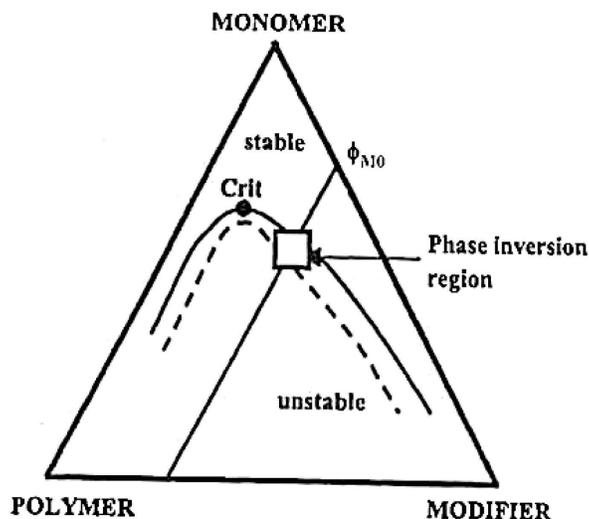


**Figure 1-19** Conversion *vs* composition transformation diagram type LCTS for a TS/TP blends in case of stepwise polymerization (M: TP phase).<sup>129</sup>

Generally, the advantages of RIPS method consist of the stability and low viscosity of initial mixtures and the morphological variation of final products. However, the correlation between curing cycles, morphology and phase composition requires to be established to control the properties of modified networks. In addition, the properties of final products can also be influenced by the interpenetration of materials between two phases.<sup>129</sup>

The most widely used thermoplastics as modifiers through RIPS methods are poly(sulfone) (PSF)<sup>131</sup>, poly(ether sulfone) (PES),<sup>132</sup> Poly(ether imide) (PEI),<sup>131</sup> Poly(ether ether ketone)

(PEEK),<sup>133</sup> poly(methyl methacrylate) (PMMA),<sup>130,134</sup> and poly(phenylene ether) (PPE).<sup>135</sup> Among them, PPE will be used as modifiers for epoxy networks in our work presented in Chapter 3. Thus, the next part is dedicated to discuss the literature about the PPE-modified epoxy networks.



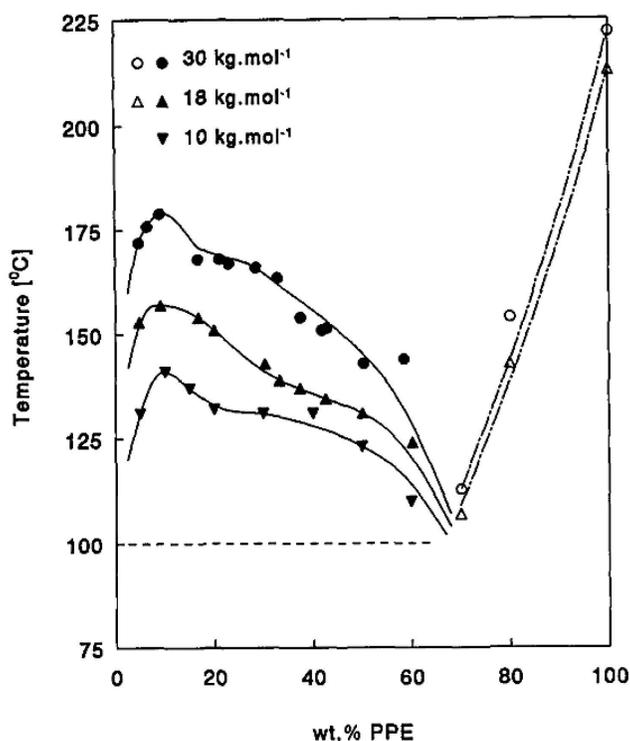
**Figure 1-20** Ternary phase diagram of TS/TP blends formed by chainwise polymerization (Crit. = critical point).<sup>129</sup>

### 1.3.2.2. PPE-modified epoxy networks

Among several thermoplastics, 2,6-dimethyl-1,4-phenylene ether (PPE) has been widely used to toughen epoxy networks thanks to their excellent physical, chemical and electrical properties.<sup>136</sup> In fact, several researches have been conducted since the 1990s on PPE-modified epoxy networks concerning the miscibility between PPE and epoxy prepolymer, the curing behavior of PPE-modified epoxy blends, the morphology and the properties of cured PPE-modified epoxy networks.

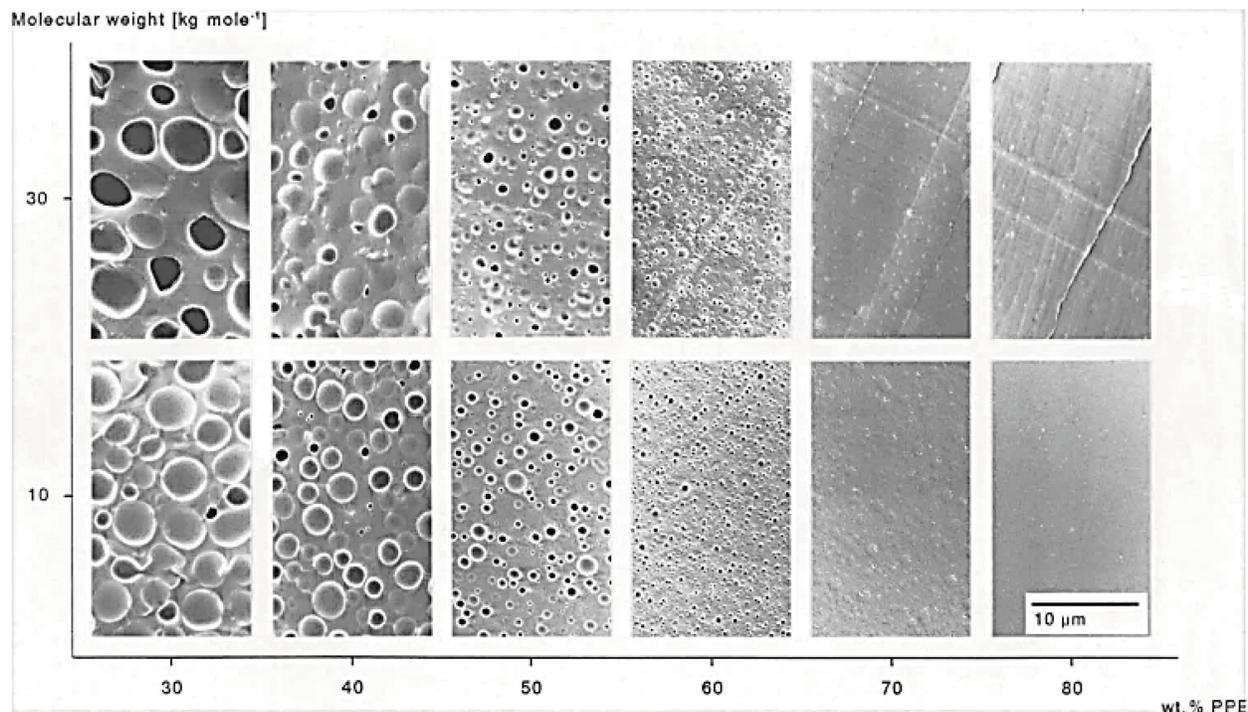
#### 1.3.2.2.1. Miscibility of PPE and epoxy prepolymer blends

The miscibility of epoxy/PPE binary blends without curing agents was followed by light transmission device which detects the cloud points (phase separation) of blends as a function of temperature or time.<sup>135,137-140</sup> An upper critical solution temperature (UCST) behavior was observed for cloud point curve of epoxy/PPE blends. Moreover, the molar mass of PPE was discovered to strongly affect the miscibility of binary blends. The decrease of PPE molar mass favors the miscibility and shifts the cloud point curve to lower temperature (Figure 1-21).<sup>135,137,138</sup> On the other hand, the functionality of PPE *i.e.* methyl capping and acid modification is unfavorable for the mixing of PPE and epoxy prepolymer resulting in a decrease of miscibility.<sup>137</sup>



**Figure 1-21** Phase diagram of epoxy/PPE blends including (—) cloud point curve, (---) calculated  $T_g$  lines and (—)  $T_g$  due to thermoreversible gelation.<sup>138</sup>

Also, the glass transition temperature of epoxy/PPE blends could be calculated from Fox equation and measured by dynamic mechanical analysis at high content of PPE. Then, Figure 1-21 presents the vitrification curves of the blends which intersect with cloud point curves at PPE content of around 70 wt% (Berghmans point).<sup>138,139,141</sup> Above this content, the vitrification of PPE will occur upon cooling before the phase separation indicating the homogeneity of epoxy/PPE blends over the entire range of temperature.<sup>138,139,141</sup> On the other hand, phase separation occurs in the case of lower PPE content. However, the completion of phase separation is restricted by the vitrification of PPE leading to the same  $T_g$  for all epoxy/PPE blends neglecting the PPE concentration, which is referred to reversible gelation (Figure 1-21).<sup>138</sup> In addition, the morphology of cooled epoxy/PPE blends containing variable PPE content was observed by scanning electron microscopy in Figure 1-22, which is in accordance with the phase diagram. No phase separation was discovered for epoxy blends containing over 70 wt% of PPE. Moreover, phase inversion occurred from 30 wt% of PPE with epoxy droplets dispersed in the PPE-rich phase.<sup>138</sup>



**Figure 1-22** Morphology of epoxy/PPE blends with PPE molar mass of 10 and 30 kg.mol<sup>-1</sup> and PPE content of 30-80 wt% after cooling from 200°C to room temperature observed by scanning electron microscopy.<sup>138</sup>

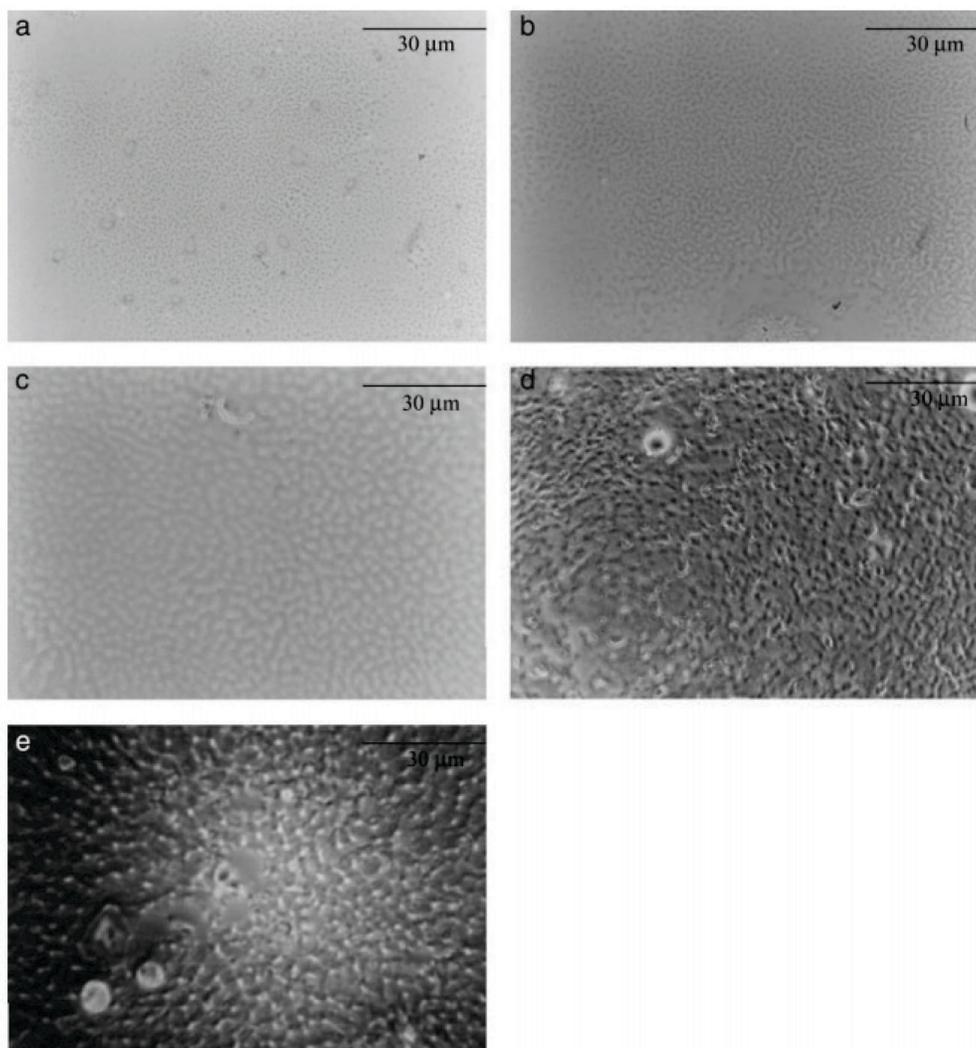
#### 1.3.2.2.2. Curing behavior of PPE-modified epoxy blends

The curing behavior of uncured PPE-modified epoxy blends combined with curing agents was studied in terms of reaction kinetics<sup>142-145</sup>, gelation time, gelation mechanism<sup>137,143,146</sup> and phase-induced mechanism<sup>137,139,145-147</sup> during the curing reaction.

The reaction kinetics of PPE-modified epoxy networks were investigated by Differential Scanning Calorimetry (DSC) and Fourier transform infrared (FTIR). The presence of PPE was found to reduce the reaction rate of epoxy/amine networks due to the dilution effect on functional group concentration and the increase of blends viscosity.<sup>143,144</sup> Otherwise, an increase of reaction rate was reported by Wu *et al.* in case of epoxy networks cured by cyanate esters in which PPE acted as catalyst of the curing reaction due to their phenolic end groups.<sup>142,145</sup> Also, the conversion of PPE modified epoxy blends was followed by DSC and FTIR under isothermal conditions at different temperatures. The final conversion of epoxy blends decreased with the amount of PPE due to the increase of bulk viscosity of mixture caused by the presence of PPE.

The influence of PPE on the gel time and gelation mechanism of epoxy blends was approached by gel time meter<sup>137</sup> and chemorheology.<sup>143</sup> Merfeld *et al.* discovered that the presence of PPE

resulted in no change of the gel time while an acid grafted PPE enhanced the reaction rate leading to a considerable decrease of blends gel time.<sup>137</sup> Moreover, Ishii *et al.* discovered that the presence of PPE in the epoxy blends lowered the conversion of the curing reaction at gelation.<sup>143</sup> They also proposed that the gelation of PPE-modified epoxy blends occurred by vitrification of PPE phase.



**Figure 1-23** Optical micrographs of PPE-modified epoxy blends (30phr) cured for different times at 180 °C showing the spinodal decomposition.<sup>145</sup>

Reaction induced phase separation was investigated by a whole of analysis such as dynamic mechanical and dielectrical measurements,<sup>144,146</sup> optical microscopy<sup>145</sup> and laser light scattering.<sup>143</sup> The effectiveness of mechanical and dielectrical measurements as a method to follow the reaction advancement of PPE-modified epoxy networks was reported in a study of Poncet *et al.*<sup>146</sup> in which the phase separation was observed to occur rapidly followed by the vitrification of PPE phase and finally the vitrification of epoxy phase. The same observations were made by Rusli *et al.*<sup>144</sup> in

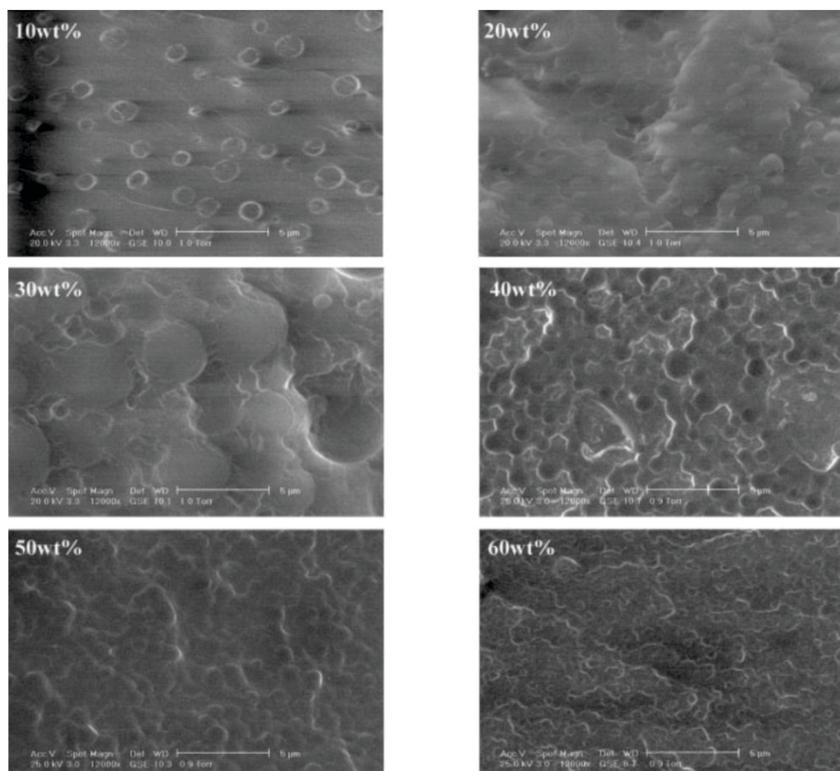
studying the dynamic rheology during cure of PPE-modified epoxy blends. Then by using optical microscopy to follow the phase separation during the curing process of PPE-modified epoxy networks, Wu *et al.* have discovered different phase separation mechanisms depending on the amount of PPE.<sup>145</sup> In details, at low PPE content, PPE particles were formed through nucleation and growth mechanism. Then, when PPE content approaches the critical point, spinodal decomposition was favored to form epoxy droplets dispersed in the continuous PPE phase (Figure 1-23).<sup>145</sup> Similarly, phase separation through spinodal decomposition was also observed by Ishii *et al.*<sup>143</sup> using a small-angle light scattering camera on epoxy blends containing 30 wt% of PPE. Phase separation occurs quickly with the curing reaction and was separated into 4 stages including reaction prior to phase separation, early stage of spinodal decomposition, late stage of spinodal decomposition and the apparent phase dissolution.<sup>143</sup> From these measurements, the Flory-Huggins parameter was also calculated and was used to construct a phase diagram for epoxy/PPE blend during reaction induced phase separation as a function of temperature and conversion. Thus, the conversion of epoxy/PPE blends at vitrification can also be predicted.<sup>148</sup>

#### 1.3.2.2.3. Morphology and properties of PPE-modified epoxy networks

Despite the different curing agents used, the morphology of cured epoxy/PPE networks obtained from reaction induced phase separation was determined by the PPE amount.<sup>135,142,144,149</sup> The morphology of PPE-modified epoxy networks varies from PPE particulate<sup>137,150,151</sup> at low PPE amount to a PPE co-continuous phase<sup>150</sup> and then phase-inversion (dispersion of epoxy phase in the PPE matrix)<sup>138,152</sup> at high amount of PPE. Scanning electron microscopy micrographs of modified epoxy networks cured by imidazole show the evolution of morphology for different PPE content from 10 wt% to 60 wt% (Figure 1-24). As expected, PPE dispersed phase increases the particles size with the PPE amount and tends to form bi-continuous morphology around the critical amount. Then from 30 wt% of PPE, epoxy particles dispersion in the PPE matrix was induced by the phase inversion. Moreover, the influence of molar mass and functionality of PPE as well as the curing temperature on the morphology of PPE-modified epoxy networks were studied by Merfeld *et al.*<sup>137</sup> The authors showed that the acid grafting onto PPE and the decrease of PPE molar mass are favorable for a better dispersion of PPE in the epoxy networks due to the increase of compatibility between epoxy matrix and thermoplastics.

On the other hand, increasing curing temperature was found to raise the molecular mobility resulting in an increase of dispersed phase size. Moreover, in order to improve the morphology of PPE-modified networks, many compatibilizers have been investigated including a block copolymer

styrene-maleic anhydride<sup>151</sup> and a triallylisocyanurate<sup>149</sup>, which eliminated the occluded PPE particles in the epoxy matrix.



**Figure 1-24** SEM micrographs of PPE modified epoxy networks cured by imidazole with different PPE content (10-60 wt%).<sup>135</sup>

The influence of PPE incorporation on the properties of modified epoxy networks were widely investigated from thermomechanical properties, thermal properties to mechanical properties. Glass transition temperature of PPE-modified epoxy networks was reported in a work of Pearson *et al.*, which showed the stability of  $T_g$  of epoxy networks with the addition of PPE and compatibilizers.<sup>151</sup> Dynamic mechanical analysis were also used to study the evolution of relaxation temperature ( $T_\alpha$ ) with the incorporation of PPE in the epoxy networks. Due to the phase separation during curing reaction (morphology), DMA curves of PPE-modified epoxy networks display two relaxation peaks corresponding to epoxy-rich phase and PPE-rich phase. Moreover, the glass transition temperature of each phase (epoxy or PPE) differed slightly from neat ones due to interpenetrating phenomenon between two phases<sup>138,142,144,149,152</sup>. In details,  $T_g$  of PPE-rich phase was found to be lower than that of pure PPE due to the existence of non-reacted epoxy monomers or of epoxy networks blended with PPE. Vice versa, the glass transition of epoxy-rich phase was also affected by the incorporation of PPE in the epoxy networks. However, the variation of  $T_g$  of epoxy phase depends

on the used curing agent *i.e.* a decrease in case of epoxy/amine networks<sup>138,144,152</sup> and an increase of  $T_g$  in the case of epoxy networks cured by dicyanamide.<sup>142,149</sup> The use of thermally stable PPE in the epoxy networks also shifted the degradation peak to higher temperature.<sup>149</sup> Likewise, studies on the mechanical properties such as tensile behaviors and fracture toughness of modified epoxy networks revealed the toughening effect of PPE while remaining the tensile modulus and strength of epoxy networks.<sup>138,142,149,150,152</sup> In fact, the addition of PPE increased linearly the fracture toughness of DGEBA/Piperidine networks from 1.1 to 1.8 MPa.m<sup>1/2</sup> respectively for unmodified and 20 phr PPE-modified epoxy networks without changing their Young's modulus (around 3 GPa) and tensile yield strength (80 MPa).<sup>150</sup> Toughening mechanism of PPE-modified epoxy networks was described as microcracking mechanism through fractography. Thus, the addition of styrene-butadiene-styrene triblock copolymers in the PPE-modified epoxy networks improved their fracture toughness thanks to the increase of microcracks density.<sup>150</sup>

### 1.3.3. Modification of epoxy networks by core-shell particles

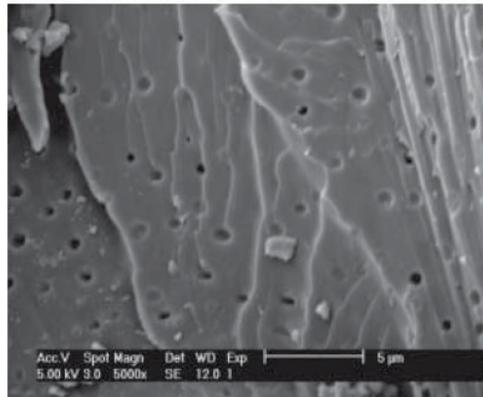
In fact, the use of thermoplastics and rubbers as modifiers of epoxy networks encounters many problems concerning the processability and the properties of modified epoxy networks. In fact, reaction induced phase separation (RIPS) leads to the difficulties of controlling the morphology and size of dispersed rubbers or thermoplastics particles which depends on the modifier content, the chemical nature of modifiers, curing agents and the curing conditions.<sup>129</sup> On the other hand, the use of rubbers as modifiers can result in a decrease of the glass transition temperature and mechanical strength due to the residual dissolved rubbers within the epoxy matrix.<sup>153,154</sup> Thus, the modification of epoxy networks with preformed particles, particularly core-shell rubber (CSR) particles has been recently gained the interest as a new strategy to overcome these drawbacks.

#### 1.3.3.1. Toughening mechanism of CSR-modified epoxy networks

Toughening mechanism of CSR-modified epoxy networks was investigated by various microscopic techniques which revealed two major mechanisms: the cavitation of CSR particles and localized shear-banding of epoxy matrix initiated by the particles.<sup>155-159</sup>

The cavitation of CSR particles is commonly observed for rubber toughened polymers causing the increase of their volume with high strain rate. In fact, during cavitation process, the original solid particles deform into a rubbery shell surrounding a void (cavities) on the fracture surface. Normally, cavitation of rubber particles is initiated by the formation of stress field ahead of the crack tip.<sup>159-161</sup> However, cavitation mechanism was found to have a slight toughening effect but rather initiation effect for shear-band yielding mechanism.<sup>162</sup> Indeed, shear-band yielding was

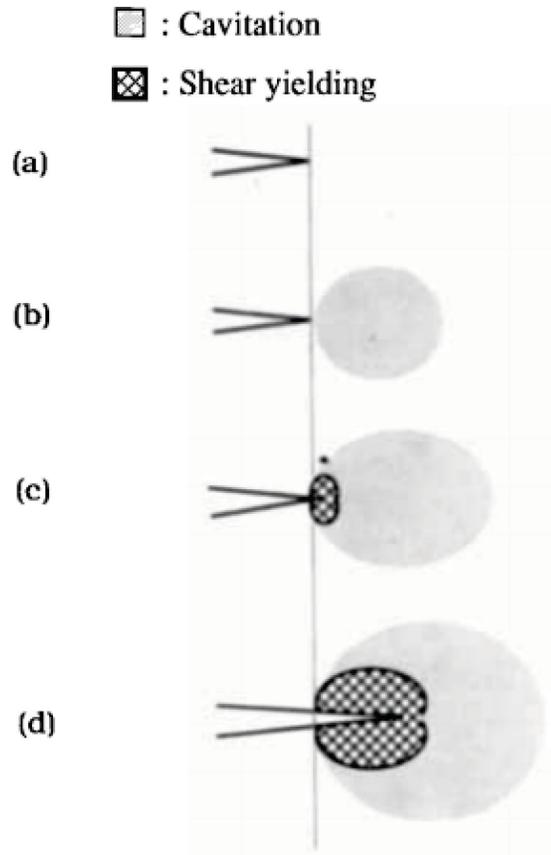
reported as a major toughening mechanism in the rubber-modified epoxy networks. Strain inhomogeneity near the crack tips due to the high stress concentrations often leads to the formation of shear band.<sup>160</sup> Additionally, this formation is enhanced by the existence of second particulate phase, *i.e.* CSR particles. Rubbery particles undergoing the cavitation can produce a higher stress concentration at their equators, which make them capable of initiating the shear yielding of the matrix. Moreover, the yielding is kept localized around virtually every particles leading to the formation of furrows running almost parallel to the principal tensile (Figure 1-25).<sup>161</sup> Also, shear-band yielding mechanism was highlighted by the elongation of rubber particles observed around the crack tip.<sup>162</sup> Thus, the toughening mechanism of CSR-modified epoxy networks can be summarized in Figure 1-26 including four main steps: *i)* the initial starter crack; *ii)* formation of cavitation zone; *iii)* formation of initial shear-yielded plastic zone; and *iv)* propagation of crack under shear yielding.



**Figure 1-25** Shear yielding mechanism of rubber-modified epoxy networks indicated by the formation of furrows running almost parallel to the principal tensile.<sup>161</sup>

The toughening mechanism of CSR particles in the epoxy networks can be influenced by the particle sizes, the crosslinking density of epoxy matrix as well as the adhesion between particles and matrix. Pearson *et al.* have demonstrated that smaller particles are favorable to follow cavitation-induced shear yielding mechanism.<sup>163</sup> In the opposite, larger particles can induce particles deflection mechanism.<sup>161,164</sup> Sue *et al.* have discovered that in some cases, the synergistic toughening effect between particle cavitation-matrix shear-yielding and crack deflection mechanism can occur. Thus, the random dispersion of CSR particles with local clusters is more desirable to upgrade the fracture toughness.<sup>164</sup> Moreover, crosslinking density of epoxy matrix plays an important role on the toughening mechanism of CSR particles in the epoxy networks. Particle-matrix debonding was suspected to be the most significant mechanisms in the highly crosslinked system instead of cavitation and shear yielding mechanism.<sup>165</sup> Similarly, the bonding between CSR-

particles and epoxy matrix has been found to have the same effect on the toughening mechanism. In case of weak CSR particles to matrix adhesion, debonding mechanism will mainly occur rather than cavitation, which decreases the toughening effect.<sup>159,161</sup>



**Figure 1-26** Toughening mechanism of CSR-modified epoxy networks summarized by four steps: a) initial starter crack; b) formation of cavitation zone; c) formation of initial shear-yielded plastic zone and d) propagation of crack under shear yielding.<sup>162</sup>

### 1.3.3.2. Different rubber core-shell particles used to modified epoxy networks

For a long time, core-shell rubber particles (CSR) with a soft rubber core and hard shell appeared as a new route to modify epoxy networks. The use of CSR particles allows to control the size and composition of dispersed phase while keeping the properties of epoxy matrix. In fact, the presence of small amount of CSR increases significantly the fracture toughness without affecting the glass transition temperature of epoxy networks. The idea of using preformed core-shell particles has been reported since 1990s with several kinds of CSR which have been employed in the epoxy matrix.<sup>166</sup> Normally, the material used for the shell is poly (methyl methacrylate) (PMMA) which is compatible with the epoxy matrix.<sup>126</sup> The most common rubbers used as the soft core of the

CSR particles include poly (styrene-co-butadiene) (SBR)<sup>151,155–158,167–170</sup>, poly (butyl acrylate) (PBA)<sup>158,167,168,171–180</sup> and polysiloxane (PDMS)<sup>158,159,181,182</sup>.

#### 1.3.3.2.1. Poly (styrene-co-butadiene) rubber (SBR) core-shell particles

Methacrylated butadiene-styrene core-shell was firstly used by Pearson *et al.* in a study about the influence of particle size and particle size distribution on the toughening mechanism of rubber-modified epoxy networks.<sup>150</sup> The toughening mechanism of core-shell particles was described as the internal cavitation of particles followed by the shear band yielding of epoxy matrix. Thus, the use of SBR core-shell particles provided more effective toughening effect than rubber particles due to the greater cavitation resistance of core-shell particles.

The toughening mechanism of CSR-modified epoxy networks was also investigated by Sue *et al.* using CSR particles composed of SBR core and multi-component shell.<sup>155,156</sup> The use of 10 wt% CSR particles in the epoxy networks increases the fracture toughness from 0.77 to 2.70 MPa.m<sup>2</sup>. The cavitation of CSR particles followed by shear yielding was proposed as the major toughening mechanism of these systems. Moreover, line arrays of cavitated rubbers particles (croids) were observed along the crack propagation through a mechanism similar to those of crazes. SBR core-shell particles also had more desirable effects on the fracture behavior of crosslinkable epoxy thermoplastic compared to a DGEBA/piperidine epoxy systems.<sup>157</sup> Indeed, CSR-modified epoxy system containing 5 wt% CSR had the fracture energy ( $G_{Ic}$ ) of over 5 times higher than the unmodified networks.

Lu *et al.* compared two epoxy systems having different crosslinking densities modified by CSR particles and discovered the relation between the crosslinking density of epoxy matrix and the toughening mechanism.<sup>165</sup> The addition of 10 wt% of CSR particles increased the fracture toughness of low and high crosslinked epoxy networks of 300 % and 100 %, respectively. In fact, the authors have explained the difference in toughening extent by the different major mechanism happening. Indeed, particles cavitation followed by shear yielding mechanism is more likely to occur in the low crosslinked epoxy networks whereas debonding mechanism was dominant in the highly crosslinked system.

Several authors have modified the structure of CSR particles, particularly functionalized PMMA shell to facilitate their dispersion in the epoxy matrix. Sue *et al.* used several types of CSR particles with the same SBR core but different shell compositions consist of monomers-styrene (MS), methyl methacrylate (MMA), acrylonitrile (AN), and glycidyl methacrylate (GMA) in order to optimize the fracture toughness of CSR-modified epoxy networks.<sup>164</sup> The authors have found that the compositions of CSR shell strongly influenced the dispersion of CSR-particles and by

consequent determined the toughening effect. In details, the existence of AN and GMA in the shell component facilitates the dispersion of CSR particles in the epoxy matrix leading to a great effect on the fracture toughness of epoxy networks. The major toughening mechanisms were determined as particle cavitation–matrix shear yielding and/or crack deflection depending on the morphology of CSR-modified epoxy networks.<sup>164</sup> Qian *et al.* have synthesized CSR particles composed of poly (styrene-co-butadiene) core and PMMA shell through seeded emulsion polymerization which allows for the modification of PMMA shell with acrylonitrile (AN), glycidyl methacrylate (GMA), and crosslinking agent divinyl benzene in order to study the role of particles-epoxy interfaces.<sup>169</sup> The dispersion of CSR particles was significantly influenced by the incorporation of acrylonitrile and glycidyl methacrylate functionality in the PMMA shell as well as the crosslinking of the shell. Thus, the importance of the functionalized shell was highlighted to reach better particle–matrix interaction and consequently an outstanding toughening effect. In addition to this, Maazouz *et al.* also studied the influence of the functionalization of PMMA shell of CSR particles on the dispersion of SBR-based CSR in epoxy/amine systems.<sup>170</sup> A more uniform dispersion of CSR particles was observed when the PMMA shell was functionalized with carboxyl groups in comparison with the agglomerations in the case of non-functionalized particles.

#### 1.3.3.2.2. Acrylate CSR

At first, core-shell particles composed of a poly (butyl acrylate) core and a poly (methyl methacrylate) shell were developed by Nakamura *et al.*<sup>179</sup> through seeded emulsion polymerization aiming to reduce the internal stress in a cured epoxy network. It was found that the internal stress of epoxy system decreased with the addition of CSR particles due to the reduction of modulus while the thermal resistance was observed to be stable.<sup>179</sup> Then in a following study, the authors have introduced crosslinks in both core and shell of CSR particles using small amount of monoethylene glycol dimethacrylate or glycidyl methacrylate (GMA).<sup>180</sup> Crosslinked CSR particles were more efficient than unmodified ones for reducing the internal stress of epoxy cured systems. In details, crosslinks in the core reduced the linear coefficient of thermal expansion of the epoxy while the presence of GMA in the shell improved the interfacial adhesion between CSR particles and epoxy matrix through the reaction between oxirane groups in the GMA comonomers and hydroxyl groups of the epoxy prepolymer during the curing process.

Then, acrylate CSR particles were used as a toughening agent for epoxy cured networks in a study of Levita *et al.* in which preformed CSR particles consisting of PBA core and PMMA shell were applied into epoxy systems up to 30 phr.<sup>171</sup> CSR particles displayed higher efficiency in toughening epoxy networks than acrylonitrile-butadiene copolymer when remaining their thermal

resistance. In addition,  $K_{Ic}$  values of modified epoxy networks were observed to increase linearly with the content of CSR particles.

Modifications on the acrylate CSR particles in particular the PMMA shell were also conducted by several authors to improve the compatibility with the epoxy matrix. Ashida *et al.* have employed CSR particles comprising of crosslinked PBA core and ion-crosslinked PMMA shell as toughening agents of epoxy networks.<sup>172,173</sup> They have demonstrated that the CSR particles swelled with the epoxy polymer during the curing process due to the penetration of epoxy polymer into the surface layer of the shell forming a bond between epoxy prepolymer and CSR particles. Thus, the addition of a small amount of CSR particles in epoxy matrix increased the energy absorption due to plastic deformation of the matrix combined with rubber particles fracture. Consequently, the toughness and adhesion strength of modified epoxy networks were enhanced. Maazouz *et al.* have used CSR particles composed of PBA core surrounded with crosslinked PMMA shell functionalized with epoxy or carboxylic groups in the epoxy/dicyanamide networks.<sup>174,175,178</sup> It was demonstrated that the use of CSR particles led to a significant toughening improvement without sacrificing thermal properties and stiffness of epoxy networks. Moreover, the authors showed the relation between the toughening level and the size of CSR particles or the core-to-shell thickness ratio.<sup>178</sup>

#### 1.3.3.2.3. PDMS CSR particles

Recently, silicon rubber or poly (dimethyl siloxane) (PDMS) were investigated as toughening agents for epoxy networks thanks to their excellent properties such as UV resistance, low surface tension and an extremely low glass transition temperature of about -120 °C. In addition, the incorporation of PDMS to epoxy networks resulted in an excellent thermal and oxygen stability. The idea of using PDMS core-shell particles as toughener for epoxy system was first published by Ebenhoch on a series of PDMS core-shell developed by Wacker-Chemie GmbH.<sup>181</sup> Due to surface modifications, CSR particles were homogeneously dispersed in the epoxy matrix. Also, the author has shown that the use of small amount of silicon CSR particles (3 wt%) could increase considerably the impact strength and fracture toughness of epoxy networks. Chen *et al.* also reported a significant increment of critical stress intensity factor  $K_{Ic}$  using 20 wt% of the CSR particles based on PDMS even at low temperature up to -100 °C.<sup>159</sup> Very recently, Roy *et al.* have used CSR particles comprising of PDMS core coated with epoxy layer as toughening agent for epoxy networks.<sup>182</sup> Improved impact strength and fracture energy of the modified epoxy networks was observed when using 5 wt% of PDMS CSR particles.

#### 1.3.3.2.4. Comparison of the toughening effect of CSR particles based on different core materials

Some studies have investigated the influence of the core materials on the toughening effect of CSR particles modified epoxy networks. Becu *et al.* compared the toughening effect of two CSR particles consisting of crosslinked PMMA shell and PBA or SBR as the core.<sup>167,168</sup> In both cases, a remarkable increase of the fracture toughness was obtained for modified epoxy networks compared to the neat ones. In addition, CSR particles with a PBA core were discovered to toughen the epoxy system better than those with a SBR core thanks to the greater cavitation resistance of the PBA. Also, the effect of three different CSR nanoparticles with rubber core of SBR, polybutadiene (PBD) or PDMS on the thermal and mechanical properties of epoxy/anhydride networks was studied by Giannakopoulos *et al.*<sup>158</sup> Neglecting the nature of core materials, the use of CSR particles led to an important increase of fracture energy of epoxy networks combined with stable glass transition temperature and mechanical modulus. Then, with the same amount of CSR particles, the particles with PDMS core presented lowest toughening effect.

#### 1.3.3.2.5. Multi-layer CSR particles

The use of multi-layer CSR particles for the modification of epoxy networks was considered. Hazot *et al.* prepared the hairy CSR particles with PBA core, PMMA shell and the outer hairy layer of poly (ethylene) oxide (PEO).<sup>176</sup> Fracture toughness of epoxy networks was highly improved by the existence of the hairy CSR particles. Also, the length and surface density of PEO chains affected the dispersion and toughening effect of CSR particles. Day *et al.* published a comparative study concerning the used of three layers CSR particles composed of an inner glassy core based on crosslinked PMA, an intermediate rubbery layer based on crosslinked PBA and a glassy outer layer of PMMA–poly(ethyl acrylate)–co–GMA copolymer (Figure 1-27).<sup>183</sup> Increases of fracture toughness of modified epoxy networks with the increasing rubber particles content were achieved in the case of using CSR particles compared to conventional liquid rubber. Moreover, the existence of GMA copolymer in the outer layer and a thick rubbery layer were found to be crucial to obtain high toughening efficiency. Very recently, Thitsartarn *et al.* developed three layers CSR particles possessing rigid polyhedral oligomeric silsesquioxane as the inner core, bonded with soft ductile PBA segments and terminated with active functional groups to strongly connect with epoxy matrix.<sup>184</sup> The use of only 1 wt% of this filler in the epoxy matrix resulted in significant enhancement of both mechanical strength (~50 %) and fracture toughness (80 %).

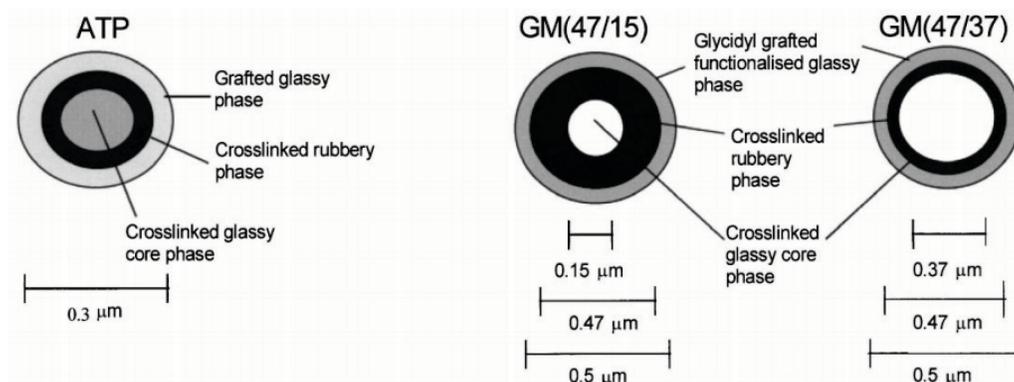


Figure 1-27 Different multi-layer CSR particles used by Day *et al.* to toughen epoxy networks.<sup>183</sup>

### 1.3.4. Conclusion

This part has reviewed different methods to improve the brittleness of epoxy networks aiming to widen their applications. In the literature, two main groups of modifiers based on the miscibility of modifiers towards epoxy prepolymer were used including thermoplastics and preformed core-shell particles. Recently, ionic liquids have demonstrated their potential as new curing agent as well as dispersion aids of nanoparticles into epoxy matrix. But does the replacement of conventional curing agent by ILs in the modified epoxy networks affect their morphology and properties? The answer to this question will be discussed in the chapter 3.

## 1.4. Bio-based epoxy networks

### 1.4.1. Introduction

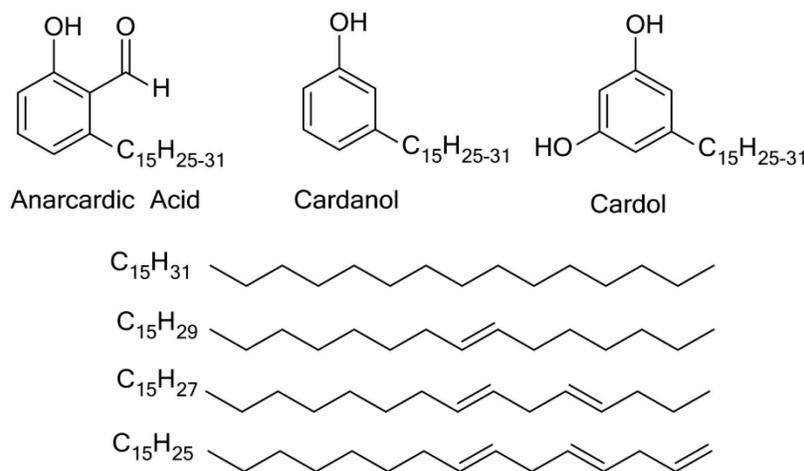
In recent years, due to the increase of oil prices, global warming, and other environmental problems, a growing demand on the bio-based polymers derived from renewable resources in order to replace partially or even totally petroleum based materials takes place. Thermosetting materials especially epoxy networks have become one of the main targets regarding their wide range of applications. In fact, 90 % of the epoxy networks are based on the diglycidyl ether of bisphenol A, DGEBA, derived from bisphenol A and epichlorohydrin. Since bio-based epichlorohydrin is commercially available<sup>185</sup> and bisphenol A has been known to have estrogenic properties,<sup>186</sup> the development of bio-based epoxy prepolymers with comparative performance to bisphenol A becomes crucial. In the literature, bio-based epoxy prepolymers are derived from vegetable oils, sucrose and cardanol, *etc.*<sup>187,188,186</sup> Among them, cardanol obtained by distillation of cashew nut

shell liquid (CNSL) appeared to be sustainable, low cost and largely available natural resources. Besides, co-reactants of epoxy prepolymers can also be developed from cardanol allowing for the formation of fully bio-based epoxy networks. The synthesis of epoxy prepolymers and co-reactants derived from cardanol as well as the formation of cardanol based epoxy networks will be discussed below.

## 1.4.2. Preparation of epoxy and curing agent monomers based on cardanol

### 1.4.2.1. Extraction of cardanol from cashew nut shell liquid

Cashew nutshell liquid (CNSL) is a natural, non-food chain, and annually renewable biomaterial, which is extracted from a soft honeycomb structure inside the cashew nutshell. CNSL consists mainly of anacardic acid (90 %) and cardol.<sup>189</sup> Through decarboxylation and distillation, a high purity monophenol with commercial name of cardanol can be obtained from CNSL.<sup>189</sup> The structures of natural compounds presented or derived from CNSL are illustrated in Scheme 1-10. In fact, chemical structure of cardanol contains a strong chemically resistant backbone based on an aromatic ring combined with hydroxyl groups providing strong adhesion and a long aliphatic side chain suggesting excellent water resistance and good flexibility.<sup>190</sup> Indeed, cardanol is highly attractive as raw materials for chemical modifications and polymerizations into special polymers.<sup>191</sup>

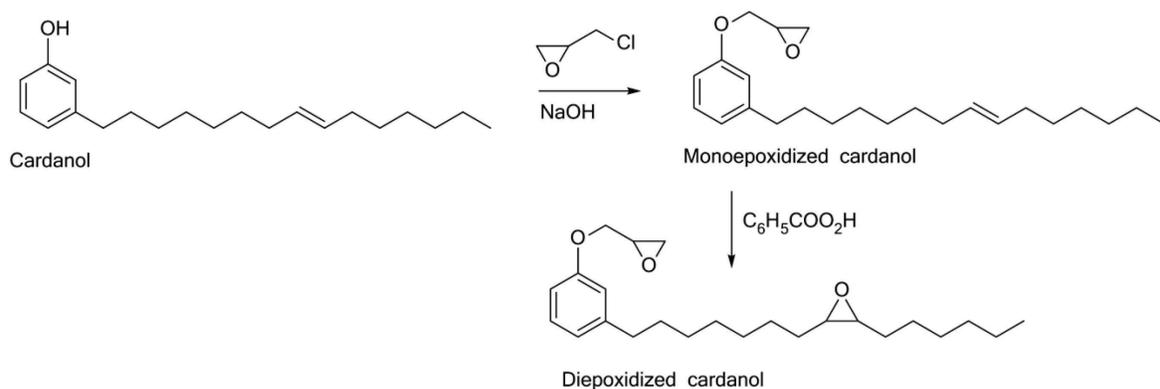


**Scheme 1-10** Natural compounds present or derived from cashew nutshell liquid.<sup>192</sup>

### 1.4.2.2. Synthesis of epoxy monomers based on cardanol

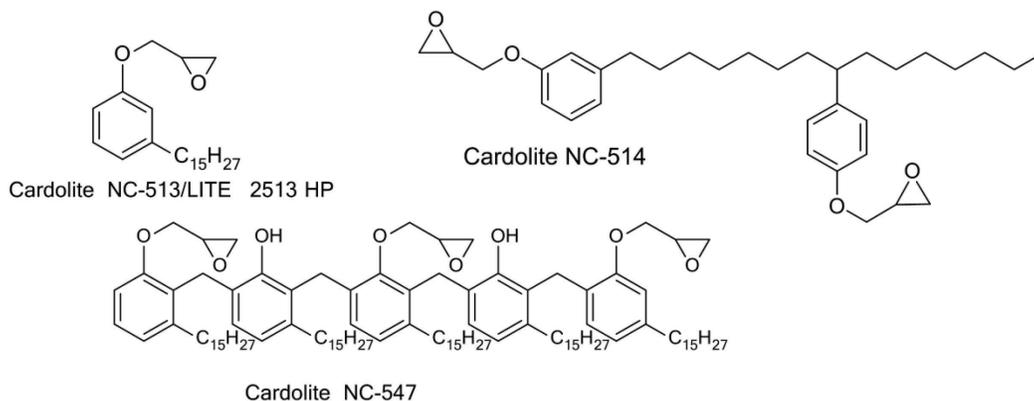
Due to the chemical structure of cardanol, various types of epoxy compounds have been synthesized from CNSL and its derivatives.

Several epoxy compounds were directly synthesized from cardanol. Using the epoxidation of cardanol with epichlorohydrin, Unnikrishnan *et al.* have prepared mono epoxy compounds to serve as toughening agents for conventional epoxy systems.<sup>193</sup> From this mono epoxy compounds, a cardanol based epoxy prepolymer was synthesized by Kanehashi *et al.* using the thermal polymerization of unsaturated bonds on the side chain.<sup>194</sup> Likewise, Zhang *et al.* synthesized cardanol based benzoxanine to introduce as partial substitution for liquid rubber in the modified epoxy/amine networks.<sup>195</sup> Moreover, thanks to the existence of double bonds in cardanol structure, the synthesis of multi-epoxide functionalized compounds were carried out. A diepoxidized cardanol (DEC) with two epoxide functional groups and an epoxy equivalent weight of 284 g.eq<sup>-1</sup> was developed by Patel *et al.* The synthesis of DEC followed a two-step process including the formation of glycidyl group by reaction between the hydroxyl group in cardanol with epichlorohydrin and the epoxidation at the double bond using preformed peroxyacid (Scheme 1-11). In order to form polyepoxide cardanol glycidyl ether (PECGE), Chen *et al.* have epoxidized the double bond of cardanol glycidyl ether using 3-chloroperbenzoic acid.<sup>196</sup> Then, PECGE was used as reactive diluent for epoxy system.



**Scheme 1-11** Synthesis of diepoxidized cardanol.<sup>197</sup>

Many cardanol-derived epoxy compounds are commercially available from Cardolite® including mono-functional epoxy diluents (Cardolite® NC-513 and LITE 2513HP) and multi-functional reactive epoxy prepolymers (Cardolite® NC-514 and NC-547) with their structures illustrated in Scheme 1-12. In fact, mono-functional reactive epoxy diluents from Cardolite have desirable properties for coatings such as very low viscosity and low volatility. Cardolite® NC-514 and NC-547 contains di-functional and tri-functional epoxy groups, respectively. The phenolic structure and aliphatic chain of these epoxy prepolymers are attractive to increase the flexibility, impact resistance, chemical resistance, and water resistance of conventional epoxy systems.<sup>198</sup>



**Scheme 1-12** Structure of commercial cardanol epoxy derivatives provided by Cardolite.<sup>192,198</sup>

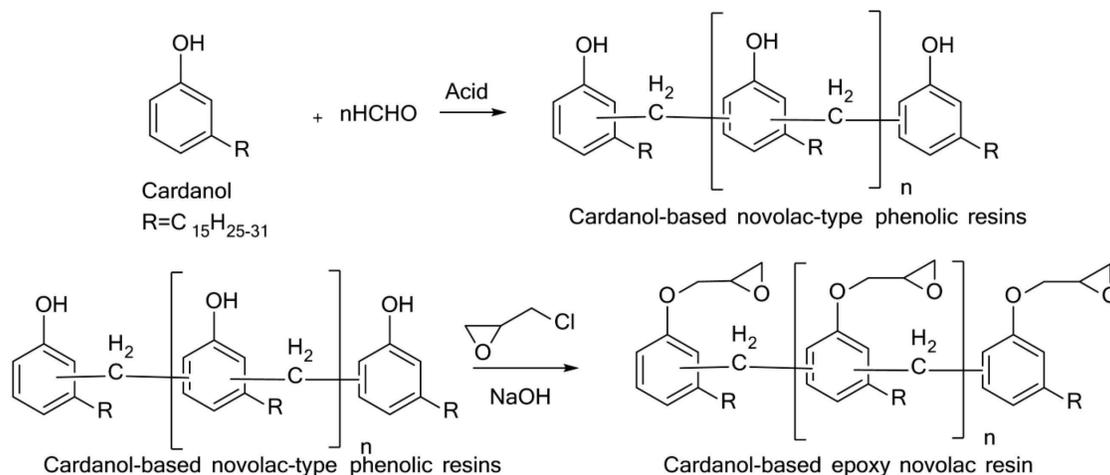
### 1.4.2.3. Synthesis of curing agent based on cardanol

Replacing all petroleum based components in the epoxy networks requires the synthesis of bio-based curing agents for epoxy prepolymers. In fact, several curing agents for epoxy prepolymers have been developed from cardanol including amines<sup>199-202</sup> and novolac polymers<sup>203</sup>.

Amines from cardanol are normally prepared from Mannich condensation reaction between aliphatic amines with cardanol and formaldehyde forming phenalkamines. Pathak *et al.* have developed different phenalkamines from cardanol by varying the structure of aliphatic amines (Scheme 1-13).<sup>199</sup> The obtained products can react with epoxy prepolymers at low curing temperature. Also, Huang *et al.* synthesized a new cardanol based amine through Mannich condensation from the cardanol butyl ether formed by the reaction between cardanol and butyl chloride.<sup>200</sup> This new curing agent has light color, good color stability and low viscosity thanks to the replacement of phenol's hydroxyl group by butoxyl functionality. Recently, the synthesis of phenalkamines through Mannich condensation using the *in situ* depolymerization of paraformaldehyde was reported by Liu *et al.* The use of paraformaldehyde instead of formalin allowed to reduce energy consumption, waste water discharge, and environmental pollution.<sup>201</sup> Nevertheless, Darroman *et al.* have used thiolene chemistry as a new synthesis method to prepare amine functionalized cardanol from cardanol and cysteamine.<sup>202</sup> The synthesis of this cardanol cysteamine which consists of the allylation of the phenol of cardanol followed by the thiolene reaction with cysteamine hydrochloride can be carried out in safe solvents such as ethanol or water (Scheme 1-14). Thus, cardanol cysteamine was reported to have similar properties to phenalkamines from Mannich reactions without the use of hazardous products such as formaldehyde or toxic amines.



observed an increasing improvement of elongation at break of modified cardanol based epoxy networks with the liquid rubber content as well as an abrupt increase of impact strength up to 15 wt% of CTBN. Besides, in their very recent study, hazardous formaldehyde involved in the formation of cardanol based novolac polymers was replaced by furfural – a heterocyclic aldehyde derived from agricultural waste product.<sup>208</sup> The novolac epoxy polymer based on cardanol and furfural exhibited equally good mechanical and chemical properties compared to phenolic based epoxy polymer.



**Scheme 1-15** Synthesis of cardanol based epoxy novolac polymer.<sup>204,205</sup>

#### 1.4.3.2. Cardanol based compounds as modifiers for conventional epoxy networks

As indicated in the previous parts, the chemical structure of cardanol based epoxy compounds contains long alkyl chains suggesting high flexibility. In fact, cardanol based compounds have been widely used as toughening agents for the conventional epoxy networks. A bisphenol A/cardanol co-epoxies was prepared by Unnikrishnan *et al.* through the reaction of epichlorohydrin with the mixture of Bisphenol A and cardanol.<sup>193</sup> The presence of cardanol based prepolymers in the epoxy systems reduced their brittle nature indicated by a sharp increase in elongation to break of cured samples. A partial substitution of conventional toughening agent of epoxy systems (CTBN) was successfully carried out by Zhang *et al.* using Cardanol based benzoxazine.<sup>195</sup> The flexibility of epoxy samples was maintained thanks to the aliphatic chain of Cardanol based benzoxazine while their thermomechanical ( $T_g$  and crosslinking density), thermal, mechanical and dielectrical properties were highly improved. Also, commercially CNSL derived epoxy prepolymers from Cardolite® (NC-514 and NC-547) have been used to toughen epoxy systems. In a study of Maiorana *et al.*,<sup>209</sup> the combination of this flexible epoxy prepolymer with a rigid bio-based epoxy networks resulted in a sharp increase in impact strength and fracture toughness *i.e.* 136 % and 66 %

respectively for a mixture containing 50 wt% of Cardolite® NC-514. The toughening effect was explained by the increase of molar mass between crosslinks thanks to the long alkyl chain of NC-514 since all obtained samples are homogenous with one transition temperature despite the difference between two epoxy prepolymers. Similarly, Gour *et al.* toughened conventional epoxy novolac polymer by Cardolite® NC-514 and NC-547.<sup>210</sup> The use of both types of Cardolite® epoxy compounds with flexible chains in the backbone was found to increase the impact strength of epoxy networks. The effect of chemical structure of flexibilizers on the toughening effect was also studied. NC-514 with flexible moiety in the main chain was more effective as toughening agent than NC-547 with close proximity of rigid phenyl groups and flexible side chains.

In addition, the research on epoxy networks containing cardanol derived epoxy prepolymers also involves the use of epoxidized cardanol as reactive diluent. Patel *et al.* investigated the effect of diepoxidized cardanol (DEC) on the curing kinetics of the system and found a slight decrease of the reactivity of the epoxy system indicated by an increase in the exothermic peak temperatures and activation energies with the amount of DEC.<sup>197</sup> In a recent study, a polyepoxide glycidyl ether synthesized from cardanol (PECGE) was applied as reactive diluent for epoxy polymer.<sup>196</sup> Using less than 20 % of PECGE, the processability of epoxy polymer was successfully enhanced with a significant reduction in blend viscosity. The overall performance especially heat resistance of obtained cured samples was improved thanks to the rigid phenol structure of PECGE and the increase of crosslinking density.

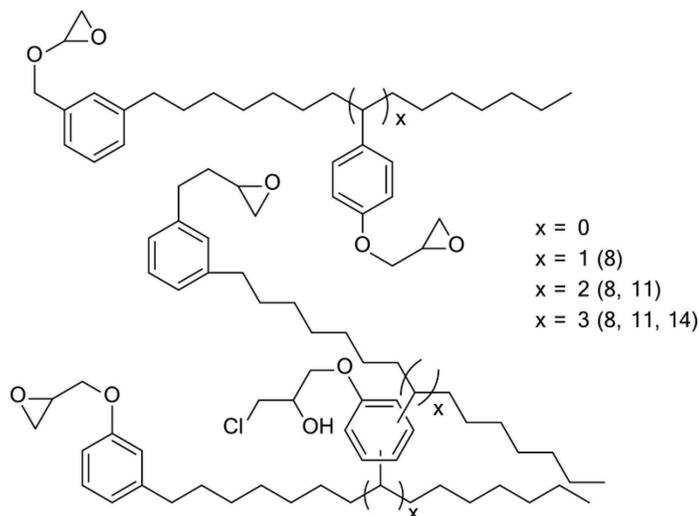
Moreover, the pending alkyl chain of cardanol based compounds opened their use as agent to improve water resistance of the epoxy coatings. Aggarwal *et al.* prepared epoxy based paint using the mixture of diglycidyl ether of cardanol and DGEBA.<sup>211</sup> The authors have found that the existence of cardanol based compounds improved the mechanical and anticorrosive properties of epoxy films. Also, the modified epoxy polymers was better binder media for paints than the neat ones regarding their 15 % higher of bond strength on subtract. Recently, a series of triglycidyl cardanol prepolymer (TGC) was developed by Kathalewar *et al.* in order to partially replace bisphenol A based epoxy prepolymer in the coating formulations.<sup>212</sup> In fact, the use of 40 % to 50 % of TGC can lead to the improved performance of epoxy coatings in terms of pencil harness, impact resistance, chemical resistance and epoxy resistance. Also, the DGEBA partial substitution by Cardolite® commercial epoxy prepolymers was also discussed by Verge *et al.*<sup>213</sup> Thanks to the hydrophobic nature of cardanol based compound, modified epoxy film outperformed in terms of adhesion and water uptake.

Finally, the mixture of cardanol based and conventional epoxy prepolymer up to 40 % of cardanol can be served as matrix for composites reinforced with natural fibers.<sup>214</sup>

### 1.4.3.3. Epoxy networks with Cardanol based prepolymer and/or curing agent

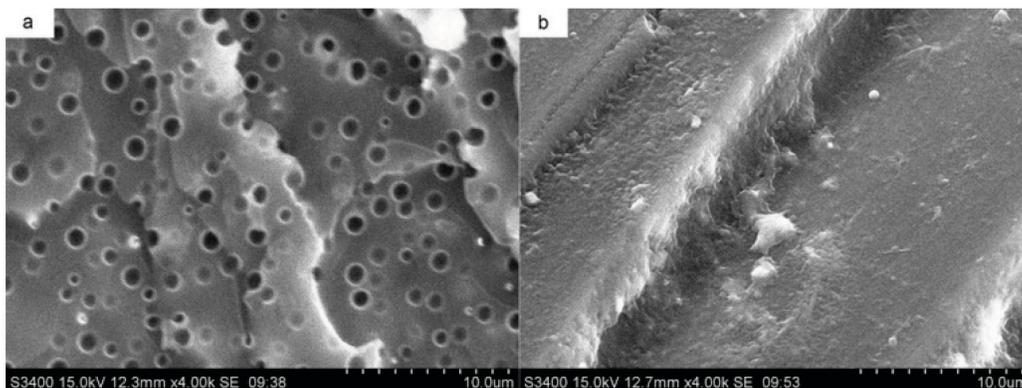
In fact, diepoxide or polyepoxide cardanol based compounds are of interest as prepolymers for the formation of bio-based epoxy systems. Cardanol based epoxy prepolymer (ECP) synthesized by Kanehashi *et al.* can form polymers films or coatings through the curing reaction with convention amines.<sup>194,215</sup> Indeed, ECP based coatings have lower drying time (less than 2 hours at room temperature) and better chemical resistance than those from commercial cashew.<sup>194</sup> In addition, the ECP films cured with diethylene triamine exhibited antibacterial activity against *E. coli* and *S. aureus* suggesting health care applications.<sup>215</sup> Moreover, commercial diepoxidized cardanol compounds from Cardolite<sup>®</sup> were widely used as prepolymers for bio-based epoxy networks. Verge *et al.* studied the substitution of DGEBA by cardanol based epoxy prepolymer and obtained a  $T_g$  of 40 °C for Cardolite<sup>®</sup> NC-514 based epoxy networks.<sup>213</sup> The hydrophobic nature of Cardolite<sup>®</sup> NC-514 also lowered the water diffusion of formed epoxy networks in respect to those based on DGEBA. Chrysanthos *et al.* investigated the gelation and reactivity of Cardolite<sup>®</sup> NC-514 with an isophorone diamine (IPDA) hardener as well as the thermal and thermomechanical properties of cured epoxy networks in comparison to other bio-based precursors from sorbitol or isosorbide and the conventional epoxy prepolymer DGEBA.<sup>191</sup> Among them, NC-514 has the lowest reactivity towards amines and longest gelation time due to low concentration of epoxide groups. Considering the long aliphatic chain of NC-514, the related epoxy networks performed a relaxation peak at around 50 °C. Similar glass transition temperature was achieved by Caillol's group for NC-514/IPDA networks.<sup>216-218</sup> The glass transition of NC-514 based epoxy networks varied in function of used conventional amines (IPDA, Jeffamine D400 and Jeffamine T403) and the epoxy/amine ratio. The authors also proposed a new chemical structure (Scheme 1-16) and epoxy equivalent weight ( $\sim 363 \text{ g.mol}^{-1}$ ) for NC-514 based on the characterization on the epoxy prepolymers by NMR and size exclusion chromatography (SEC).<sup>216</sup> However, the properties of amine cured NC-514 was found to be not sufficient to replace the DGEBA in the epoxy networks. Sucrose epoxy derivatives from sorbitol and isosorbide were considered to improve the performance of epoxy cardanol derived materials for coating applications.<sup>217</sup> In fact, the glass transition and hardness of materials were enhanced by the existence of epoxidized sorbitol and isosorbide. Very recently, Caillol's group also reported the use of three different epoxy reactants as modifiers for cardanol derived epoxy coatings.<sup>218</sup> They have demonstrated that comparative properties to DGEBA based coatings can be reached with the right choice of epoxy monomer indicating the possibility of fully DGEBA-substituted coatings. Another way to enhance the properties of cardanol based epoxy networks for high performance applications concerns the incorporation of nanofillers particularly graphene nanoplatelets (GNP).<sup>219</sup> The Young's Modulus, tensile strength and stress intensity factor of neat NC-514/IPDA were 474 MPa, 17 MPa and  $0.7 \text{ MPa.m}^{1/2}$ , respectively. Then, only 5 wt%

of GNP incorporated into NC-514/IPDA systems led to remarkable improvement of mechanical properties *i.e.* + 258 % of Young's Modulus, + 94 % of tensile strength and + 157 % of  $K_{Ic}$  values.



**Scheme 1-16** Chemical structure of cardanol NC-514 proposed by Caillol's group.<sup>216</sup>

Besides, curing agents derived from Cardanol reported in the previous part can react with conventional epoxy prepolymer (DGEBA) to form epoxy networks. Phenalkamines synthesized from Mannich reactions are the most common cardanol based curing agent used for epoxy prepolymers aiming for coating applications. In fact, it was demonstrated by Pathak *et al.* that epoxy/phenalkamines blends can be cured at room temperature and the obtained samples exhibited good adhesion with metal surface particularly with copper.<sup>199</sup> Liu *et al.* also showed the formation of epoxy/phenalkamines networks with excellent thermal and mechanical properties.<sup>201</sup> In fact, the use of phenalkamines with high molar mass and soft segment alkyl side chain resulted in a higher fracture toughness of epoxy networks compared to those cured with diethylene triamine *i.e.* 81 % improvement in impact strength. From Mannich reaction, another cardanol based curing agent (Mannich base of cardanol butyl ether - MBCBE) was also synthesized by Huang *et al.* and was used as curing agent for DGEBA.<sup>200</sup> The morphology of cured DGEBA/MBCBE samples observed by SEM presented a phase separation of MBCBE or incompletely crosslinked DGEBA/MBCBE in the epoxy matrix similar to the reaction induced phase separation. Then this dispersed phase promoted the formation of cavities in the epoxy networks leading to remarkable improved impact strength compared to systems cured with phenalkamines (Figure 1-28). Nevertheless, novolac polymers based on cardanol can be served as curing agents for epoxy prepolymers leading to the formation of epoxy networks with excellent thermal stability (400 °C).<sup>203</sup>



**Figure 1-28** SEM micrographs of the fracture surface of DGEBA based epoxy networks cured with a) MBCBE showing the cavities and b) Phenalkamines with no phase separation.<sup>200</sup>

By combining the cardanol based epoxy prepolymers and a bio-based curing agent, fully bio-based epoxy networks can also be synthesized.<sup>202,220</sup> Caillol's group reacted cardanol based epoxy with amine derived from vegetable oil in presence of blowing agent in order to develop bio-based epoxy foams. The obtained foams possessing good thermal stability of over 200 °C and a glass transition of 20 °C can be considered as environmentally friendly foams for structural applications.<sup>220</sup> Additionally, in their recent study, epoxy networks were prepared from epoxy prepolymers and curing agents both derived from cardanol providing fully bio-based epoxy coatings. In fact, the authors compared two fully cardanol based epoxy systems using commercial phenalkamines and a synthesized cardanol cysteamine.<sup>202</sup> The properties of two epoxy networks was examined indicating that cardanol cysteamine provided epoxy networks with similar properties of those using phenalkamines without the use of hazardous formaldehyde or toxic amines in the synthesis.

#### 1.4.4. Conclusion

This part summarized the literature on the development of bio-based epoxy networks in general and especially from cardanol aiming to replace petroleum based epoxy precursors (DGEBA). In fact, cardanol based compounds possess exceptional combination of properties due to the chemical structure containing both aromatic rings and long aliphatic chains. Cardanol based compounds can be served as modifiers for conventional epoxy networks such as tougheners or agent to improve chemical resistance and hydrophobicity. In addition, cardanol based epoxy networks prepared by several authors provide good performances suggesting a new way to develop sustainable materials.

## 1.5. Conclusion of chapter 1

In the last few years, ionic liquids possessing excellent properties have become new multifunctional additives of polymers in designing new materials with outperformed properties. Not only limiting as an additives for thermoplastics, ionic liquids have expanded their applications in the field of thermosetting polymers *i.e.* as modifiers or comonomers for epoxy networks. While ionic liquids based on imidazolium have been widely investigated, the studies on those based on phosphonium are still limited. In fact, phosphonium based ionic liquids having high thermal stability and hydrophobicity are promising as the alternatives for conventional epoxy curing agents. In addition, a series of commercial phosphonium based ionic liquids are commercially available for the development of epoxy/phosphonium based IL networks. Thus, studies are required to a better understanding of the role of phosphonium based IL in the formation of epoxy networks, the influence of the chemical nature of ILs on the final properties of networks as well as the mechanism of the curing reaction (Chapter 2). Moreover, ILs are well known as an efficient solvent, does the presence of ionic liquids also affect the incorporation of modifiers in the epoxy matrix leading to good properties? (Chapter 3) Finally, the combination of ionic liquids with bio-based materials can be interesting to develop a new generation of “sustainable materials” for future applications (Chapter 4).

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## Chapter 2:

# Ionic liquids: A new route for the design of epoxy networks

In the field of epoxy networks, ionic liquid based on phosphonium cations have recently shown their ability to act as a co-monomer in order to develop new epoxy networks. However, to our knowledge, very few studies mention their use as reactive additives of epoxy prepolymers. In this second chapter, our research group has investigated the effect of phosphonium IL in these systems and this chapter has been divided in three parts: *i)* The first part includes a preliminary work on epoxy/IL systems where the kinetics of polymerization as well as the thermal and thermomechanical properties was studied. *ii)* The second part focuses more particularly on the influence of ILs nature on the mechanical properties of epoxy networks such as flexural properties and fracture toughness. At the same time, a comparative study between epoxy/amine and epoxy/IL networks was presented. *iii)* Finally, the last part of this chapter discusses the mechanism of the curing reaction between epoxide functional group and ionic liquids during the curing process.

## Table of contents

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<b>2.1. Introduction</b> .....	<b>97</b>
<b>2.2. Experimental</b> .....	<b>98</b>
2.2.1. Materials and methods .....	98
2.2.2. Preparation of samples .....	100
2.2.3. Characterization of epoxy/IL mixtures and networks.....	100
<b>2.3. Results and Discussions</b> .....	<b>103</b>
2.3.1. Ionic Liquids as reactive additives for the preparation and modification of Epoxy networks .....	103
2.3.1.1. Curing sample.....	103
2.3.1.2. Curing behavior of epoxy amine and epoxy/IL blends .....	104
2.3.1.3. FTIR Analysis .....	106
2.3.1.4. Thermal Stability of epoxy networks .....	107
2.3.1.5. Hydrophobic behavior of epoxy networks.....	109
2.3.1.6. DSC analysis of epoxy networks.....	109
2.3.1.7. Dynamic Mechanical Properties of epoxy networks.....	110
2.3.2. Effect of ILs nature on the design of Epoxy networks .....	114
2.3.2.1. Reactivity of epoxy amine and epoxy/IL systems .....	114
2.3.2.2. FTIR Analysis .....	115
2.3.2.3. Morphology of the resulting epoxy networks.....	116
2.3.2.4. Surface properties of epoxy networks .....	117
2.3.2.5. Thermal behavior of epoxy networks .....	119
2.3.2.6. Dynamic Mechanical properties of epoxy networks .....	120
2.3.2.7. Mechanical behavior of epoxy networks .....	122
2.3.3. Conclusion .....	124

<b>2.4. Polymerization Mechanism between phosphonium ionic liquids and the epoxide functional group of epoxy prepolymer .....</b>	<b>125</b>
2.4.1. Introduction and materials.....	125
2.4.2. Preparation of samples.....	126
2.4.3. Characterization of epoxy/IL mixtures.....	126
2.4.4. Results and discussion.....	127
2.4.4.1. Curing behavior of mono-epoxy and IL systems (blends or cured materials).....	127
2.4.4.2. Polymerization Mechanism between EPP and ILs .....	129
2.4.5. Conclusion .....	137
<b>2.5. Conclusion of chapter 2 .....</b>	<b>137</b>
<b>References of chapter 2 .....</b>	<b>138</b>
<b>Supporting Information of chapter 2.....</b>	<b>143</b>

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## 2.1. Introduction

Nowadays, there is a growing demand to design and develop new high-performance materials that are sustainable and environmentally friendly. Recently, thanks to their unique properties such as excellent thermal stability, good ionic conductivity, low saturated vapor pressure, non-flammability, but also high versatility, ionic liquids (ILs) have become excellent functional additives to polymer matrices.<sup>1,2</sup> In fact, ILs are more and more used as processing aids of renewable resources,<sup>3,4</sup> as a solvent of polymerization,<sup>5-8</sup> lubricants,<sup>9-11</sup> or plasticizers<sup>12-14</sup> in advanced polymer materials, compatibilizers of thermoplastic and biopolymer blends,<sup>15-17</sup> building blocks for designing nanostructured polymers,<sup>18,19</sup> or as surfactant agents in nanocomposites.<sup>20</sup> Very recently, ionic liquids have been also investigated as reactive additives within epoxy networks to develop new polymer electrolytes, anticorrosive coatings, or for composite applications.<sup>21-23</sup>

According to the literature, two main ways have been studied to combine ILs and epoxy networks: *i*) synthesis and development of new functionalized ILs in order to provide ionic conductivity to the polymer electrolytes based on an epoxy/amine network for energy applications.<sup>24-29</sup> Thus, ILs bearing epoxide groups either on the cation or the counter anion were synthesized by Matsumoto *et al.*<sup>24-26</sup> to design ionic conductive epoxy/amine networks.<sup>27</sup> Other authors synthesized new bis epoxide ILs monomers to prepare polymeric ionic liquids (PILs) and PIL/IL ion-gels based on epoxy/amine networks revealing significant improvements in CO<sub>2</sub> permeability and selectivity.<sup>28,29</sup> *ii*) ILs can be also combined as additives or comonomers to conventional epoxy prepolymers or epoxy/amine reactive systems.<sup>30-39</sup> In fact, the incorporation of a small amount of ionic liquids (a few wt%) can lead to increase reaction (curing) kinetics and to modify the resulting morphologies leading to improvements of the properties of the networks such as the thermomechanical behavior, ionic conductivity, and scratch resistance.<sup>30,31,35</sup> For example, Sanes *et al.* have demonstrated an improvement of wear and scratch resistance of epoxy/amine networks by using only 1.5 wt% of imidazolium IL.<sup>33</sup> On the other hand, Saurin *et al.* have shown that the use of 9 wt% of IL in an epoxy/amine system led to a self-healing effect after abrasion damage under multiple scratch tests.<sup>34</sup>

In recent years, ILs have been also reported as new alternatives to conventional amines used as hardeners (comonomers) of epoxy prepolymer.<sup>22,39</sup> In 2009, Rhamathullah *et al.* highlighted that imidazolium salt associated with a dicyanamide counter anion could be used as a latent curing agent.<sup>36</sup> In addition, various authors have demonstrated that ILs based on imidazolium and pyridinium cations acted as initiators and curing agents of diglycidyl ether of bisphenol A prepolymer (DGEBA) through cationic polymerization to prepare epoxy/IL networks.<sup>30,31,37</sup>

However, high temperatures are required for the processing of these networks. More recently, other authors as well as our research group have found that phosphonium ILs combined with different counter anions were also very good candidates to replace amines.<sup>39,40</sup> In fact, Soares *et al.*, Livi *et al.*, and Maka *et al.* clearly demonstrated that the basic nature of the phosphinate and dicyanamide anions allowed the polymerization of the epoxy prepolymer via anionic polymerization.<sup>22,39,40</sup> In addition, they have demonstrated that these new epoxy/IL networks have excellent thermomechanical properties, including thermal stability under nitrogen (>400 °C) and a glass transition temperature between 80 and 140 °C depending on the chemical nature of the anion. These authors have highlighted the occurrence of nanostructuring of the resulting networks due to the limited miscibility between an epoxy prepolymer, *i.e.*, DGEBA, and IL.<sup>39</sup> Very recently, Maka *et al.* have also studied epoxy networks cured with imidazolium and phosphonium ILs combined with dicyanamide anion.<sup>23</sup> They have obtained epoxy/IL networks with high transparency (85 %) combined with a glass transition temperature of 170 °C.

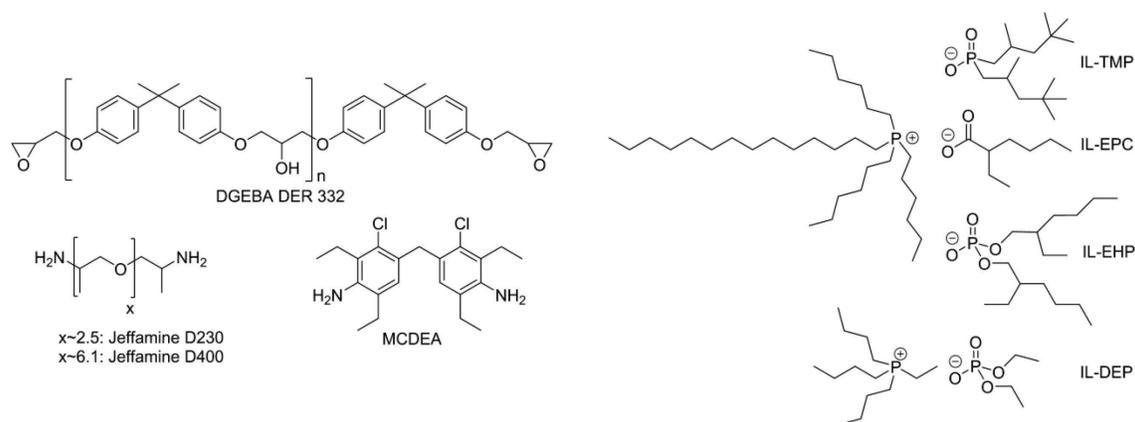
In this work, different phosphonium ionic liquids combined with phosphinate, carboxylate, and phosphate counter anions have been used as new reactive components of epoxy systems. Thus, the influence of the chemical nature of the anion (phosphinate versus carboxylate) and the cation (phosphonium functionalized with short versus long alkyl chains combined with the same phosphate counter anion) was investigated on the polymerization kinetics of epoxy prepolymer, thermal (ATG, DSC), and thermomechanical properties (DMA) as well as on the morphology and surface properties of epoxy/IL networks. In addition, to highlight the contribution of the ionic liquid on the properties of the networks, reference systems based on a mixture of DGEBA and conventional amine *i.e.* Jeffamine D230, Jeffamine D400 and MCDEA was also studied. Thus, for the first time to our knowledge, a comparative study on the mechanical behavior (flexural properties and fracture toughness) of these new epoxy networks versus conventional epoxy/amine systems was studied.

## 2.2. Experimental

### 2.2.1. Materials and methods

Diglycidyl ether of bisphenol A (DGEBA) based epoxy prepolymer (DER 332, DOW Chemical company) with epoxide equivalent weight (EEW) of 175 g.mol<sup>-1</sup> was considered. Three conventional diamine comonomers, *i.e.* an aromatic diamine, 4,4'-methylene bis(3-chloro-2,6-diethylaniline) - MCDEA (Lonzacure, Amine Hydrogen Equivalent Weight -AHEW = 95 g.mol<sup>-1</sup>) and two aliphatic diamines, polyoxy-propylene-diamine - Jeffamine D230 (Hunstmann, AHEW = 60 g.mol<sup>-1</sup>) and Jeffamine D400 (Hunstmann, AHEW = 115 g.mol<sup>-1</sup>) were used as the reference

curing agents. Four types of phosphonium ionic liquids were kindly supplied by Cytec, Inc. All the chemical structures are presented in Figure 2-1 with their principal properties in Table 2-1. The ionic liquids denoted IL-EPC (Trihexyl(tetradecyl) phosphonium 2-ethylhexanoate), IL-EHP (Trihexyl(tetradecyl) phosphonium bis(2-ethylhexyl)phosphate), and IL-TMP (trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate) have the same cation combined with carboxylate, phosphate, and phosphinate counter anions, respectively. IL-DEP (tributyl(ethyl)phosphonium diethyl phosphate) possesses the same phosphate anion as IL-EHP but combined with a phosphonium cation functionalized with shorter alkyl groups.



**Figure 2-1** Chemical structure of DGEBA, Jeffamine D230, Jeffamine D400, MCDEA, and phosphonium ionic liquids.

**Table 2-1** Principal properties of used materials: DGEBA, Jeffamine D230, Jeffamine D400, MCDEA, and phosphonium ionic liquids.

Material	Glass transition temperature $T_g$ (°C)	Degradation temperature			Surface Tension (mJ · m <sup>-2</sup> )
		$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	$T_{max\ DTGA}$ (°C)	
DGEBA	-22	256	272	335	44.6 <sup>a</sup>
D230	--	95	115	165	28.6 ± 0.3
D400	--	182	209	299	31.7 ± 0.3
MCDEA	--	218	233	283	52.6
IL-TMP	--	234	304	382	28.3 ± 0.3
IL-DEP	--	226	286	357	29.4 ± 0.2
IL-EPC	--	269	299	348	29.3 ± 0.4
IL-EHP	--	313	338	271	28.2 ± 0.2

<sup>a</sup> value from the study of Chen *et al.*<sup>41</sup>

### 2.2.2. Preparation of samples

DGEBA and curing agents (ionic liquid or diamine) were mixed with a suitable ratio under stirring at room temperature for 30 minutes. The mixture was then degassed in an ultrasonic bath during 15 minutes, was poured into silicone molds and was cured under different conditions to confirm the formation of epoxy/ionic liquid networks. The ratio between DGEBA and hardeners as well as the curing procedure are given in Table 2-2.

**Table 2-2** Curing conditions of epoxy/amine and epoxy/IL systems.

Epoxy	Curing agent	Concentration (phr)	Curing protocol
DGEBA	D400	66 (a/e =1) <sup>a</sup>	2h@80 + 3h@140
	MCDEA	54 (a/e =1)	1h@150 + 2h@180 + 1h@200
	D230	34 (a/e =1)	2h@80 + 3h@125 + 1h@200
	IL-TMP	10, 20, 30 (a/e =0.02, 0.04, 0.07) <sup>b</sup>	2h@80 + 3h@120 + 1h@200
	IL-DEP	10, 20, 30 (a/e = 0.05, 0.09, 0.14)	2h@80 + 3h@160 + 3h@200
	IL-EPC	10 (a/e=0.03)	2h@80 + 3h@120 + 1h@200
	IL-EHP	30 (a/e=0.06)	2h@80 + 3h@180 + 3h@200

<sup>a</sup> a/e is the amino hydrogen to epoxy ratio

<sup>b</sup> In the case of IL, a/e is the IL anion to epoxy ratio considering that each IL anion reacts to one epoxide group.

### 2.2.3. Characterization of epoxy/IL mixtures and networks

*Differential Scanning Calorimetry* measurements (DSC) of epoxy/IL reactive mixtures and resulting networks were carried out by using Q20 (TA instruments) from 20 to 250 °C at a rate of 10 K.min<sup>-1</sup> under nitrogen flow of 50 mL.min<sup>-1</sup>. The weight of samples was included between 9 – 10 mg in all the cases.

*Fourier Transform Infrared* absorption spectra (FTIR) were recorded using a Thermo Scientific Nicolet iS10 Spectrometer in a transmission mode (32 scans, resolution 4 cm<sup>-1</sup>) from 4,000 to 500 cm<sup>-1</sup> to follow the curing reaction. The conversion of epoxide group was calculated from the

area of absorption peaks at 1,184 cm<sup>-1</sup> (corresponding to the C-O bonds) and 914 cm<sup>-1</sup> (epoxy function) at a given reaction time, t, using the following equation.<sup>22</sup>

$$\chi\% = \frac{(A^o - A^t)}{A^o} \times 100\% \quad (\text{Equation 2-1})$$

where A<sup>o</sup> and A<sup>t</sup> are the A<sub>914</sub>/A<sub>1,184</sub> area ratio for the reactive system at t = 0 and at a reaction time t, respectively.

*Surface energy* of epoxy networks was determined from the sessile drop method using a Dataphysics goniometer. Water and diiodomethane were used as probe liquids for contact angle measurements on compacted MCDEA pellets and resulting epoxy networks. Non-dispersive (polar and H-bond) and dispersive components of surface energy were determined according to the Owens-Wendt theory.<sup>42</sup> Surface tensions of phosphonium ionic liquids (denoted IL-TMP, IL-EPC, IL-DEP and IL-EHP) and Jeffamine D230 were measured from pendant drop method.<sup>43</sup>

*Thermogravimetric Analyses* (TGA) of resulting epoxy networks were performed using a Q500 Thermogravimetric analyzer (TA instruments) from 30 to 600 °C for a heating rate of 20 K.min<sup>-1</sup> under nitrogen atmosphere.

*Dynamic Mechanical Analysis* (DMA) was carried out on a Rheometrics Solid Analyzer RSAII at 0.01 % tensile strain and a frequency of 1 Hz. The heating rate was 3 K.min<sup>-1</sup> for a temperature range from 30 °C to 200 °C.

*Flexural tests:* Three points bending tests were conducted under ISO 178:2001(F) standard with the samples geometries of 75×10×4 mm<sup>3</sup>. Five samples for each system were analyzed using a MTS tensile instrument with a 1kN load cell and a fixed span length of 60 mm at a speed of 2 mm.min<sup>-1</sup> at room temperature. Flexural strength at break was calculated using the equation:

$$\text{Flexural strength} = \frac{3FL}{2bh^2} \quad (\text{Equation 2-2})$$

Where F (N) is the load at break, L (m) the span length, b (m) and h (m) the width and the thickness of specimens, respectively. The flexural modulus was calculated from the force deflection curve using the following equation:

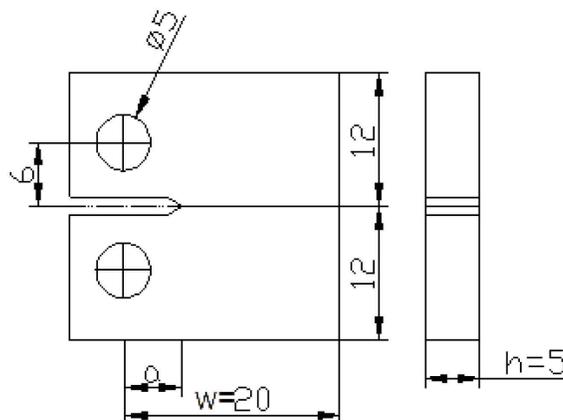
$$E_f = \frac{L^3}{4bh^3} \frac{F}{d} \quad (\text{Equation 2-3})$$

where F (N) and d (m) is the load and the deflection at break, respectively.  $\frac{L^3}{4bh^3}$  is the correction factor for the slope of load-deflection curve.

*Fracture Toughness* ( $K_{Ic}$ ) of epoxy/IL samples was determined using compact tension specimen figuration according to ISO 13586 Standard (Figure 2-2). The initial portion of V notch was machined with a milling cutter and the starter crack was introduced at the root of the notch by tapping a fine razor blade. The ratio of crack length to width ( $a/w$ ) is to be maintained between 0.2 and 0.8. The  $K_{Ic}$  specimens were then tested in tension mode using a MTS tensile instrument with a 1kN load cell at a speed of 10 mm.min<sup>-1</sup>. Then fracture toughness was calculated using the following equation:  $K_{Ic} = f(a/w) \frac{F_Q}{h\sqrt{w}}$  (Equation 2-4)

where  $F_Q$  (N) is the load at the initiation of crack,  $a$  (m) is the crack length,  $w$  (m) is the width of the specimen,  $h$  (m) is the thickness of the specimen and  $f(a/w)$  is the geometry constant (Equation 2-5):

$$f(a/w) = \frac{(2+a)}{(1-a)^{3/2}} (0.886 + 4.64a - 13.32a^2 + 14.72a^3 - 5.6a^4) \quad (\text{Equation 2-5})$$



**Figure 2-2** Compact Tension specimen configuration.

*Transmission electron microscopy* (TEM) was carried out at the Technical Center of Microstructures (University of Lyon) using a Phillips CM 120 microscope operating at 80 kV to characterize the structuration of ILs in the epoxy networks. The 60-nm-thick ultrathin sections of samples were obtained using ultramicrotome equipped with a diamond knife and were then set on copper grids. The size of ionic domains was estimated using ImageJ Software (U.S National Institutes of Health).

*Scanning electron microscopy* (SEM) on a Phillips XL20 microscope with a tension of acceleration of 25 kV was used to characterize the fracture surface of  $K_{Ic}$  specimens. The samples were cleaned using ethanol<sup>44</sup> and then coated with gold.

## 2.3. Results and Discussions

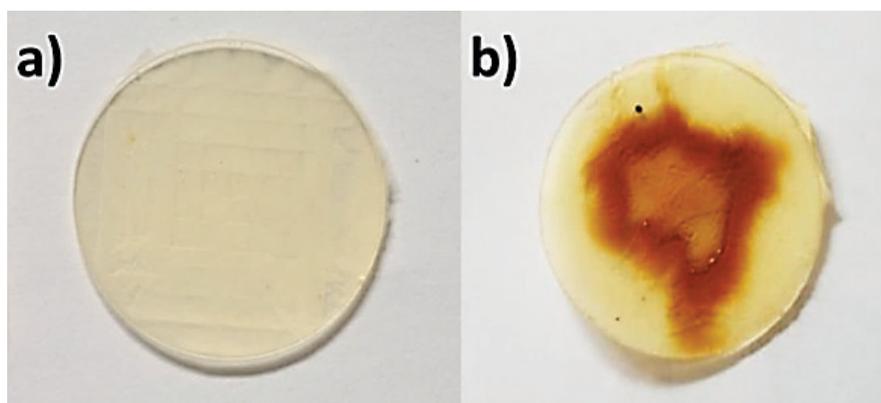
The results of epoxy/IL networks were divided into two parts: *i)* A preliminary study on IL effect (IL-TMP *vs.* IL-DEP) on the polymerization kinetics and thermomechanical properties of epoxy networks. The results were compared with reference epoxy/amine networks *i.e.* Jeffamine D400. *ii)* Effect of the chemical nature of ILs (IL-TMP, IL-EPC, IL-DEP and IL-EHP) on the final properties of epoxy networks compared to conventional systems based on aromatic amine (MCDEA) and aliphatic amine (Jeffamine D230).

### 2.3.1. Ionic Liquids as reactive additives for the preparation and modification of Epoxy networks

The results presented in this part concerns the use of two commercially available ionic liquids containing phosphinate (IL-TMP) and phosphate (IL-DEP) anion at different IL amounts of 10, 20 and 30 phr. Jeffamine D400 was used as reference curing agent due to its similar structure to ILs. IL-TMP and IL-DEP were chosen for this part owing to their commercial availability at industrial scale. The results presented below were published in *the Journal of Polymer Science Part A: Polymer Chemistry*, 2014, Volume 52, Pages 3463–3471.

#### 2.3.1.1. Curing sample

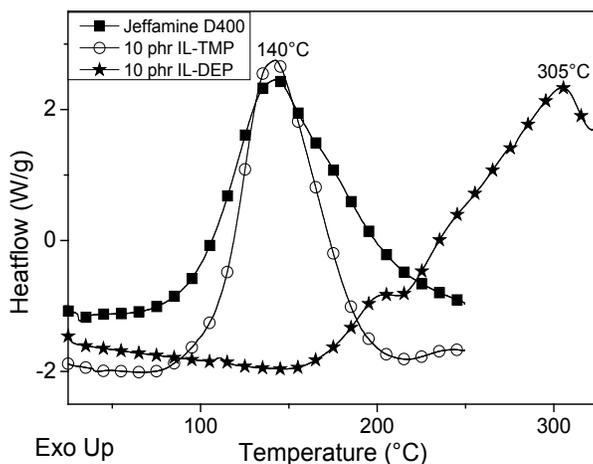
In both cases, all the samples are homogenous except the epoxy prepolymer containing 20 phr and 30 phr of IL-TMP where one exudation is observed. Samples of epoxy cured with 10 and 20 phr of IL-TMP are presented in Figure 2-3.



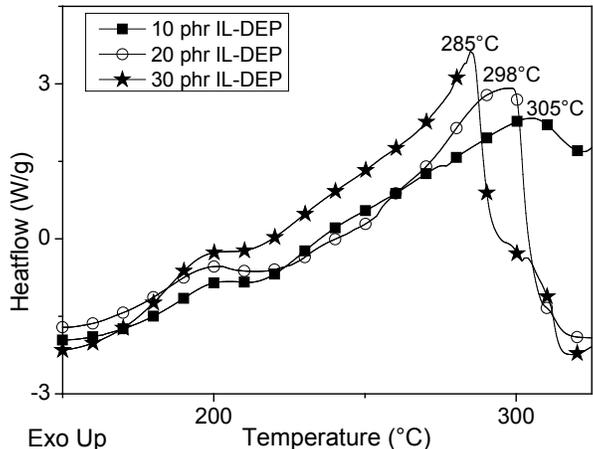
**Figure 2-3** Samples of epoxy prepolymer containing different amount of IL-TMP of (a) 10 phr and (b) 20 phr (Exudation of IL on the surface of samples with color change due to the oxidation).

### 2.3.1.2. Curing behavior of epoxy amine and epoxy/IL blends

The curing process of epoxy/curing agents mixtures was studied by DSC and FTIR techniques. The DSC thermograms of the corresponding blends are reported in Figure 2-4 and Figure 2-5. The DSC curves are performed under dynamical mode in the exotherm region.



**Figure 2-4** DSC thermograms of epoxy/Jeffamine D400 (■), epoxy/ 10 phr IL-TMP (○) and epoxy/ 10 phr IL-DEP (★).

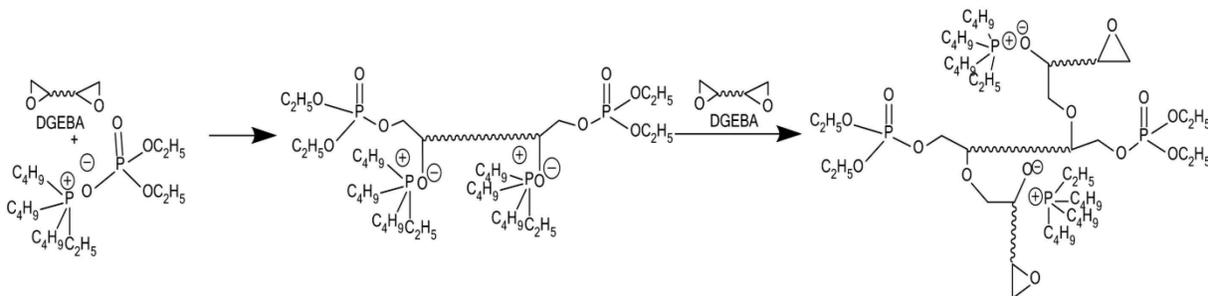


**Figure 2-5** DSC thermograms of epoxy/ 10phr IL-DEP (■), epoxy/ 20phr IL-DEP (○) and epoxy/ 30phr IL-DEP (★).

In both cases, the use of Jeffamine D400 or phosphonium ionic liquids combined with phosphate or phosphinate anions highlight an exothermic peak which clearly indicates the ability of comonomer to be used as a curing agent for epoxy prepolymer *i.e.* the conventional hardener but also ionic liquids. Thus, 10 phr of the ionic liquid coupled with phosphinate counter anion leads to the same exothermic temperature (140 °C) as the Jeffamine D400, conventionally used in the

preparation of epoxy/amine networks. These results clearly show that a small amount of IL (10 phr) is an excellent alternative to large amount of amines required for the crosslinking of the network (in this case, 66 phr of Jeffamine D400) and corroborate a previous study on epoxy systems based on ionic liquids.<sup>22</sup> Indeed, comparing the exothermic peak reported in literature for epoxy systems cured by other conventional amines, epoxy/ IL-TMP system containing 10 phr of IL gives an exothermic peak at similar temperature as that found for the system cured with 20 phr of 4,4-diaminodiphenylamine (DDA)<sup>45</sup> and at lower one than those found for systems cured with 30 phr of 4,4'-methylenedianiline (DDM) (176 °C),<sup>46</sup> or a mixture of aromatic imide-amines (180 – 230 °C).<sup>47</sup> In contrast, a large difference in reactivity between the two phosphonium ionic liquids (phosphate *vs.* phosphinate) was observed. In fact, an exothermic peak temperature of 305 °C is obtained when the phosphonium coupled with phosphate anion was used instead of 140 °C for IL combined with phosphinate counter anion. This difference of reactivity observed is due to the basicity of ionic liquids.<sup>39</sup> Indeed, the lower reactivity of the phosphate anion is due to its lower basicity compared to the phosphinate anion which has longer alkyl groups (Pentyl for IL-TMP *versus* ethyl for IL-DEP) inducing an inductive donor effect which leads to enrichment of electrons for the OH bond and makes very difficult the rupture of the OH bond. Thus, the phosphinate anion is more basic (higher pKa) compared with phosphate anion. The basicity of ionic liquid may also be presented by the Kamlet - Taft  $\beta$  parameter or the basic part of the tension surface of ILs. However, these values are not available in the literature for the phosphonium ILs used in this research.

Taking into account the similarity between the two ionic liquids, a mechanism was also suggested for the polymerization of epoxy prepolymer initiated by phosphate ionic liquid in Figure 2-6 according to the proposed mechanism with phosphinate ionic liquid presented in literature.<sup>22</sup> Thus, the basicity of the two counter anions initiates the polymerization of the epoxy prepolymer as others bases such as imidazoles or tertiary amines.<sup>30,48</sup>



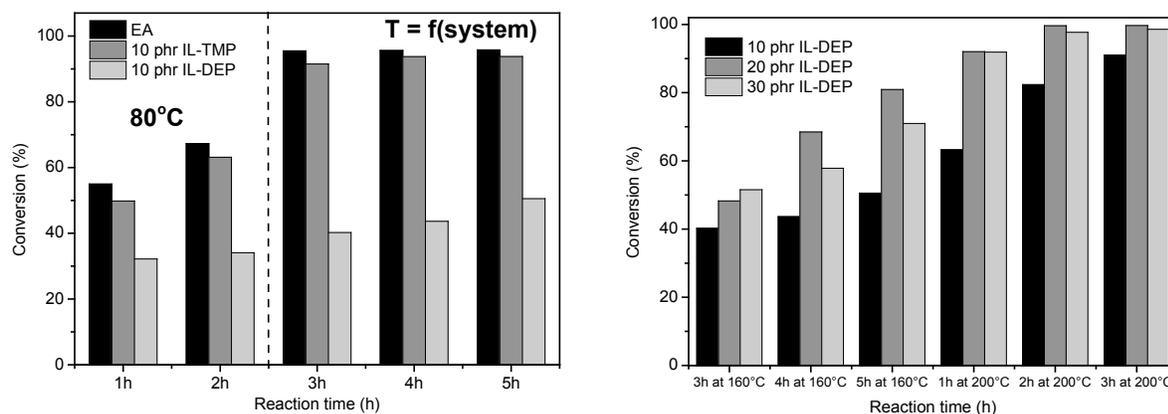
**Figure 2-6** Proposed curing mechanism for the polymerization of epoxy prepolymer initiated by phosphate ionic liquid.

In addition, Figure 2-5 presents the DSC thermograms of epoxy/IL-DEP blends containing different amounts of IL. Thus, an increase in the amount of IL-DEP (20 and 30 phr) leads to a decrease of only 20 °C of the exothermic peak (285 °C compared to 305 °C for 10 phr of IL).

In conclusion, the influence of the chemical nature of the counter anion plays a key role on the polymerization kinetics of epoxy prepolymer by using ionic liquid.

### 2.3.1.3. FTIR Analysis

In order to evaluate the effect of ionic liquid and to confirm the curing process, FTIR analysis was used to follow the reaction between DGEBA and the corresponding curing agents. All the epoxy/hardener blends were analyzed in the wavelength region of 800 – 1300  $\text{cm}^{-1}$  in which there are the absorption peaks corresponding to epoxide group at 914  $\text{cm}^{-1}$  and C–O group of the ether linkage at 1184  $\text{cm}^{-1}$ .<sup>22</sup> In addition, to follow the evolution of polymerization reaction, the IR spectra of epoxy networks were recorded at different time. The conversion of epoxide group was then calculated from the relation between two absorption peaks at 914  $\text{cm}^{-1}$  and 1184  $\text{cm}^{-1}$  based on the Equation 2-1).<sup>22</sup> Then the conversion of epoxide group versus reaction time was demonstrated in Figure 2-7 as a function of different curing agents (Figure 2-7a) *i.e.* Jeffamine D400, IL-TMP and IL-DEP while Figure 2-7b shows the influence of the amount of phosphonium ionic liquid combined with phosphate anion.



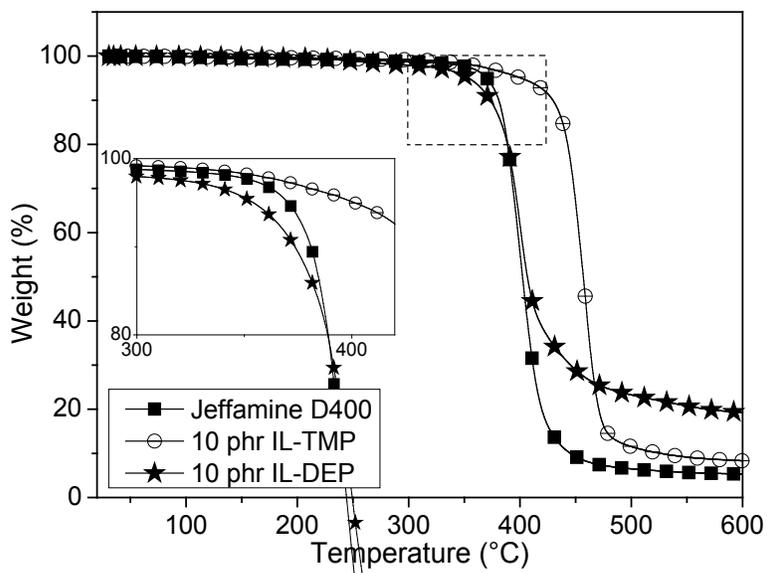
**Figure 2-7** Conversion of epoxide groups versus reaction time of (a) epoxy/different curing agents and (b) epoxy/different amounts of IL-DEP.

These results confirm that ionic liquids are able to cure the prepolymer with a conversion of epoxide group higher than 90 % after the full curing process. Also, in agreement with DSC results, the phosphonium ionic liquid with phosphate anion is less reactive than IL-TMP which leads to a system with the same reactivity as epoxy/Jeffamine D400 system. In Figure 2-7a, after 5 hours of curing at 160 °C, only 50 % of epoxide group was converted in the case of 10 phr of phosphate

ionic liquid. This result can explain why epoxy/phosphate ionic liquid blends need a longer curing process at higher temperature than other systems (see in Table 2-2). Furthermore, the effect of phosphate ionic liquid amounts on the epoxide group conversion was also investigated at 160 °C and 200 °C (Figure 2-7b). In fact, the increase of the amount of IL-DEP (10 phr and 20 phr) leads to an improvement of the conversion rate. Nevertheless, 30 phr of ionic liquid coupled with phosphate counter anion generates a slight decrease of the epoxy conversion rate. These results highlight a threshold value corresponding to a critical concentration of ILs in epoxy networks.<sup>22</sup> After reaching a critical concentration, a part of ionic liquid will not participate in the curing reaction but will act as a plasticizer agent.

#### 2.3.1.4. Thermal Stability of epoxy networks

The influence of the Jeffamine D400 and the ionic liquids on the thermal stability of epoxy networks was investigated by TGA. The weight loss (TGA) curves and the corresponding derivative curves (DTGA) as a function of temperature for different curing agents and different IL-DEP amounts were illustrated in Figure 2-8 and Figure 2-9, respectively. In addition, the thermal stability among these systems was also compared by determining the degradation temperature at 5 % and 10 % of weight loss and the maximum peak of DTGA with all the results are summarized in Table 2-3.

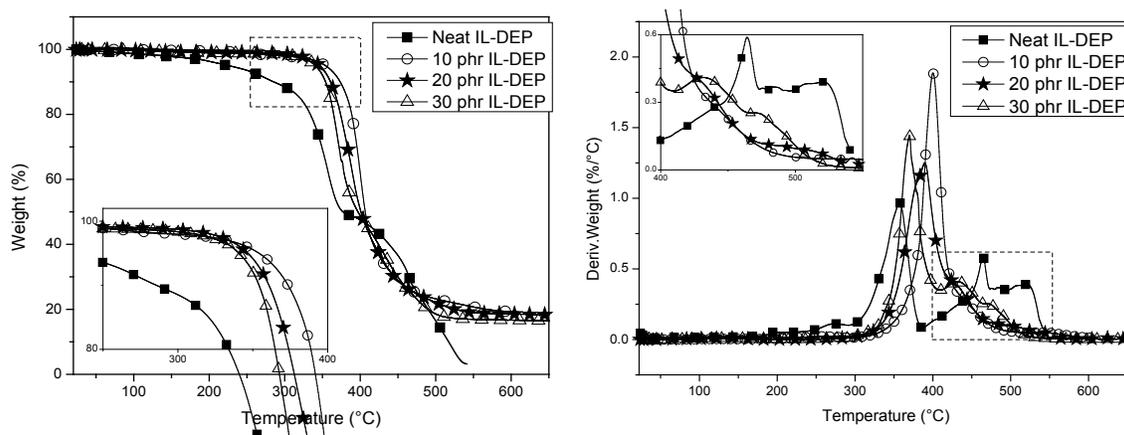


**Figure 2-8** Evolution of weight loss as a function of temperature (TGA) of epoxy networks with different curing agents: Jeffamine D400 (■), 10 phr IL-TMP (○) and 10 phr IL-DEP (★).

**Table 2-3** Decomposition temperatures  $T_d$  of different DGEBA networks under inert atmosphere.

System	$T_{d5\%}$ ( $^{\circ}\text{C}$ )	$T_{d10\%}$ ( $^{\circ}\text{C}$ )	$T_{d_{\max}} \text{DTGA}$ ( $^{\circ}\text{C}$ )
Jeffamine D400	370	381	400
10 phr IL-TMP	400	430	458
10 phr IL-DEP	354	373	400
20 phr IL-DEP	347	361	390
30 phr IL-DEP	341	354	370

In Figure 2-8, TGA analyses confirm the homogeneity of epoxy samples because one only step of degradation was observed in all cured systems. Moreover, in comparison with the conventional curing agent (Jeffamine D400), the use of phosphinate ionic liquid improves the thermal stability which leads to an increase of about  $50^{\circ}\text{C}$  of the degradation temperature at the maximum peak of DTGA curve ( $458^{\circ}\text{C}$ ). On the contrary, epoxy/IL-DEP at 10 phr presents nearly the same degradation temperature as that of epoxy system cured with Jeffamine D400. Also, a small change in the slope of TGA curves of DGEBA/10 phr IL-DEP is due to the degradation of the ionic liquid. These results are corroborated by the Figure 2-9 where a peak broadening is observed when the amount of ionic liquid is increased.

**Figure 2-9** Evolution of weight loss as a function of temperature (TGA, DTGA) of neat ionic liquid IL-DEP (■) and epoxy/IL-DEP networks: 10 phr (○), 20 phr (★) and 30 phr (Δ).

### 2.3.1.5. Hydrophobic behavior of epoxy networks

Surface energy was determined by sessile drop method on cured epoxy samples. The dispersive and non-dispersive components were calculated by using Owen-Wendt method<sup>42</sup> from the contact angles with water and diiodomethane and are presented in Table 2-4.

**Table 2-4** Determination of dispersive and non-dispersive components of the surface energy on epoxy/ amine and epoxy/ionic liquid network from contact angles with water and diiodomethane.

System	$\Theta_{\text{water}}$ ( $^{\circ}$ )	$\Theta_{\text{CH}_2\text{I}_2}$ ( $^{\circ}$ )	$\gamma_{\text{non-dispersive}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_{\text{dispersive}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_{\text{total}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )
Jeffamine D400	59.5	36.9	12.2	41.1	53.3
10 phr IL-TMP	91.4	44.4	1.0	37.3	38.3
10 phr IL-DEP	96.3	66.6	1.5	24.8	26.4
20 phr IL-DEP	102.6	63.6	0.4	26.5	26.9
30 phr IL-DEP	101.8	72.9	1.1	21.2	22.3

The DGEBA networks cured by the ionic liquids (phosphate and phosphinate) lead to the much more hydrophobic surfaces than DGEBA/Jeffamine D400 network. The use of ionic liquid results in a significant decrease of surface energy and in particular the non-dispersive component. In fact, the non-dispersive component of the conventional epoxy/amine networks ( $12.2 \text{ mJ}\cdot\text{m}^{-2}$ ) decreases to 1.0 and 1.5  $\text{mJ}\cdot\text{m}^{-2}$  by replacing Jeffamine D400 by 10 phr of phosphinate or phosphate ionic liquids, respectively. These results are also lower than those of epoxy matrix modified by fillers such as 3.5 phr of silica,<sup>49</sup> or 10 phr of CNTs.<sup>50</sup> This phenomenon can be explained by the hydrophobicity of phosphonium ionic liquid known to have low surface tension<sup>51</sup> (Table 2-1) due to the presence of long alkyl chains. In addition, the non-dispersive component of epoxy/ phosphate ionic liquids varies with the amount of ionic liquids. The increase of the IL amount decreases the total surface energy from  $26.4 \text{ mJ}\cdot\text{m}^{-2}$  (10 phr IL) to  $22.3 \text{ mJ}\cdot\text{m}^{-2}$  (30 phr IL), similar to a polyolefin surface.

### 2.3.1.6. DSC analysis of epoxy networks

DSC Analysis was also used to confirm the curing process and to determining the glass transition temperature ( $T_g$ ) of epoxy systems. The values of  $T_g$  were determined from the inflection point of endothermic stepwise change in the DSC heat flow at the third cycle and are listed in Table 2-5.

**Table 2-5** Variation of glass transition temperature  $T_g$  of DGEBA systems.

System	Jeffamine D400	10 phr IL-TMP	IL-DEP (phr)		
			10	20	30
$T_g(^{\circ}\text{C})$	44	141	110	108	93

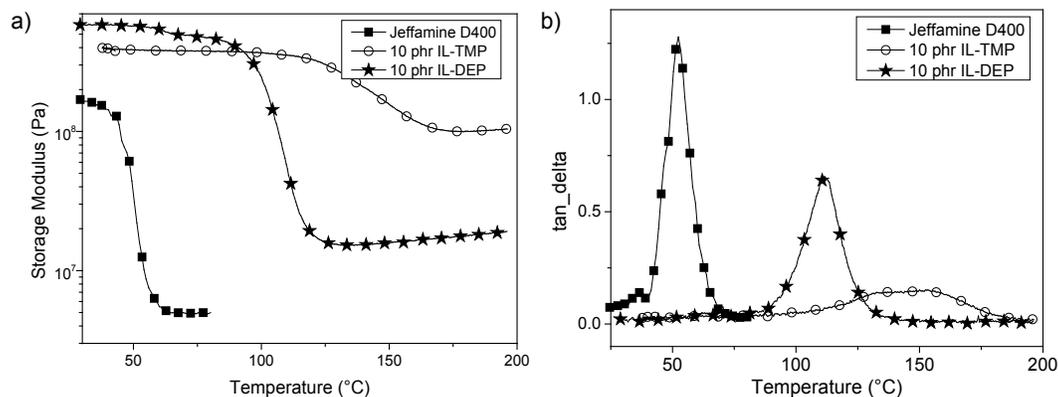
It is observed that the epoxy prepolymer cured with the ionic liquids leads to high glass transition temperatures ( $> 90^{\circ}\text{C}$ ). Moreover, the phosphinate ionic liquid induces a network with a higher crosslink density which is expressed by the highest  $T_g$  (141  $^{\circ}\text{C}$ ) among all systems. This value is also higher than the glass transition temperature measured by DSC of different systems described in the literature such as the DGEBA/TETA system, where a glass transition of 130  $^{\circ}\text{C}$  was obtained.<sup>52</sup> The effect of the amount of phosphate ionic liquid was also studied. A plasticizing effect of IL-DEP was observed since a decrease of the  $T_g$  is obtained with the increase of phosphate ionic liquid in the network. Thus, the glass transition temperature observed by DSC of epoxy systems containing 10 phr, 20 phr and 30 phr of IL-DEP were 110  $^{\circ}\text{C}$ , 108  $^{\circ}\text{C}$  and 93  $^{\circ}\text{C}$ , respectively. These results highlight that a quantity of ILs between 10 and 20 phr participates in the formation of the network whereas the remainder of the IL acts as plasticizer agent.

### 2.3.1.7. Dynamic Mechanical Properties of epoxy networks

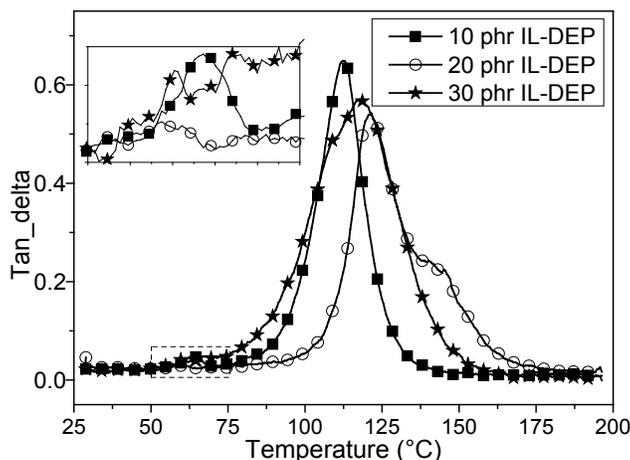
The effect of curing agents and the IL amount (10, 20, 30 phr) on the dynamic mechanical properties of epoxy networks was studied by DMA. Storage Modulus  $E'$  and loss factor  $\tan\delta$  curves obtained from DMA are presented in Figure 2-10 and Figure 2-11 as a function of curing agent but also as a function of the amount of phosphate ionic liquid, respectively. The relaxation temperatures ( $T_{\alpha 1}$  and  $T_{\alpha 2}$ ) from the maximum value of  $\tan\delta$ , storage modulus  $E'$  and maximum value of  $\tan\delta$  are listed in Table 2-6.

**Table 2-6** DMA values of epoxy/ amine and epoxy/ionic liquid systems (measurement rate of 3  $^{\circ}\text{C}\cdot\text{min}^{-1}$ ).

System	$T_{\alpha}$ ( $^{\circ}\text{C}$ ) Max $\tan\delta$		$E'$ (MPa)		$\tan\delta_{\text{max}}$
	$\alpha_2$	$\alpha_1$	Glassy state	Rubbery State	
Jeffamine D400	-	52	145	5	1.28
10 phr IL-TMP	-	150	391	104	0.14
10 phr IL-DEP	62	112	584	18	0.65
20 phr IL-DEP	62	121	520	13	0.54
30 phr IL-DEP	67	117	795	16	0.58



**Figure 2-10** Storage Modulus  $E'$  (a) and loss factor  $\tan\delta$  (b) as a function of temperature of DGEBA systems with different types of curing agent: Jeffamine (■), 10 phr IL-TMP (○) and 10 phr IL-DEP (★) from DMA with measurement rate of 3 °C.min<sup>-1</sup>.

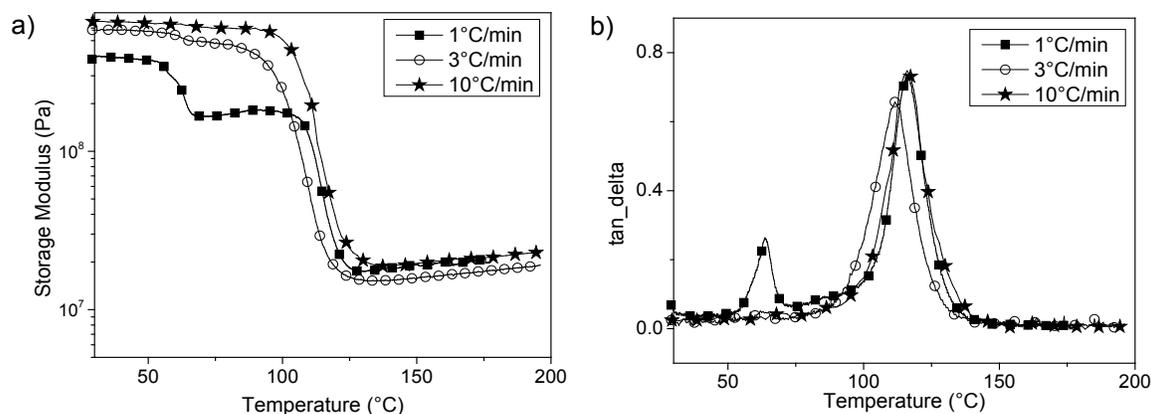


**Figure 2-11** Loss factor  $\tan\delta$  as a function of temperature of epoxy/phosphate ionic liquid IL-DEP at different contents: 10 phr (■), 20 phr (○) and 30 phr (★).

The storage modulus in the rubbery state and the maximum value of  $\tan\delta$  give information on the crosslink density of epoxy network.<sup>37</sup> The lowest storage modulus and the highest  $\tan\delta$  obtained for DGEBA/Jeffamine D400 suggest the lowest crosslink density and lead to lowest value of relaxation temperature at 52 °C. On the contrary, the epoxy/phosphinate network have the highest  $T_\alpha$  and the highest crosslink density in agreement with their storage modulus and their  $\tan\delta$  of 104 MPa and 0.14, respectively. In the case of epoxy/IL-DEP systems, the relaxation temperature and the crosslink density do not change dramatically with the percentage of ionic liquid. However, a plasticizing effect is also observed when 30 phr of IL-DEP are introduced in epoxy prepolymer. In fact, a decrease of  $T_\alpha$  and an increase of the value of  $\tan\delta$  are observed. This can be explained by the rise of the second phase corresponding to a second relaxation peak in the epoxy/IL networks.

The appearance of this second phase may be related to the appearance of the second network corresponding to the homopolymerization of the epoxy prepolymer. In addition, when 20 phr of ionic liquid combined with the phosphate counter anion is used; a shoulder peak is observed in the  $\tan\delta$  curve. This shoulder peak could correspond to the poor distribution of the free ionic liquid in the epoxy network. Then, from 30 phr, we can assume a better dispersion of the IL in the polymer matrix which induces a broader peak combined with a decrease of the glass transition temperature. In fact, above 20 phr of ionic liquid introduced into the epoxy network, ionic liquid acts as a plasticizer.

In order to investigate the second relaxation peak in the case of phosphate ionic liquid, a variation of measurement rate was investigated in the epoxy/IL networks. Thus, the samples were tested at different velocity of 1 °C, 3 °C and 10 °C per minute. Storage Modulus and  $\tan\delta$  curves of samples are illustrated in Figure 2-11 with the values of relaxation temperature ( $T_{\alpha 1}$ ,  $T_{\alpha 2}$ ), storage modulus  $E'$  and maximum value of loss factor  $\tan\delta$  listed in Table 2-7.

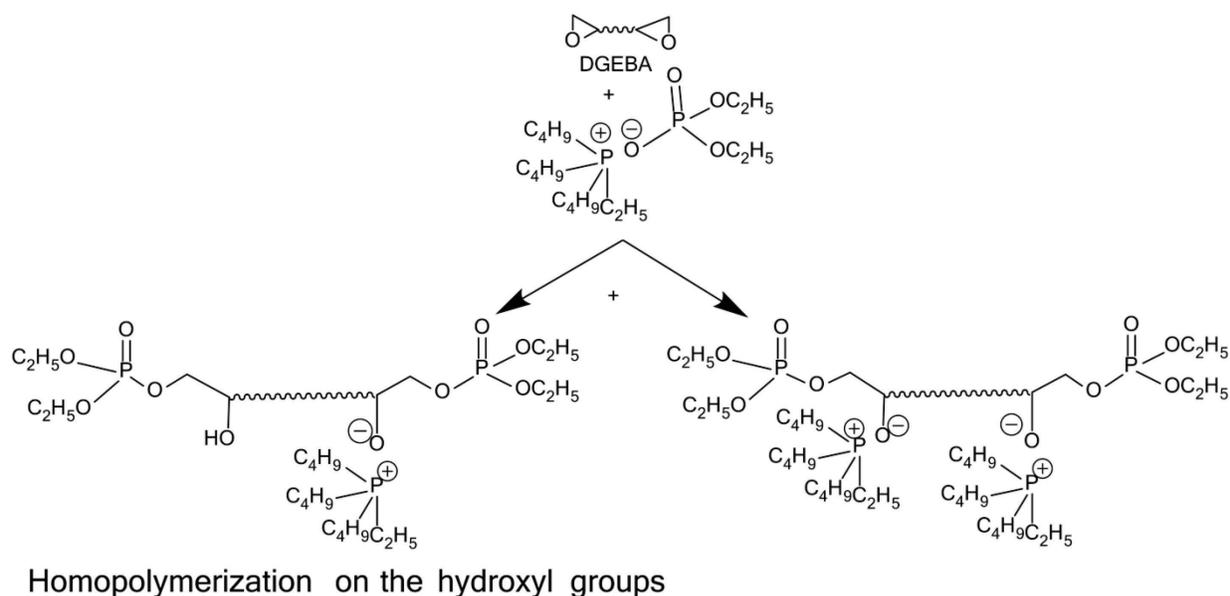


**Figure 2-12** Storage Modulus  $E'$  (a) and loss factor  $\tan\delta$  (b) as a function of temperature of epoxy/10 phr IL-DEP at different DMA measuring velocity: 1 °C.min<sup>-1</sup> (■), 3 °C.min<sup>-1</sup> (○) and 10 °C.min<sup>-1</sup> (★).

**Table 2-7** DMA Modulus value of DGEBA system with 10 phr of phosphate ionic liquid.

Methods	$T_{\alpha}$ (°C) Max $\tan\delta$		$E'$ (MPa)	Tan $\delta$ max
	$\alpha_2$	$\alpha_1$	Rubbery State	
1 °C.min <sup>-1</sup>	64	116	19.95	0.73
3 °C.min <sup>-1</sup>	62	112	18.00	0.65
10 °C.min <sup>-1</sup>	-	116	21.44	0.75

It is evident that the relaxation temperature corresponding to the glass transition, storage modulus  $E'$  at rubbery state and maximum value of  $\tan\delta$  of sample do not change with the measurement rate, which means that measurement rate does not influence the thermo-mechanical properties as well as the crosslink density of samples. However, when the temperature is slow, the second relaxation peak around 60 °C appears more clearly, because the polymer chains have more time to move and to relax and are more sensitive to the thermomechanical effect. As previously described, when 10 phr of ionic liquid denoted IL-DEP is introduced in the epoxy prepolymer, one competition between the homopolymerization of the epoxy network (by the presence of OH groups) and the formation of epoxy/ionic liquid network takes place (Figure 2-13). Thus, 20 phr of the ionic liquid leads to an improvement of the glass transition temperature  $T_g$  (Figure 2-11) due to the additional formation of ionic bonds  $O^-P^+$  which confirms the formation of epoxy/IL network.



**Figure 2-13** Proposed mechanism for the polymerization of phosphate ionic liquid with epoxy prepolymer.

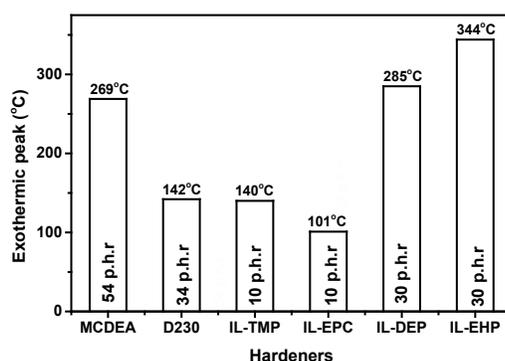
In conclusion, the thermo-mechanical analysis highlighted the key role of the chemical nature of the counter anion of the phosphonium ILs. In fact, the phosphinate anion (IL-TMP) acts as hardener of epoxy network while the phosphate anion (less reactive) also acts as a catalyst for the homopolymerization of the epoxy prepolymer. Thus, a larger amount of ionic liquid is required to prevent this reaction.

### 2.3.2. Effect of ILs nature on the design of Epoxy networks

This part will focus on the effect of the chemical nature of ILs on the design of epoxy/IL networks. Thus, four kinds of ILs will be concerned *i.e.* IL-TMP, IL-EPC, IL-DEP and IL-EHP. The amount of ionic liquids depending on the chemical structure of ILs was chosen based on previous study (2.3.1) on the use of ionic liquids combined with phosphinate and phosphate counter anions as initiator of the epoxy polymerization. The optimal concentrations was identified *i.e.* 10 phr (phosphinate) and 30 phr (phosphate) to obtain solid samples with better properties and without exudation phenomenon. In addition, the effect of IL amount was investigated for systems based on IL-EPC and IL-EHP using the same test described in Part 2.3.1. The results indicated the same reactivity of IL-EPC to IL-TMP and of IL-EHP to IL-DEP, respectively suggesting the use of the same amount of ILs *i.e.* 10 phr for IL-EPC and 30 phr for IL-EHP. The curing protocol was also tuned for each epoxy/IL system in order to complete the curing reaction and obtain the fully cured networks. Two different amines were chosen as the reference comonomers: Jeffamine D230 and 4,4'-methylene-bis 3-chloro-2,6-diethylaniline (MCDEA) based on their glass transition temperatures which are more similar to epoxy/IL networks than Jeffamine D400 of the previous part. The results presented below were published on the *ACS Sustainable Chemistry & Engineering*, 2016, Volume 4, Issue 2, Pages 481- 490.

#### 2.3.2.1. Reactivity of epoxy amine and epoxy/IL systems

The reaction kinetics of the epoxy/curing agents reactive systems were investigated using DSC from the reaction enthalpy. Thus, the position of exothermic enthalpy peak is illustrated in Figure 2-14.



**Figure 2-14** Reaction enthalpy peak temperature (DSC, 10 K.min<sup>-1</sup>) of different epoxy reactive systems.

Concerning epoxy combined with conventional diamines, exothermic peaks occurred at temperatures of 140 °C (with Jeffamine D230) and 269 °C (with MCDEA). This difference is

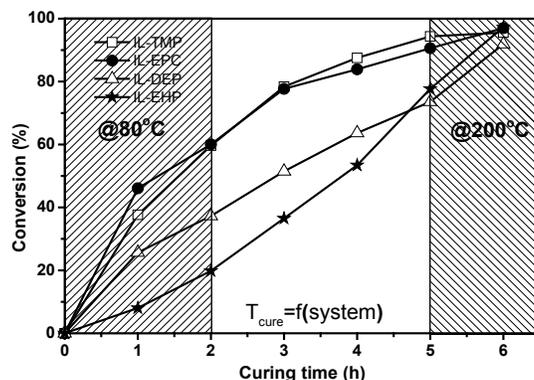
explained by the aromatic nature of the MCDEA, which requires higher curing temperatures compared to aliphatic Jeffamine D230.<sup>53</sup> In all the cases, phosphonium ILs combined with phosphinate, carboxylate, and phosphate counter anions induce reaction enthalpy highlighting the ability of ILs to act as initiators and hardeners of DGEBA epoxy prepolymer. Thus, 10 phr of IL-EPC (carboxylate) and IL-TMP (phosphinate) led to exothermic peaks at 100 and 140 °C, respectively. This result confirms our previous work on the use of IL-TMP as a hardener but demonstrates a better reactivity of IL-EPC.<sup>22</sup> In contrast, ILs combined with phosphate counter anions denoted IL-DEP and IL-EHP led to higher temperatures, *i.e.*, close to 285 and 344 °C, confirming a lower reactivity of these anions. These observations were reported in the previous part. Indeed, the reactivity of the ionic liquids is controlled by their basicity. Thus, ILs may be ranked according to their basicity in the following order: IL-EPC > IL-TMP > IL-DEP > IL-EHP, which corresponds to their reactivity. The basicity of ionic liquid may also be presented by the Kamlet-Taft  $\beta$  parameter or the basic part of the tension surface of ILs. However, these values are not available in the literature for the phosphonium ILs used in this research. Other authors have shown that the Lewis base such as imidazoles initiates a self-perpetuating anionic polymerization. The NMR analyses show that the imidazole participates in the formation of the network by covalent bonds, confirming the role of imidazole as a curing agent.<sup>54,55</sup> These results confirm the mechanisms that we have proposed in the previous works where the phosphinate and dicyanamide counter anions bind covalently to the network and initiate the polymerization.<sup>22,39</sup> However, compared to epoxy/amine networks where a stoichiometric composition is required to form and to obtain the optimum properties, the use of a small amount of ionic liquids is sufficient to prepare the epoxy/IL networks.

In conclusion, ILs are excellent alternatives to conventional amines as lower amounts are required for reaction: 10 phr for IL-TMP and IL-EPC, 30 phr for IL-DEP and IL-EHP compared to 34 phr for Jeffamine D230 and 54 phr for MCDEA. In addition, the reactivity of the phosphonium ILs plays a key role on the kinetics of polymerization, *i.e.*, on the formation of the epoxy network as well as on its final properties.

### **2.3.2.2. FTIR Analysis**

As the Jeffamine D230 and MCDEA amines have been widely studied as epoxy hardeners in the literature,<sup>56-58</sup> only the influence of ILs are discussed in this section. To highlight the influence of the chemical nature of the ionic liquid and to investigate precisely the reaction paths, FTIR analysis was used to follow the reaction between epoxy prepolymer (DGEBA) and ILs. Thus, FTIR spectra of each system were recorded at different reaction times during curing. The epoxide group

conversion of different epoxy/IL systems calculated according to  $\chi\% = \frac{(A^o - A^t)}{A^o} \times 100\%$  (Equation 2-1) is presented in Figure 2-15 as a function of curing time.

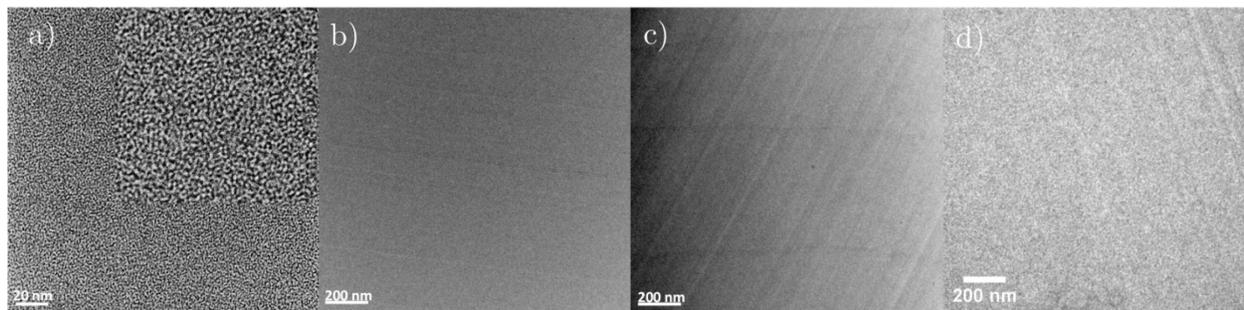


**Figure 2-15** Epoxide group conversion as a function of curing time calculated from FT-IR spectra of different epoxy/IL systems during cure (see Table 2-2 for curing schedules which differ for each reactive system).

As expected, FTIR spectra of epoxy/IL mixtures during the reaction show a decrease of absorption peak at  $914\text{ cm}^{-1}$  corresponding to epoxide group justifying the opening of epoxide ring during curing process.<sup>22,39</sup> At the end of each curing protocol, this absorption peak was nearly disappeared suggesting a total conversion. In fact, a constant increase in the conversion of the epoxide groups is observed in Figure 2-15 to achieve at 6 h a conversion of about 90 % for all the epoxy/IL blends. However, for the same curing time (1 h at 80 °C), epoxy systems based on IL-TMP and IL-EPC (10 phr) have exhibited a higher conversion of epoxide groups (40 % and 50 %) and are in the solid state compared to epoxy networks with 30 phr of IL-DEP and IL-EHP (30 % and 10 %). In addition, the curing conditions of epoxy/IL networks are different depending of the chemical nature of the ILs: 3 h at 180 and 160 °C as well as a post-curing at 200 °C during 3 h are required for IL-EHP and IL-DEP, respectively. In contrast, 3 h at 120 °C and 1h at 200 °C are necessary for IL-TMP and IL-EPC. These results still show the best reactivity of epoxy systems containing IL-TMP and IL-EPC as all the reactive systems were cured at 80°C for the two first hours (confirming the DSC analysis). This analysis also demonstrates that after curing schedule completion, the epoxy conversion is higher than 90 %.

### 2.3.2.3. Morphology of the resulting epoxy networks

To reveal a possible structuration of ILs in the epoxy networks, transmission electronic microscopy (TEM) is the suitable tool. TEM micrographs of epoxy cured with IL-TMP, IL-EPC, ILDEP, and IL-EHP are presented in Figure 2-16.



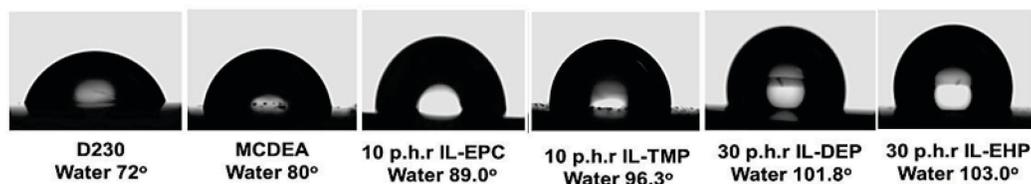
**Figure 2-16** TEM micrographs of IL-EPC (a), IL-TMP (b), IL-DEP (c) and IL-EHP (d) networks.

In the case of epoxy systems containing IL-TMP (10 phr), IL-DEP (30 phr), and IL-EHP (30 phr), no phase separation is observed, which could be attributed to *i*) good miscibility between the ionic liquid and the epoxy prepolymer along the reaction as well as *ii*) a slight difference in electronic densities between phases which prevents their identification.<sup>39</sup> Nevertheless, in contrast, IL-EPC led to a (nano)phase separation characterized by the appearance of small IL inclusions due to the limited miscibility between the phosphonium salt and the growing epoxy polymer during curing (Figure 2-16, left). This phenomenon is commonly encountered in the modified reactive systems (thermosets) using elastomers, thermoplastics, or block copolymers.<sup>59-63</sup>

ILs have a similar behavior to ionomers that are polymers in which a relatively small number (up to 15 %) of the monomer units consist of ionic moieties.<sup>64,65</sup> The morphology of such ionomers consists of small dispersed ionomer particles embedded in the polymer matrix when the ionomer constitutes the minor phase. It is well known that the polar ionic groups of the ionomer tend to form aggregates, commonly referred to as multiplets and clusters. Multiplets are considered to consist of a small number of interacting ion pairs; whereas clusters are thought to arise from overlapping regions of restricted mobility surrounding multiplets.<sup>66</sup> With a similar behavior to ionomers, ILs open a new route in the preparation of nanostructured thermosets.

#### **2.3.2.4. Surface properties of epoxy networks**

The surface energy of epoxy networks was determined by the sessile drop method. Then, the dispersive and non-dispersive components of the epoxy networks were calculated by using the Owens–Wendt method from the contact angles with water (Figure 2-17), and diiodomethane and are summarized in Table 2-8.



**Figure 2-17** Contact angle with water on surfaces of epoxy networks cured with different types of IL and different ILs amount.

**Table 2-8** Contact angles and surface energy of epoxy networks measured by sessile drop method.

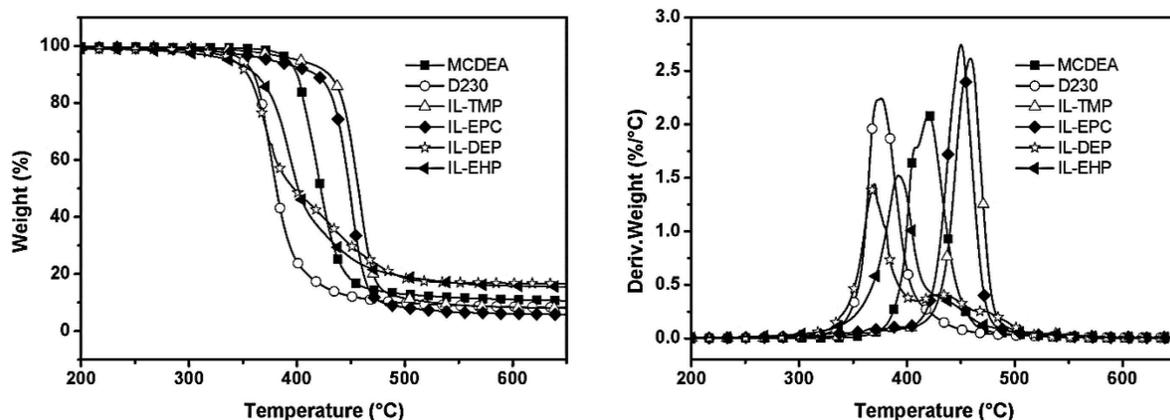
System	$\Theta_{\text{water}}$ ( $^{\circ}$ )	$\Theta_{\text{CH}_2\text{I}_2}$ ( $^{\circ}$ )	$\gamma_{\text{non-dispersive}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_{\text{dispersive}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_{\text{total}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )
MCDEA	81	50	4.5	29.8	34.3
D230	72	50	9.2	27.5	36.7
IL-TMP	91	44	1.0	37.3	38.3
IL-EPC	89	62	3.0	24.4	27.4
IL-DEP	102	73	1.1	21.2	22.3
IL-EHP	103	69	0.3	23.1	23.4

The incorporation of ILs, whatever their chemical nature (ILTMP, IL-EPC, IL-EHP, and IL-DEP) as hardeners in the epoxy prepolymer (DGEBA), induces a more significant hydrophobic behavior compared to conventional epoxy/amine networks. These results are explained by the hydrophobic nature of ionic liquids that is characterized by surface energy values from 29 to 33  $\text{mJ}\cdot\text{m}^{-2}$ <sup>51,67</sup> (Table 2-1). Slight differences are observed depending on the chemical nature of the ionic liquids. Indeed, among the ionic liquids IL-EPC, IL-EHP, and IL-TMP having the same phosphonium cation, the use of IL-EPC (with  $\text{COO}^-$  group) leads a relatively higher non-dispersive component (3  $\text{mJ}\cdot\text{m}^{-2}$ ). On the opposite, IL-EHP and IL-TMP generate a reduction in the non-dispersive component of epoxy systems due to the presence of long alkyl chains on the phosphinate (1  $\text{mJ}\cdot\text{m}^{-2}$ ) and phosphate (0.3  $\text{mJ}\cdot\text{m}^{-2}$ ) counter anions. Thus, the chemical nature of the ILs also plays a key role in the hydrophobic behavior of thermosets.

In conclusion, the use of ionic liquids as reactive additives of epoxy matrix could open new perspectives in the development of coatings having a hydrophobic surface, similar to a polyolefin surface.

### 2.3.2.5. Thermal behavior of epoxy networks

The influence of the conventional amines and phosphonium ILs on the thermal stability of epoxy networks was investigated by thermogravimetric analysis (TGA). The evolution of the weight loss as a function of the temperature of all the epoxy networks is presented in Figure 2-18.



**Figure 2-18** Weight loss as a function of temperature (TGA, DTGA) of epoxy networks: MCDEA (■), Jeffamine D230 (○), IL-TMP (△), IL-EPC (◆), IL-DEP (☆) and IL-EHP (◄) (heating ramp 20 K.min<sup>-1</sup>, N<sub>2</sub> atmosphere).

In all the cases, the TGA curves highlight an excellent thermal behavior of the epoxy/amine and epoxy/IL networks, *i.e.*, degradation temperature at maximum of DTG curve of over 350°C. In the case of epoxy cured with Jeffamine D230 and MCDEA, the thermal degradation temperatures of 375 and 418 °C are obtained. According to the literature, this higher degradation temperature (418 °C) for the epoxy/MCDEA system is explained by the presence of aromatic groups.<sup>68</sup> Concerning the epoxy networks based on 10 phr of phosphonium ILs, *i.e.*, IL-TMP and IL-EPC, the degradation temperatures determined at the maximum of the DTG peaks are included between 450 and 460 °C. However, the use of ionic liquids combined with phosphate counter anions, denoted IL-EHP and IL-DEP (30 phr) leads to lower degradation temperatures of 390 and 370 °C, respectively. The slight improvement of IL-EHP thermal stability is due to the functionalization of IL by long alkyl chains on the cation but also on the counter anion (Figure 2-18). Thus, two types of behavior are observed: epoxy cured with IL-EHP and IL-DEP have a similar thermal behavior to an epoxy/Jeffamine network whereas the use of IL-EPC and IL-TMP as hardeners leads to a better thermal stability (+40 °C) compared to the thermostable epoxy/MCDEA network. This difference in thermal behavior between the epoxy/IL systems is attributed to their chemical nature but also to the amount of ionic liquid introduced (10 phr for IL-EPC and IL-TMP; 30 phr for IL-DEP and IL-EHP). Indeed, the use of a larger amount of ionic

liquids denoted IL-DEP and IL-EHP generates more free ionic liquids in epoxy systems acting as plasticizers.<sup>39</sup> Thus, this phenomenon may explain the better thermal stability of epoxy/IL networks based on IL-TMP and IL-EPC.

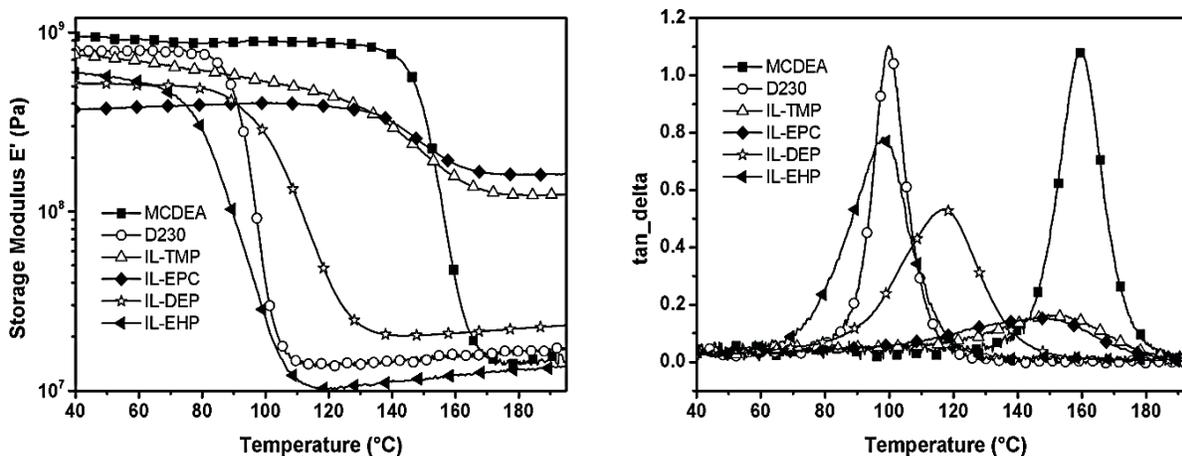
In conclusion, phosphonium ionic liquids are an excellent alternative as curing agents to conventional amines. In fact, the use of these new curing agents leads to very thermally stable epoxy networks and the presence of phosphorus compound could be an asset to the fire properties of these systems. Moreover, lower amounts of ionic liquids are required (10 phr for IL-EPC and IL-TMP and 30 phr for IL-EHP and IL-DEP) compared to stoichiometric ratios of 34 phr and 54 phr for diamines, *i.e.*, Jeffamine D230 and MCDEA.

### 2.3.2.6. Dynamic Mechanical properties of epoxy networks

The influence of the chemical nature of the curing agents (diamines versus ILs) on the dynamical mechanical properties of epoxy networks was investigated by DMA. The temperature of  $\alpha$ -relaxation related to the glass transition  $T_\alpha$  from the maximum of  $\tan\delta$  as well as the storage modulus,  $E'$ , in the rubbery state ( $E'_R$ ) are listed in Table 2-9 and the DMA spectra are given in Figure 2-19. In addition, crosslink density,  $\nu_e$ , ( $\text{mol.m}^{-3}$ ) of epoxy networks (assuming homogeneous

networks) was also estimated using the elasticity theory:<sup>40,69,70</sup>  $\nu_e = \frac{E'_R}{3RT_R}$  (Equation 2-6).

Where  $E'_R$ (Pa) is storage modulus determined in the rubbery state, *i.e.*, at  $T_R = T_\alpha + 30$  (K) and R is ideal gas constant ( $R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ ).



**Figure 2-19** Storage modulus  $E'$  and loss factor  $\tan\delta$  as a function of temperature of DGEBA-based networks cured with different types of curing agent: MCDEA (■), Jeffamine D230 (○), IL-TMP (△), IL-EPC (◆), IL-DEP (☆), and IL-EHP (◄) at 1Hz.

**Table 2-9** Thermo-mechanical behavior of epoxy networks cured by different curing agents.

System	$T_{\alpha}^a$ (°C)	$E'_R{}^b$ (MPa)	$\nu_e^c$ (mol.m <sup>-3</sup> )
MCDEA	160	16	1,385
D230	100	16	1,591
IL-TMP	150	104	9,201
IL-EPC	144	124	11,121
IL-DEP	117	16	1,527
IL-EHP	98	14	1,399

<sup>a</sup>  $\alpha$  Relaxation Temperature from DMA at 1Hz

<sup>b</sup> Rubbery state storage modulus from DMA, determined at  $T_{\alpha} + 30$  (K)

<sup>c</sup> Crosslink density calculated from DMA

For all epoxy systems, DMA spectra display only one relaxation peak suggesting the homogeneity of epoxy networks. Even, in the case of IL-EPC, the phase separation observed by TEM micrographs cannot be evidenced with an additional relaxation peak in DMA spectrum.

The glass transition temperatures (considering  $T_{\alpha}$  value) and crosslink densities of the epoxy/amine systems (MCDEA and D230) are in agreement with the literature.<sup>31,71-73</sup> The same ranges of crosslink density (1,400-1,600 mol.m<sup>-3</sup>) are obtained for the two amines. As expected, MCDEA cured epoxy networks have higher  $T_{\alpha}$  (160 °C) compared to Jeffamine D230 cured epoxy networks (100 °C). This difference of  $T_{\alpha}$  is mainly due to the more rigid and more hindered structure of MCDEA based on aromatic rings preventing chain mobility and increasing the glass transition temperature.<sup>74</sup>

In the cases of epoxy/IL networks, two different behaviors have been observed. In fact, epoxy networks cured by phosphate ILs (IL-DEP and IL-EHP) display almost the same glass transition region as Jeffamine D230, *i.e.* 100-110 °C while epoxy networks cured by IL-TMP and IL-EPC are close to epoxy/MCDEA networks with  $T_{\alpha}$  above 140 °C. Moreover, the crosslink density of epoxy networks filled with IL-EPC (11,121 mol.m<sup>-3</sup>) and IL-TMP (9,201 mol.m<sup>-3</sup>) are significantly higher compared to epoxy/MCDEA networks and epoxy networks based on phosphate -ILs. In the case of phosphate counter anions based ILs, *i.e.* IL-EHP and IL-DEP, the long alkyl chains of IL-EHP increase the flexibility of epoxy/IL networks leading to lower  $T_{\alpha}$  compared to IL-DEP-based epoxy network one.

Overall, the chemical nature of the ionic liquid controls the formation and the final properties of epoxy networks.

### 2.3.2.7. Mechanical behavior of epoxy networks

The mechanical properties such as the flexural properties and the fracture toughness,  $K_{Ic}$ , of epoxy networks were investigated. As the mechanical tests require thick samples, the low reactivity of IL-EHP did not allow to process the samples. As a consequence, only the epoxy/amine and epoxy/IL networks containing IL-TMP, IL-EPC, and IL-DEP were studied.

#### 2.3.2.7.1. Fracture Toughness ( $K_{Ic}$ )

The values of the critical stress intensity factor  $K_{Ic}$  were measured for epoxy/amine and epoxy/IL networks (Table 2-10).

**Table 2-10** Mechanical behavior (determined at room temperature) of epoxy networks cured by different curing agents.

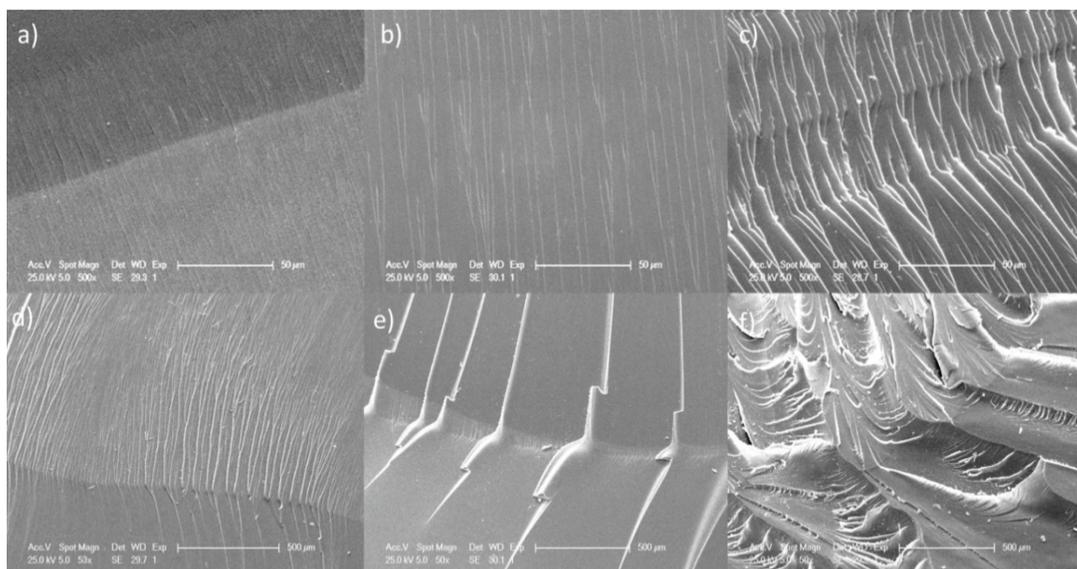
System	$E_f^a$ (GPa) $\pm 0.1$	$\sigma_R^b$ (MPa) $\pm 4$	$K_{Ic}$ (MPa.m <sup>1/2</sup> ) $\pm 0.05$
MCDEA	2.3	77	0.56
D230	2.7	82	1.05
IL-TMP	1.6	25	0.39
IL-EPC	2.4	50	0.37
IL-DEP	2.2	69	0.64
IL-EHP	-	-	-

<sup>a,b</sup>Flexural modulus and Flexural Strength from Flexural Tests

In the case of epoxy networks cured with Jeffamine D230 and MCDEA, the values of the fracture toughness are similar to those reported in the literature. In fact, many authors reported  $K_{Ic}$  values of about of 0.60 MPa.m<sup>1/2</sup> and 1.24 MPa.m<sup>1/2</sup> for epoxy/MCDEA and epoxy/Jeffamine networks, respectively.<sup>75-78</sup> This difference in the mechanical behavior between the two diamine hardeners provides from their different chemical structure. Indeed, the aromatic amine, *i.e.* MCDEA which has a rigid structure and a high steric hindrance leads to the formation of a more brittle epoxy network while the aliphatic amine, *i.e.* Jeffamine D230, composed of long ether chains induces a more flexible epoxy system confirming its higher value of the fracture toughness.

The fracture toughnesses of the epoxy/IL networks containing IL-EPC and IL-TMP are in the same range whereas the epoxy system based on IL-DEP has a higher  $K_{Ic}$  of  $0.64 \text{ MPa}\cdot\text{m}^{1/2}$ . This difference in fracture toughness between epoxy/IL networks is related to their crosslink densities. In fact, the epoxy/IL networks having the highest crosslink densities (IL-EPC and IL-TMP) are more brittle than the epoxy/MCDEA network. In fact, Chang and Brittain have shown a general trend in which an increase in the crosslink density has led to a decrease in fracture toughness.<sup>79</sup> Other authors have also reported the same phenomenon on epoxy/amine networks in the literature.<sup>80-85</sup> However, the relationship between the crosslink density of a network and the fracture toughness remains ambiguous knowing as several other parameters are also involved such as chain flexibility, free volume, and intermolecular packing.

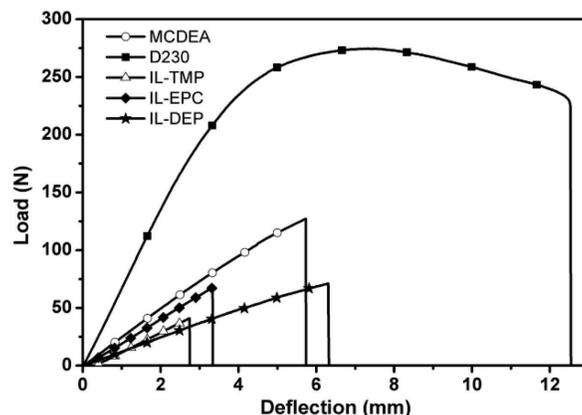
SEM micrographs of fractured surface after crack initiation and catastrophic failure are presented in Figure 2-20. Two types of fracture behaviors are evidenced depending on the nature of curing agents used. Indeed, the fracture surfaces of brittle networks, *i.e.* IL-EPC, IL-TMP and MCDEA are very smooth which can be denoted as mirror-like fracture surfaces (Figures 2-20a, 2-20b, and 2-20c). On the opposite, epoxy cured with Jeffamine D230 and also IL-DEP show a very rough fracture surface with ridges, river marks, and tortuous cracks (Figure 2-20e, 2-20f). According to the literature, such features are the signature of a higher energy for the crack propagation, *i.e.* a higher fracture toughness.<sup>44,86</sup>



**Figure 2-20** Fractured surfaces of epoxy networks cured with IL-EPC (a), IL-TMP (b), and MCDEA (c) at magnification of  $\times 500$  (up) and MCDEA (d), IL-DEP (e) and D230 (f) at magnification of  $\times 50$  (down).

2.3.2.7.2. Flexural properties

The flexural modulus and the flexural strength of epoxy/amine and epoxy/IL networks are summarized in Table 2-10. The load-deflection traces are also given in Figure 2-21.



**Figure 2-21** Load-deflection curves of epoxy/different curing agents: MCDEA (○), Jeffamine D230 (■), IL-TMP (△), IL-EPC (◆) and IL-DEP (★) (2 mm.min<sup>-1</sup>).

Overall, the obtained values of the flexural modulus and flexural strength for the epoxy cured with Jeffamine D230 and MCDEA are close to the values reported in the literature<sup>44,86-90</sup>. Thus, the addition of the flexible amine (Jeffamine D230) leads to a ductile behavior with a high flexural modulus of 2.7 GPa while the use of the aromatic amine (MCDEA) displays a brittle behavior with a lower Flexural Modulus (2.30 GPa).

Then, the addition of ILs as reactive additives leads to the formation of stiff epoxy networks. Indeed, a similar behavior to the conventional system using MCDEA is obtained for epoxy cured with IL-EPC (2.4 GPa) and IL-DEP (2.2 GPa). Only the network containing IL-TMP displays a very different behavior with a lower value of flexural modulus (1.6 GPa).

In conclusion, these first results on the mechanical performances such as the flexural properties and the fracture toughness of epoxy/IL networks have shown similar results to an epoxy prepolymer cured with MCDEA. Thus, it becomes possible to replace the conventional diamine hardeners by ionic liquids. Depending on the numerous cation/anion combinations, this new route for the preparation of epoxy networks looks very promising.

### 2.3.3. Conclusion

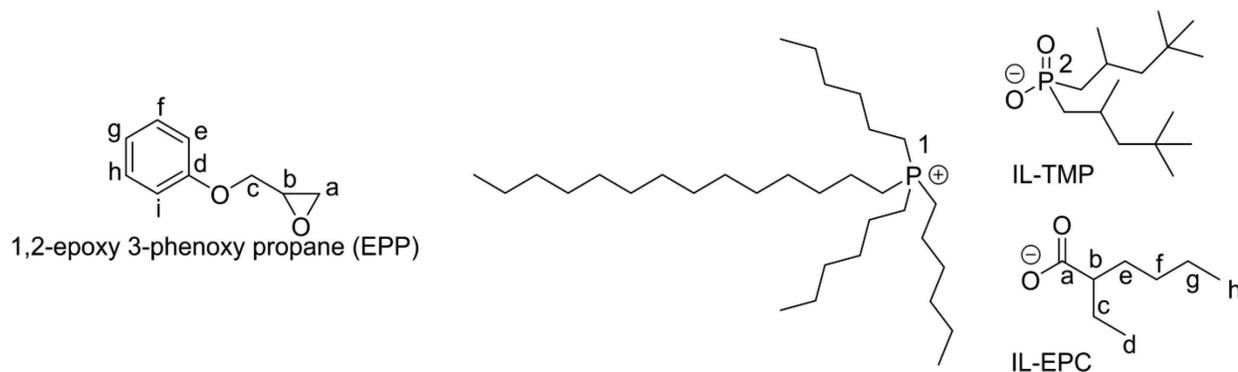
In conclusion, different phosphonium ionic liquids were studied as new curing agents of epoxy prepolymer and were compared to epoxy cured with conventional aliphatic or aromatic diamines

(Jeffamine D230, Jeffamine D400 and MCDEA). Thus, we demonstrated that a small amount of ILs (from 10 to 30 phr) could lead to the formation of epoxy/IL networks with improved final properties. In fact, the use of ionic liquids as reactive additive leads to poly-epoxy networks with excellent thermal properties ( $> 350$  °C), glass transition temperatures tunable between 90 and 150 °C as well as highly hydrophobic networks. Furthermore, in terms of mechanical properties, the values of the fracture toughness and flexural moduli are similar to epoxy/MCDEA networks. In summary, ILs open a new route for the design of new epoxy networks. Nevertheless, further studies are required to demonstrate the real relevancy of ionic liquids as comonomers in thermosetting materials.

## 2.4. Polymerization Mechanism between phosphonium ionic liquids and the epoxide functional group of epoxy prepolymer

### 2.4.1. Introduction and materials

In this chapter, we have shown that the use of phosphonium ILs represents a new alternative to conventional amines used as curing agents (comonomers) of epoxy prepolymer. In fact, our research has demonstrated that phosphonium ILs combined with basic counter anions such as carboxylate, phosphinate or phosphate anions led to new epoxy/IL networks. However, no proofs confirm the anionic polymerization mechanism and due to the high crosslink density of epoxy/IL networks, liquid NMR is not possible. In order to better understand the reaction between epoxy prepolymer and the counter anion of IL, a modeling of the reaction was considered by using a mono-epoxy. Thus, a mono-epoxy denoted 1,2-epoxy 3-phenoxy propane (EPP) with a similar structure to DGEBA was used to react with phosphonium ionic liquids combined with carboxylate (IL-EPC) and phosphinate (IL-TMP) counter anions (see Figure 2-22).



**Figure 2-22** Chemical structures of phosphonium ILs (IL-EPC, IL-TMP) and mono-epoxy denoted 1,2-epoxy-3-phenoxypropane (EPP).

### 2.4.2. Preparation of samples

EPP was mixed with 30 phr of phosphonium ILs at room temperature. In all the cases, the amounts of IL-TMP, and IL-EPC were chosen to be higher than stoichiometry given in Part 2.3 (see Table 2-2) in order to improve the signals of ILs analyzed by liquid NMR. The epoxy/IL mixtures were then cured according to the protocol described in Part 2.1, *i.e.* 2h at 80 °C and 3h at 120 °C for EPP/IL-TMP and EPP/IL-EPC. In all the cases, samplings were made at different times to follow the reaction. In addition, various methods have been used to characterize epoxy/IL mixtures (TGA, DSC, FTIR, SEC and NMR).

### 2.4.3. Characterization of epoxy/IL mixtures

*Differential Scanning Calorimetry* thermograms (DSC) of epoxy networks samples were performed on DSC Q20 TA instruments from 20 to 250 °C at a rate of 10 K.min<sup>-1</sup> under nitrogen flow of 50 mL.min<sup>-1</sup>.

*Thermogravimetric Analyses* (TGA) of epoxy networks were carried out using a Q500 Thermogravimetric analyzer (TA instruments) from 30 to 700 °C at a heating rate of 20 K.min<sup>-1</sup> under nitrogen.

*Size-exclusion chromatography* (SEC) was carried out in THF with 3 Shimadzu Stryragel HR 5E columns in series (35°C, 1ml.min<sup>-1</sup>) with Shimadzu UFLC pump using RID-10A detection. Molar mass  $M_n$  was calculated using PS standard calibration.

*Fourier transform infrared* (FTIR) absorption spectra (32 scans, 4 cm<sup>-1</sup>) were recorded on a Thermo Scientific Nicolet iS10 spectrometer in transmission mode in the wavelength range of 4000 to 500 cm<sup>-1</sup>.

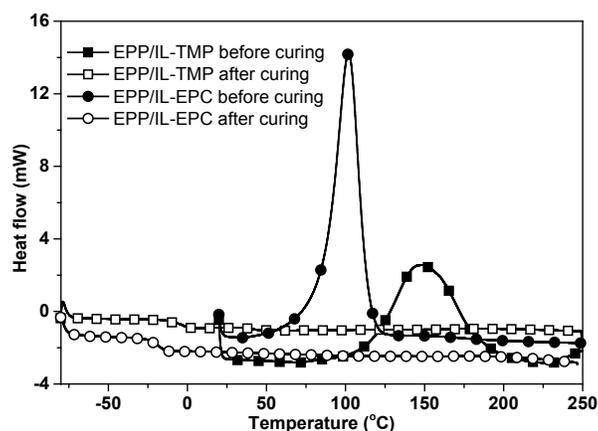
<sup>13</sup>C, <sup>1</sup>H and <sup>31</sup>P *Nuclear magnetic resonance* (NMR) spectra were recorded using a Bruker Avance 400 spectrometer (resp. 400, 100 and 162 MHz) in CDCl<sub>3</sub>. In particular, <sup>31</sup>P NMR spectra of IL-TMP and EPP/IL-TMP mixtures were prepared directly in NMR tube with co-axial tube containing DMSO to avoid the solvation effect on NMR peaks. However, this method can only be used before gel time of the epoxy/IL mixtures due to the increase of system viscosity. Moreover, NMR peak shifting was confirmed by NMR prediction tool provided by Chemdraw, PerkinElmer Informatics, United States.

## 2.4.4. Results and discussion

### 2.4.4.1. Curing behavior of mono-epoxy and IL systems (blends or cured materials)

The curing behavior of EPP with IL-TMP and IL-EPC was investigated using DSC, TGA and SEC.

DSC analysis test revealed the reactivity of ILs towards EPP and confirmed the completion of the curing reaction. In fact, DSC thermograms of EPP/IL systems (IL-TMP and IL-EPC) before and after the curing protocol were presented in Figure 2-23. Thus, exothermic peaks at 149 °C and 102 °C were obtained for EPP/IL-TMP and EPP/IL-EPC blends before the curing procedure, respectively suggesting high reactivity of IL with EPP. Moreover, these temperature values are similar to DGEBA/ILs systems *i.e.* 140 °C and 101 °C for systems containing IL-TMP and IL-EPC, respectively (Part 2-3). These values once again confirm the higher reactivity of IL-EPC than IL-TMP thanks to the higher basicity of carboxylate anion. The disappearance of these peaks after curing step clearly indicates the completion of curing reaction which forms EPP/ILs oligomers with low  $T_g$  below 0 °C.



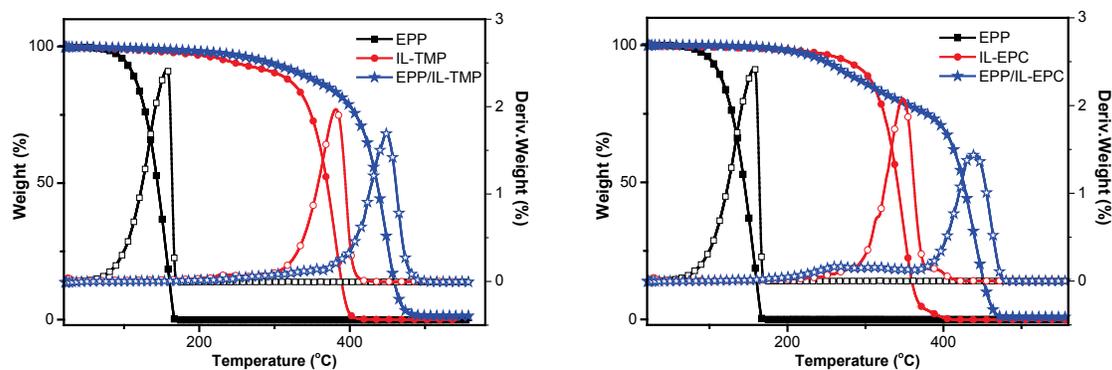
**Figure 2-23** DSC thermogram of EPP/IL-TMP (■, □) and EPP/IL-EPC (●, ○) systems: before (■, ●) and after the curing procedure (□, ○).

Thermogravimetric (TGA) analysis was also carried out on neat ionic liquids and EPP compounds as well as on the EPP/ILs after curing protocol. TGA and DTGA curves are presented in Figure 2-24 and the degradation temperatures at 5 %, 10 % of weight loss and at the maximum of DTGA curve are listed in Table 2-11. The formation of a new product based on EPP and ILs is confirmed by the observed degradation temperatures such as the maximum degradation temperature at over 440 °C. These values are much higher than degradation temperature of neat materials (EPP and ILs) and are similar to the degradation peak of DGEBA/ILs networks based

on IL-TMP and IL-EPC. In summary, these results highlighted that phosphonium ionic liquids *i.e.* IL-TMP and IL-EPC can react with epoxide group in order to form a network in the case with DGEBA or an oligomer in the case of EPP.

**Table 2-11** TGA data of EPP, IL-TMP, IL-EPC, EPP/IL-TMP and EPP/IL-EPC network

Material	T <sub>d5%</sub> (°C)	T <sub>d10%</sub> (°C)	T <sub>dmax</sub> (°C)
EPP	98	110	157
IL-TMP	234	305	382
EPP/IL-TMP	282	337	449
IL-EPC	269	300	348
EPP/IL-EPC	240	274	440

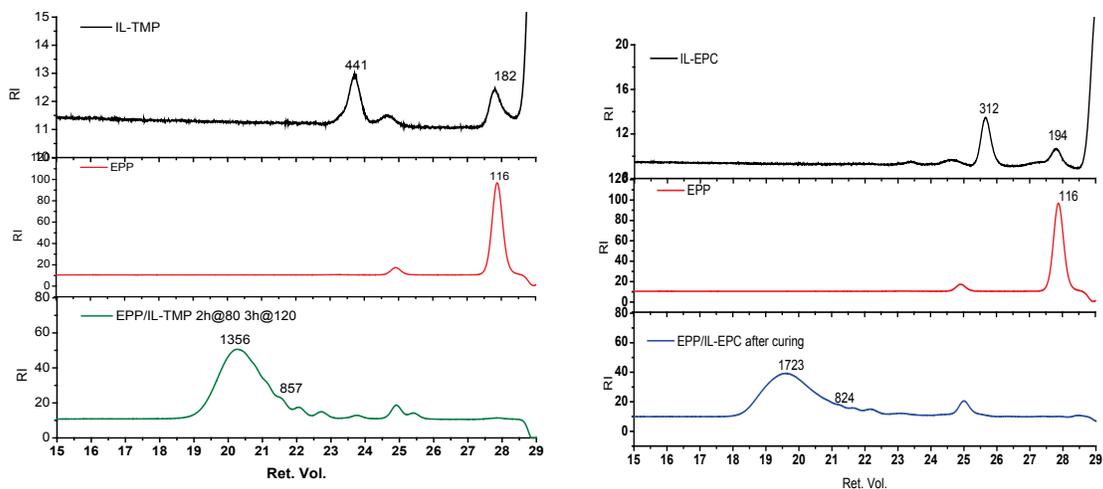


**Figure 2-24** TGA (■,●,★) and DTGA (□,○,☆) curves of EPP (■,□), neat IL (●,○) and EPP/ILs (★,☆) for EPP/IL-TMP (left) and EPP/IL-EPC (right) systems.

To investigate the evolution of molar mass of EPP/ILs systems, SEC analysis was carried out for neat materials (EPP, IL-TMP and IL-EPC) as well as EPP/IL mixture after curing process (Figure 2-25).

In the case of neat ILs, two SEC peaks are present corresponding to cation and counter-anion. In details, cation and anion peaks were related to molar mass  $M_n$  of 441 and 182 g.mol<sup>-1</sup> for IL-TMP and  $M_n$  of 312 and 194 g.mol<sup>-1</sup> for IL-EPC, respectively. However, the SEC signal of neat ILs is so small compared to EPP signal that it cannot be observed in the SEC signal of EPP/IL mixture. Thus, curing reaction was characterized based on SEC peak of EPP at  $M_n$  of 116 g mol<sup>-1</sup>. As expected, at the end of curing process, this peak disappears completely indicating the completion of curing reaction. Moreover, after curing process of 2h at 80 °C and 3h at 120 °C,

various peaks can be detected for  $M_n$  varying from 600 to 1400 g mol<sup>-1</sup> for EPP/IL-TMP system and from 600 to 1800 g mol<sup>-1</sup> for the case of EPP/IL-EPC corresponding to the formation of EPP/ILs oligomers.

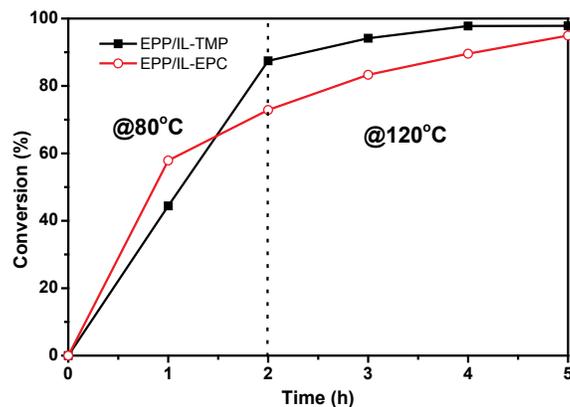


**Figure 2-25** SEC analysis for IL, EPP, EPP/ILs systems after curing for IL-TMP (left) and IL-EPC (right).

In conclusion, DSC, TGA and SEC analysis highlighted the reaction between EPP and ionic liquids in particular IL-TMP and IL-EPC to form a relatively high molar mass product with a high thermal stability.

#### 2.4.4.2. Polymerization Mechanism between EPP and ILs

In this section, the polymerization mechanism between EPP and phosphonium ILs was studied using FTIR and NMR test.



**Figure 2-26** Epoxy conversion as a function of curing time of EPP/IL-TMP (■) and EPP/IL-EPC (○) systems.

FTIR was used to follow the curing reaction. The conversion of epoxide groups as a function of curing time is presented in Figure 2-26 for EPP/IL-TMP and EPP/IL-EPC systems. The conversion of epoxide group increases during the curing process confirming the opening of epoxide groups by ILs. At the end of curing reaction, the epoxide group conversion is over 90 % for both ILs suggesting the completion of curing reaction.

NMR tests were also carried out on neat ionic liquids, EPP and EPP/IL mixtures before and after reaction as well as different times during the curing protocol.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded for EPP as received presented in Figure S2-1, S2-2.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.5 – 7.2 (m, 2H), 7.1 – 6.8 (m, 3H), 4.2 (dd,  $J = 11.0, 3.2$  Hz, 1H), 4.0 (dd,  $J = 11.0, 5.6$  Hz, 1H), 3.3 (m, 1H), 2.9 (dd,  $J = 5.0, 4.1$  Hz, 1H), 2.7 (dd,  $J = 5.0, 2.6$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 158.5, 129.5, 121.2, 114.6, 68.7, 50.1, 44.7.

For neat ionic liquids,  $^{13}\text{C}$  NMR was measured for IL-EPC (Figure S2-3) while  $^{31}\text{P}$  NMR spectra were recorded for both types of ILs, IL-EPC and IL-TMP (Figure S2-4 a,b).  $^{13}\text{C}$  NMR for anion of IL-EPC (101 MHz,  $\text{CDCl}_3$ ) 181.3, 51.4, 30.6, 29.1, 26.5, 22.7, 14.00, 12.8.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  33.4 ( $\text{P}^1$  cation) for IL-EPC and  $\delta$  33.3 ( $\text{P}^1$  cation), 26.4 ( $\text{P}^2$  anion) for IL-TMP.  $^{31}\text{P}$  NMR peaks of IL-TMP are the same as previous study.<sup>91,92</sup>

#### 2.4.4.2.1. NMR test on EPP/IL-TMP systems

Curing reaction between EPP and IL-TMP was followed by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR methods.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were also carried out for EPP/IL-TMP mixture after 2 h at 80 °C and after 5 hours of curing (2h at 80 °C and 3h at 120 °C) in  $\text{CDCl}_3$  compared to neat EPP. As can be seen in Figure 2-27,  $^1\text{H}$  NMR peaks at 4.2, 4.0, 3.3, 2.9, and 2.7 ppm corresponding to  $\text{H}_a$ ,  $\text{H}_b$  of epoxide group and  $\text{H}_c$  next to epoxide group decreased and then nearly disappeared after the curing protocol. A similar decline was observed in the  $^{13}\text{C}$  NMR spectra with peaks at 68.7, 50.1 and 44.7 ppm corresponding to  $\text{C}_a$ ,  $\text{C}_b$  and  $\text{C}_c$ , respectively (Figure 2-28). These results are in agreement with FTIR spectra indicating the open of epoxide group during curing reaction.

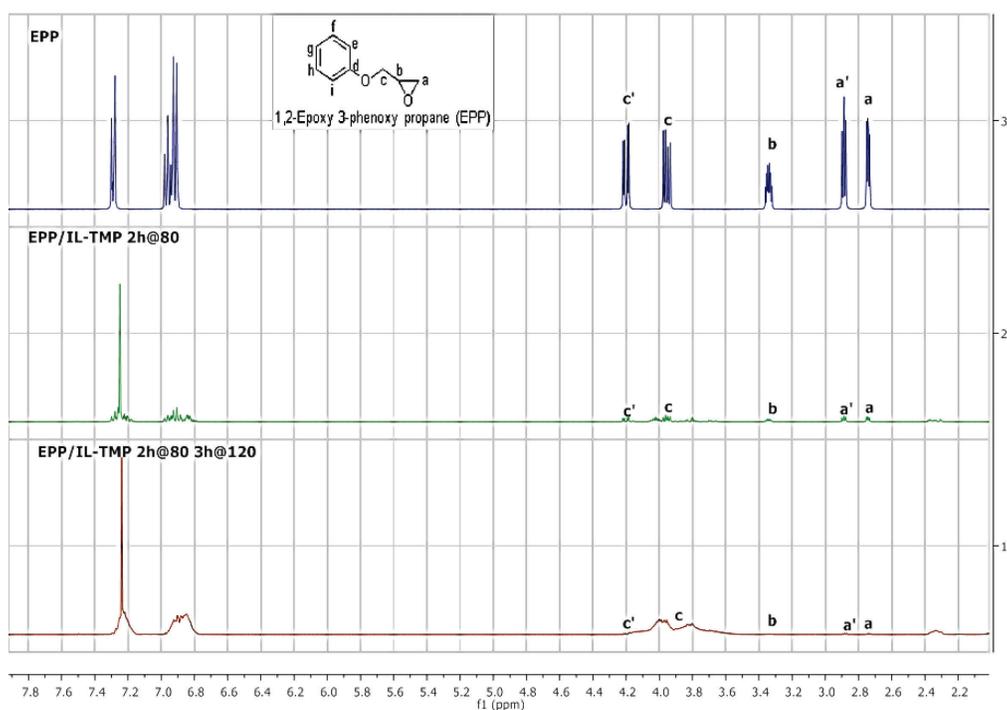


Figure 2-27  $^1\text{H}$  NMR of EPP and EPP/IL-TMP system after 2h and 5h of curing.

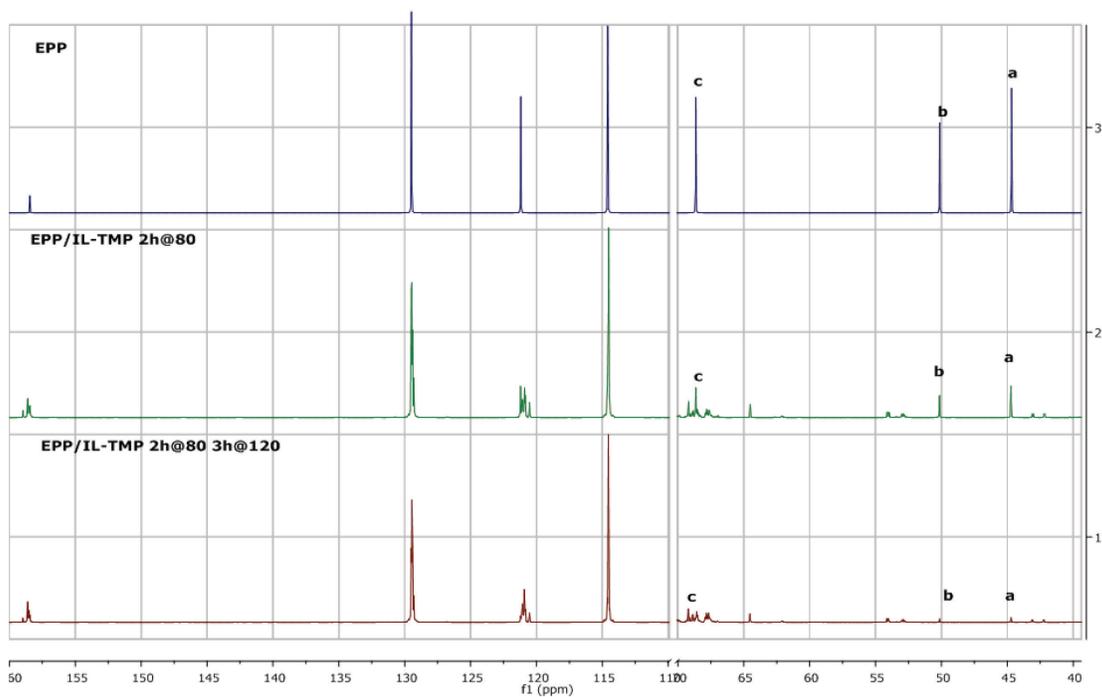
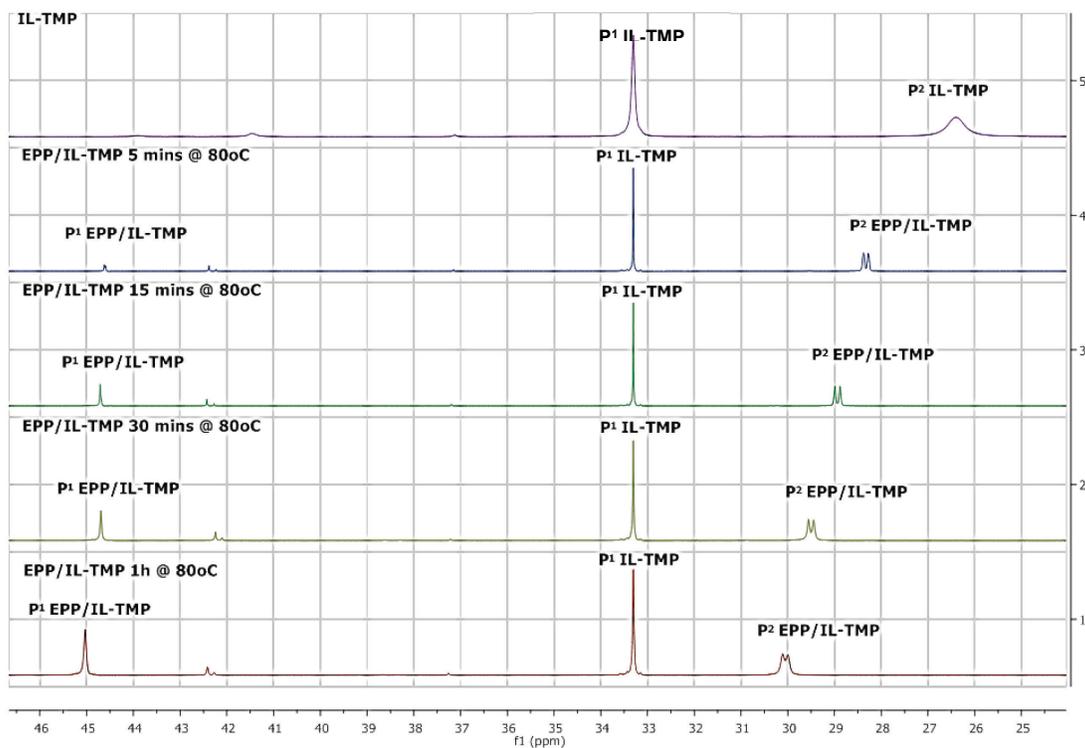


Figure 2-28  $^{13}\text{C}$  NMR of EPP and EPP/IL-TMP system after 2h and 5h of curing.

In addition,  $^{31}\text{P}$  NMR was also carried out for EPP/IL-TMP systems at different curing times of 5 minutes, 15 minutes, 30 minutes and 1 hour at  $80\text{ }^{\circ}\text{C}$ . The mixture of EPP and IL-TMP was mixed and poured directly in NMR tube coupled with an empty coaxial tube. Deuterated solvent could be added later into the inside tube to proceed the NMR measurement. NMR measurement without solvent contact allows to eliminate solvation effect which merged the two nearby peaks. The measurement was stopped after 1h at  $80\text{ }^{\circ}\text{C}$  due to the high viscosity of EPP/IL-TMP system, which prevents NMR signals. NMR spectra of EPP/IL-TMP system and IL-TMP are presented in Figure 2-29. It can be noted that after only 5 minutes at  $80\text{ }^{\circ}\text{C}$ ,  $^{31}\text{P}$  NMR peak corresponding to phosphorous of the counter anion (denoted  $\text{P}^2$ ) is moved to higher chemical shift at 28.5 ppm compared to 26.4 ppm for the phosphinate anion of neat IL-TMP. After 1h at  $80\text{ }^{\circ}\text{C}$ , only one peak at 30 ppm is observed. Concerning the phosphonium cation (denoted  $\text{P}^1$ ),  $^{31}\text{P}$  NMR highlighted one peak at 33.3 ppm and no change is observed whatever the temperature used. These results confirm the anionic polymerization proposed in Part 2.3. Also,  $^{31}\text{P}$  NMR on EPP/IL-TMP systems shows the appearance of a new peak at around 45 ppm which grows steadily during curing time. In order to define this peak,  $^{31}\text{P}$  NMR was recorded for IL-EPC and EPP/IL-EPC systems because IL-EPC has the same cation as IL-TMP.

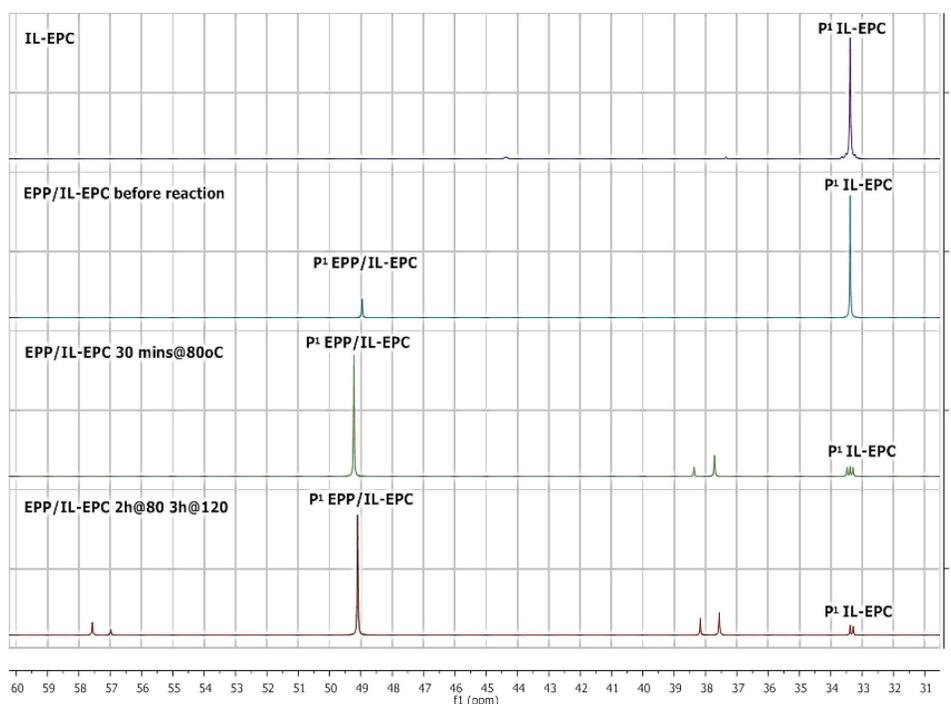


**Figure 2-29**  $^{31}\text{P}$  NMR of IL-TMP and EPP/IL-TMP system after 5 minutes, 15 minutes, 30 minutes and 1 hour at  $80\text{ }^{\circ}\text{C}$ .

2.4.4.2.2. NMR test on EPP/IL-EPC systems

NMR test was conducted on EPP/IL-EPC systems in order to fully understand the role of IL cation and counter anion in the curing reaction with epoxy monomer.

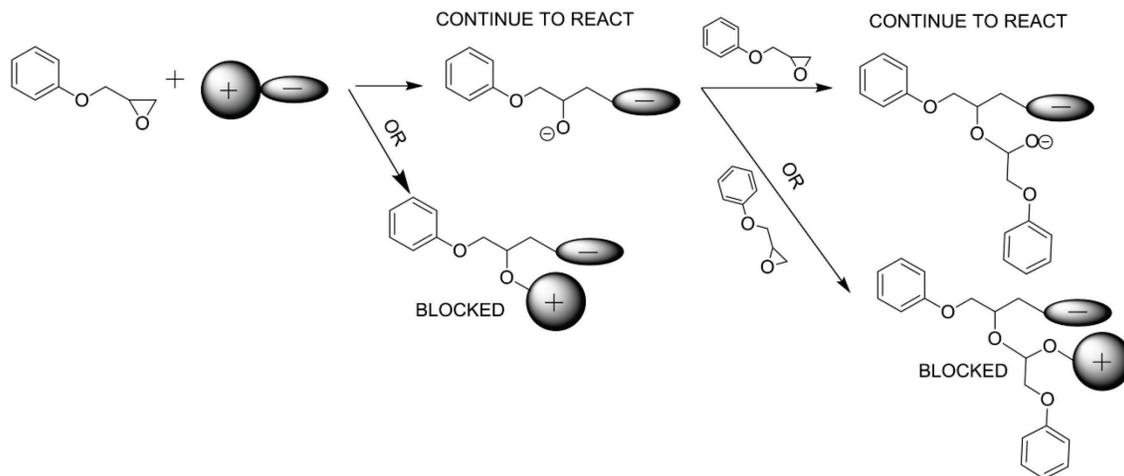
Figure 2-30 presents the  $^{31}\text{P}$  NMR on IL-EPC and EPP/IL-EPC systems before and after the reaction *i.e.* at 30 minutes and 5 h of the curing process.  $^{31}\text{P}$  NMR measurements on EPP/IL-EPC allow to follow the shift of NMR peak corresponding to phosphorous of IL cation (denoted  $\text{P}^1$ ). Moreover, as IL-EPC contains only one phosphorous in the cation, the solvation effect is not concerned in this case. Thus,  $^{31}\text{P}$  NMR measurement for EPP/IL-EPC system can be executed with samples solubilized in  $\text{CDCl}_3$  from the beginning to the end of curing process.



**Figure 2-30**  $^{31}\text{P}$  NMR of IL-EPC and EPP/IL-EPC systems before the reaction and after 30 minutes and 5 h of curing process.

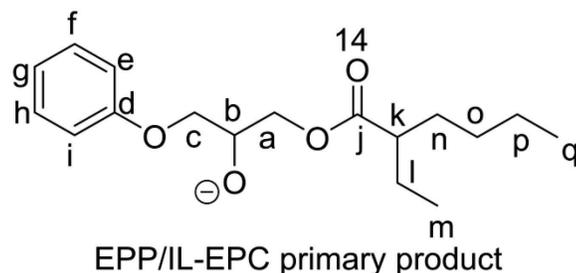
It can be seen in Figure 2-30 that from the beginning of the reaction (after mixing) a second  $^{31}\text{P}$  NMR peak appeared at around 49 ppm. This peak continues to grow as a function of the curing reaction. At the same time,  $^{31}\text{P}$  NMR peak corresponding to IL-EPC cation at 33.4 ppm decreased and nearly disappeared at the end of curing process. This means that during the curing reaction, IL-EPC cation also interacts with EPP resulting in the shift of corresponding  $^{31}\text{P}$  NMR peak. Moreover, the chemical shift of this peak is very close to the new peak observed on the  $^{31}\text{P}$  NMR of EPP/IL-TMP after 1h of reaction (45 ppm). The difference may be explained by the influence

of different counter anion: hexanoate and phosphinate. As a result, during the reaction between EPP and IL-TMP or IL-EPC, while counter anion react to open epoxide group, a part of cation also form an ionocovalent bonds with the O<sup>-</sup> of epoxide group. This bonding will block the epoxide group, which then stops the reaction center. However, the rest of O<sup>-</sup> will not be bonded and continue to react with epoxide group of free EPP to form longer oligomers. Thus, the mechanism of curing reaction between EPP and ionic liquid can be summarized in Scheme 2-1.

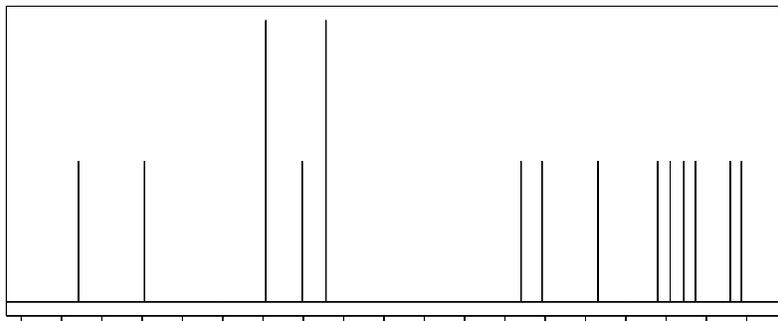


**Scheme 2-1** Possible mechanism of curing reaction between EPP and ionic liquid.

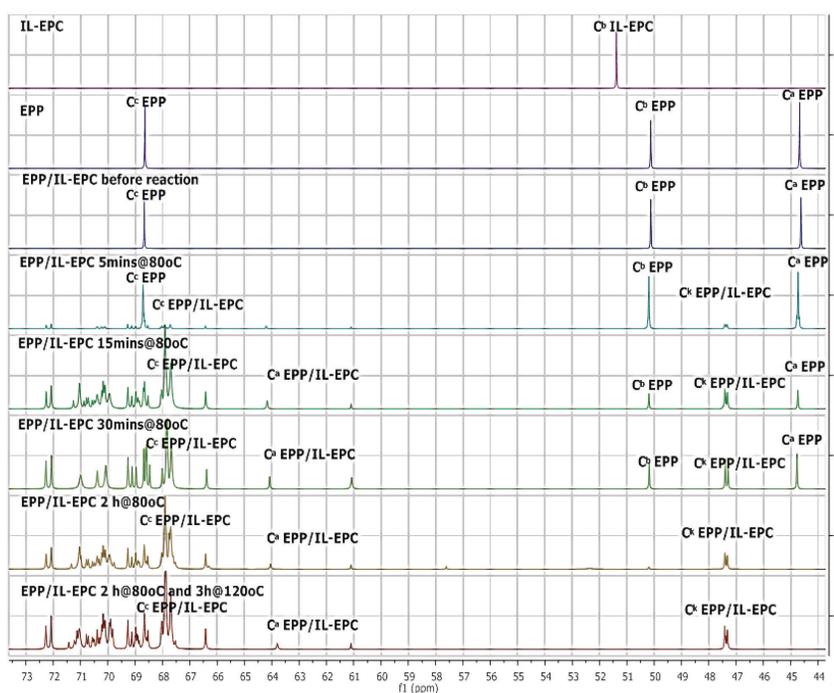
Furthermore, the effect of hexanoate anion of IL-EPC on the polymerization mechanism was also investigated using <sup>13</sup>C NMR. Based on the mechanism on Scheme 2-1, the primary product of EPP and IL-EPC reaction was demonstrated in Scheme 2-2 with the <sup>13</sup>C NMR spectrum predicted using Chemdraw presented in Figure 2-31. Otherwise, <sup>13</sup>C NMR was measured for IL-EPC and EPP/IL-EPC systems to follow the displacement of IL-EPC counter anion. Figure 2-32 and Figure 2-33 shows the evolution of <sup>13</sup>C NMR peak chemical shift from 44 to 74 ppm and from 173 to 184 ppm, respectively.



**Scheme 2-2** Proposed chemical structure of EPP/IL-EPC primary product based on proposed mechanism.

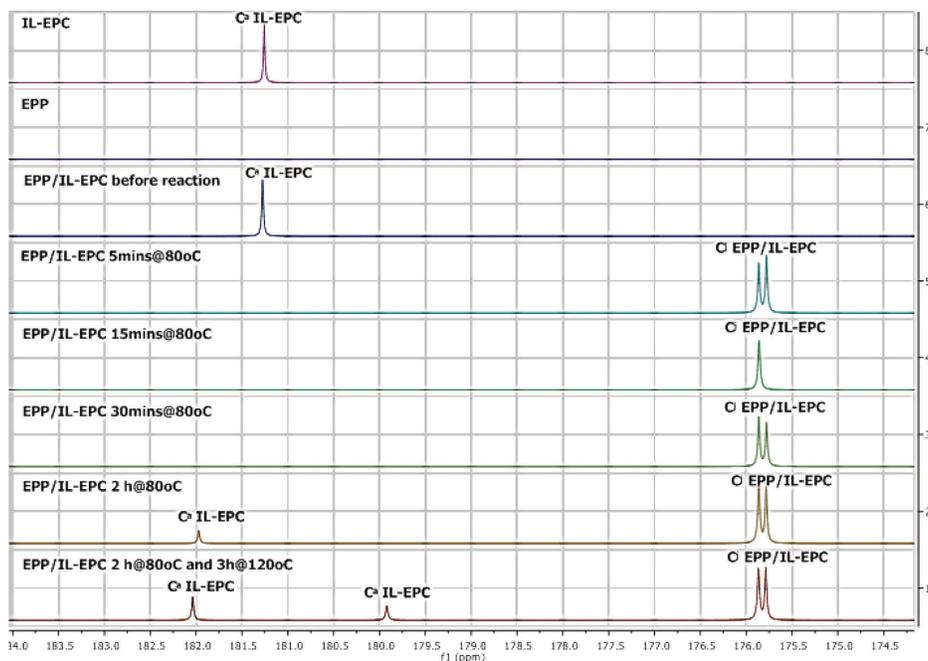


**Figure 2-31** Predicted  $^{13}\text{C}$  NMR of EPP/IL-EPC primary product by Chemdraw.



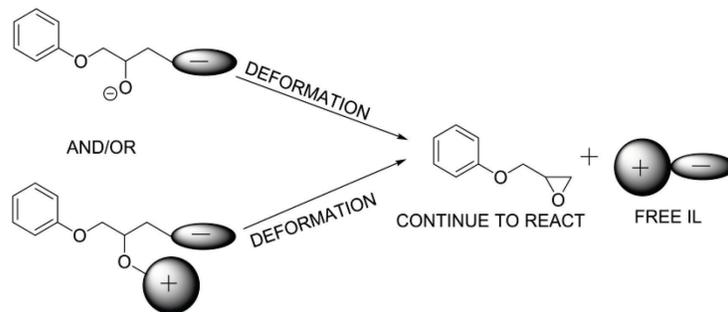
**Figure 2-32**  $^{13}\text{C}$  NMR of IL-EPC, EPP and EPP/IL-EPC systems before the reaction and after 5, 15, 30 mins, 2 hours and 5 hours of curing (chemical shift from 44 to 74 ppm).

At first, comparing Figure 2-31 and Figure 2-32, it can be deduced again that the  $^{13}\text{C}$  NMR peaks corresponding to  $C_a$ ,  $C_b$ ,  $C_c$  of EPP ( $-\text{CH}_2-$ ,  $-\text{CH}-$  of epoxide group and  $-\text{CH}_2-$  connecting to epoxide group) decrease during curing protocol and then disappear totally at the end of curing process. Along with this change, new peaks gradually appear at 47, 61, 67 ppm corresponding to  $C_k$ ,  $C_a$  and  $C_c$  of EPP/IL-EPC primary product, which is similar to Chemdraw prediction. These peaks increase gradually with reaction time. In addition to this, many other peaks appear around these peaks suggesting a mixture of products. This can be explained by the broad dispersity of molar mass of EPP/IL-TMP products observed by SEC (Figure 2-25).



**Figure 2-33**  $^{13}\text{C}$  NMR of IL-EPC and EPP/IL-EPC systems before the reaction and after 30 mins and 5 hours of curing (chemical shift from 173 to 184 ppm).

At the same time, the evolution of  $^{13}\text{C}$  NMR peak corresponding to IL-EPC counter anion  $\text{C}_a$  was presented in Figure 2-33. As expected, after only 5 mins of curing reaction, IL-EPC  $\text{C}_a$  peak at 180 ppm is completely displaced to 175 ppm corresponding to  $\text{C}_k$  of EPP/IL-EPC primary product (Figure 2-31) suggesting that all the IL-EPC counter anion was coupled with EPP to form primary product. However, this peak is separated in two, which may be due to the influence of other counter elements or the mixture of molecular chains of different lengths. Besides, it has to be noted that from 2 hours of curing, other small peaks appear around 180 ppm, which may be attributed to the  $\text{C}_a$  of IL-EPC counter anion. We consider the reversible character of the ionic bonding. We propose that along the curing reaction, some coupled IL-EPC counter anions are liberated from the primary product to reform EPP. The free epoxide group of EPP is then free to react with O of primary products in order to prolong the molecular chain. The decomposition mechanism of EPP/IL-EPC primary products can be summarized in Scheme 2-3. This also indicates that at the end of curing reaction, some free ILs will exist in the final product despite the completion of curing reaction in the form of IL inclusions *i.e.* the case DGEBA/IL-EPC systems observed by TEM (Figure 2-16).



**Scheme 2-3** Decomposition mechanism of EPP/IL-EPC primary product to form EPP and free IL.

### 2.4.5. Conclusion

In conclusion, the use of EPP helped us to better understand the curing mechanism between DGEBA and ILs. The same protocol for DGEBA/IL systems was suitable to EPP/IL system to complete the curing reaction. Instead of thermosetting networks, EPP/IL oligomers have high thermal stability and high molar mass with a broad dispersity. NMR results on EPP/ILs systems confirm the mechanism for DGEBA/IL systems proposed in the previous part.

## 2.5. Conclusion of chapter 2

Firstly, a comparative study was conducted to demonstrate the potential of ionic liquids as reactive additives of epoxy prepolymers. We have demonstrated that phosphonium ILs combined with different counter anions lead to epoxy networks having glass transition temperatures higher than 90 °C as well as high storage moduli. In addition, the chemical nature of the anion plays an important role in the reactivity of the epoxy network formation. In fact, the versatility of ionic liquids allowed preparing epoxy networks tunable to the desired properties. In all the cases, the use of phosphonium ionic liquid leads to thermosetting networks with a higher hydrophobicity and higher thermal stability as well as similar mechanical properties in comparison to epoxy/amine networks

Secondly, we have also demonstrated by NMR that the reaction between the epoxy prepolymer and ionic liquid occurred through an anionic polymerization initiated by the counter anion of ILs. Moreover, the existence of free ILs in the epoxy networks has been proven by NMR explaining the phase separation observed by TEM particularly for the case of IL-EPC.

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## Supporting Information of chapter 2

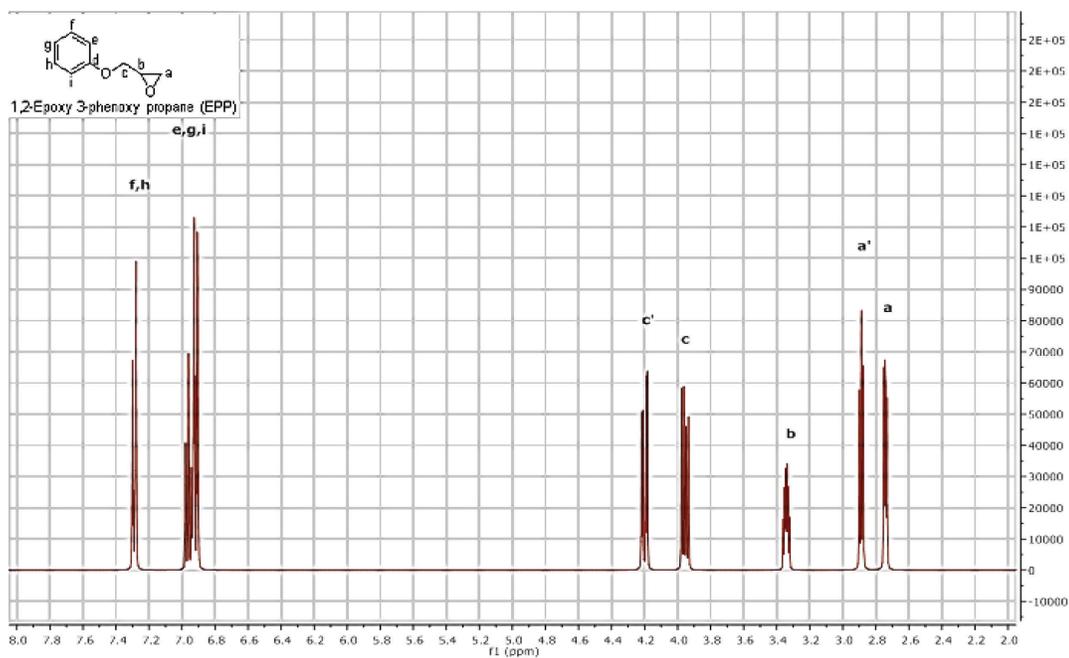


Figure S2-1  $^1\text{H}$  NMR of 1,2-epoxy 3-phenoxy propane (EPP).

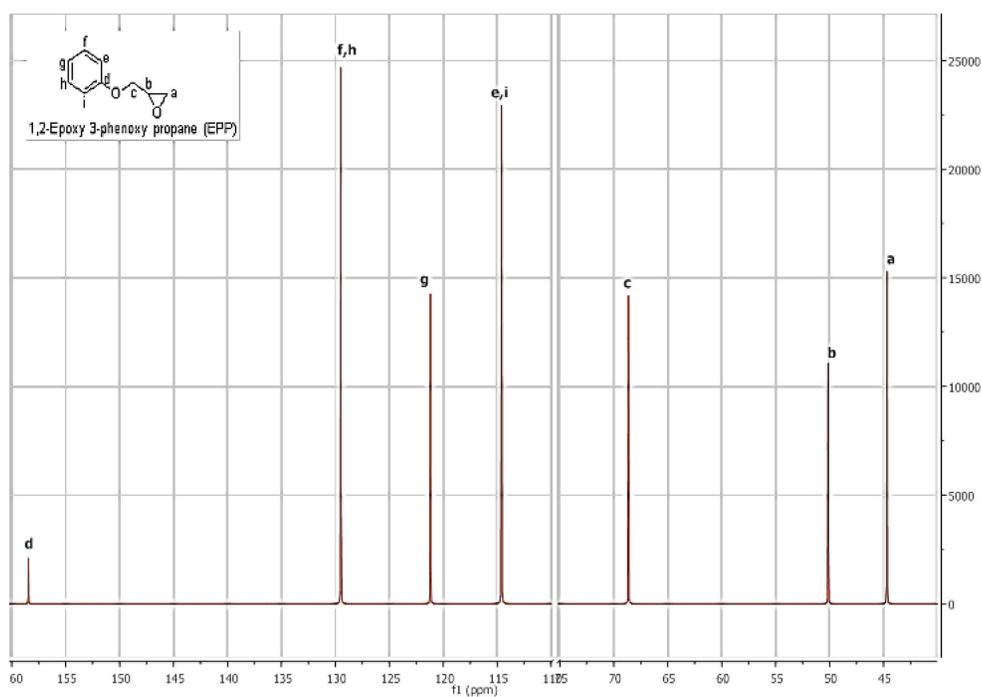


Figure S2-2  $^{13}\text{C}$  NMR of 1,2-epoxy 3-phenoxy propane (EPP).

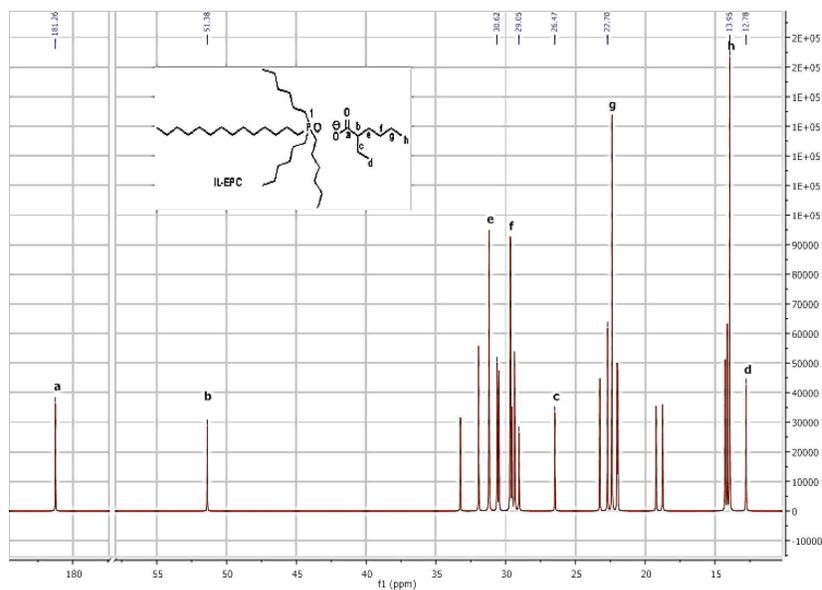


Figure S2-3  $^{13}\text{C}$  NMR of IL-EPC.

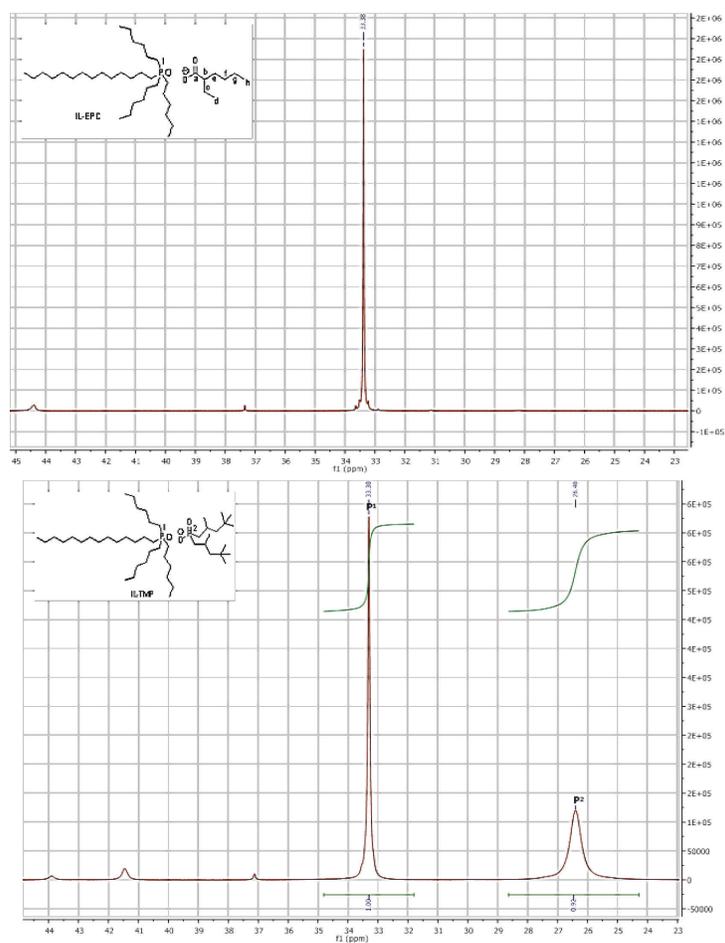


Figure S2-4  $^{31}\text{P}$  NMR of IL-EPC, IL-TMP and IL-DEP.

## Chapter 3:

# Modification of Epoxy/Ionic Liquid networks

As indicated in the previous chapter, despite the excellent thermal and mechanical properties of epoxy networks, their brittleness limits their applications and requires modifications. In this chapter, two kinds of modifiers have been applied into epoxy/IL networks in order to improve their fracture toughness:

- i)* Poly (phenylene ether) with reaction induced phase separation mechanism;
- ii)* Preformed core-shell particles.

In these systems, ILs will act not only as curing agent to replace conventional amine but also as dispersion aids for the modifiers in the epoxy networks. The effect of ILs on the morphology and properties of modified epoxy networks will be demonstrated.

## Table of contents

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<b>3.1. Toughening of epoxy/ionic liquid networks with thermoplastics based on poly (2,6-dimethyl-1,4-phenylene ether) (PPE).....</b>	<b>148</b>
3.1.1. Introduction .....	148
3.1.2. Experimental.....	149
3.1.2.1. Materials.....	150
3.1.2.2. Samples processing.....	151
3.1.3. Results and discussion.....	152
3.1.3.1. Morphology of PPE-modified epoxy networks.....	152
3.1.3.2. Thermomechanical properties of PPE-modified epoxy networks.....	155
3.1.3.3. Thermal stability of PPE-modified epoxy networks .....	158
3.1.3.4. Surface energy of PPE-modified epoxy networks.....	160
3.1.3.5. Mechanical properties of PPE-modified epoxy networks .....	161
3.1.4. Conclusion .....	164
<b>3.2. Dual functions of IL in the core-shell particle reinforced epoxy networks: curing agent vs dispersion aids.....</b>	<b>165</b>
3.2.1. Introduction .....	165
3.2.2. Experimental.....	165
3.2.2.1. Materials.....	167
3.2.2.2. Samples preparation.....	167
3.2.3. Results and discussions .....	167
3.2.3.1. Curing behavior of CSR-modified epoxy blends .....	167
3.2.3.2. Effect of IL on the morphology of CSR-modified epoxy networks .....	167
3.2.3.3. Properties of CSR-modified epoxy/IL networks .....	173
3.2.4. Conclusion .....	179
<b>3.3. Conclusion of chapter 3 .....</b>	<b>180</b>

**References of chapter 3 ..... 181**  
**Supporting Information of chapter 3..... 181**

## 3.1. Toughening of epoxy/ionic liquid networks with thermoplastics based on poly (2,6-dimethyl-1,4-phenylene ether) (PPE)

### 3.1.1. Introduction

Epoxy networks are considered as one of among the most important thermosetting polymers thanks to their excellent thermal and mechanical properties. In addition, the versatility of epoxy networks with highly commercial availability allows to broaden their applications in various fields from coatings or adhesives to matrices of composite materials.<sup>1</sup> Nevertheless, in some cases, the modifications of epoxy networks are required to improve their performances. . Recently, ionic liquids (ILs) have gained a lot of interest as they could be considered as excellent alternatives of conventional additives in polymer matrices as thermoplastics<sup>2-6</sup> or thermosets. Indeed, ionic liquids are well known to be used as multifunctional additives such as plasticizers, compatibilizing agents, structuration agents, interfacial agents of nanoparticles, and reactive additives. In addition, thanks to their outstanding properties,<sup>6,7</sup> low contents of ionic liquids can be considered in the epoxy networks issued from copolymerization of epoxy prepolymer and amines or anhydrides in order to enhance their physical properties such as thermomechanical behavior,<sup>8,9</sup> ionic conductivity,<sup>10</sup> and scratch resistance.<sup>11,12</sup> The addition of some glycidyl-functionalized ionic liquids into conventional epoxy/amine networks could also contribute to improve ionic conductivity,<sup>13-16</sup> as well as the permeability and selectivity for CO<sub>2</sub>.<sup>17,18</sup> Nevertheless, ILs could also substitute amines and anhydrides as hardeners of epoxy prepolymers.<sup>19-23</sup> In fact, in spite of their lower loadings compared to conventional curing agent, ionic liquids have been reported in the Chapter 2 to have high reactivity towards epoxy prepolymer suggesting low curing temperature. Moreover, the obtained networks provide outstanding thermal and mechanical properties combined with a high hydrophobic character,<sup>23</sup> which allow them to be an excellent fiber-based composite or nanocomposite matrix.<sup>24,25</sup> The changes of networks properties with the ionic liquid structure including the glass transition temperature, thermal stability and nanostructure-based morphology also makes them relevant in a wide range of applications (Chapter 2). However, as for conventional epoxy based networks, the high crosslink density of epoxy/ILs networks makes them very brittle,<sup>1</sup> which reduces their applications. According to Chapter 2, epoxy/ILs networks display similar flexion modulus as conventional epoxy/amine-based networks but, their stress intensity factor ( $K_{Ic}$ ) was about 0.4-0.6 MPa · m<sup>1/2</sup>, *i.e.* comparable to aromatic amines (MCDEA) based epoxy networks but lower than those based on aliphatic amines (Jeffamine D230). Thus, some modifications should be considered to improve the mechanical properties of epoxy/ILs networks.

In the literature, many modifiers have been added to epoxy networks in order to improve their toughness such as reactive rubber,<sup>26</sup> inorganic fillers,<sup>27</sup> and high  $T_g$  thermoplastics.<sup>28</sup> Among all of these components, high performance thermoplastics are interesting according to the fact that they could improve fracture toughness of epoxy/amines networks without loss in their thermomechanical properties.<sup>28</sup> In particular, poly phenylene ether (PPE) has been widely investigated to toughen epoxy based networks for structural applications. Several papers have been published for PPE/epoxy blends prepared from different epoxy reactive systems differing from the curing agents, *i.e.* conventional amines (piperidine,<sup>29,30</sup> MCDEA,<sup>31–37</sup> MDEA,<sup>32,33,38</sup> or DETDA<sup>39–42</sup>) to cyanate ester,<sup>43,44</sup> phenolic hardeners,<sup>45</sup> imidazoles,<sup>46</sup> or even a mixture of curing agents of such as ones based on diamine and imidazole.<sup>47,48</sup> The influence of changing the PPE molar mass<sup>29,38,49,50</sup> and functionalization<sup>38,45</sup> on morphology and properties was also demonstrated. Moreover, properties of reactive PPE-modified epoxy blends such as solubility,<sup>36</sup> curing reaction behavior,<sup>37,41,44</sup> and gelation time<sup>34,41</sup> were studied using the combination between Differential Scanning Calorimetry (DSC), Fourier transform infrared (FTIR) and rheology analysis. The reaction induced mechanism (RIPS) during curing reaction was followed by optical microscopy,<sup>44</sup> dielectrical and dynamic mechanical measurements,<sup>34</sup> as well as small angle light scattering combined with DSC.<sup>40</sup> The resulting morphology of PPE/epoxy blends can be tailored from the knowledge of the reaction kinetics, *i.e.* conversion as a function of time, and conversion at which separation occurs. For example, Ishii *et al.* using Flory-Huggins model proposed a phase diagram to predict the generation of morphologies.<sup>42</sup> The morphology of PPE/epoxy blends was also investigated at the final stage, *i.e.* for fully cured material. Whatever the curing agents or epoxy prepolymer structure, PPEs with different molar masses or functional end group undergo the same reaction-induced phase separation phenomenon for PPE/epoxy blends. Depending on the PPE amount, the samples morphology varies from dispersed PPE particles base morphology<sup>29,30,38</sup> at low PPE amount to a co-continuous phase<sup>30</sup> and then phase-inversion<sup>35,39</sup> as the PPE content increases.<sup>37,43,46,47</sup> Dynamical mechanical spectroscopy of such blends revealed two relaxation mechanisms corresponding to the ones of the two phases, *i.e.* the main mechanical relaxations of the epoxy and of the thermoplastic phases which do not occur at the same temperatures as epoxy network and neat PPE due to the non-complete phase separation during curing.<sup>30,35,37,39,43,47</sup> In fact, some TP chains remain in the epoxy-rich phase as well as epoxy and amine comonomers remain dissolved in the PPE-rich phase. According to the high  $T_g$  of PPE, thermal stability and tensile properties of PPE-modified epoxy networks were reported to be similar to neat networks,<sup>35,39,47</sup> which is relevant for industrial applications. Moreover, PPE successfully leads to toughen epoxy based networks displaying significant improvements of fracture toughness  $K_{Ic}$  and fracture energy

$G_{IC}$ , especially for co-continuous morphologies.<sup>30,35,39,47</sup> Therefore, PPE-modified epoxy networks have been used as matrix for high performance composites.<sup>31,32</sup>

In this work, two kinds of PPE of different molar mass will be considered into two different epoxy/ionic liquids blends in order to improve the fracture toughness. The effect of ionic liquid structure as well as PPE type on the morphology, thermal and thermomechanical properties, hydrophobic character and mechanical properties (Flexural properties and Fracture toughness) of PPE-modified epoxy systems will be investigated and compared to a conventional PPE/epoxy networks cured by MCDEA.

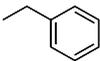
### 3.1.2. Experimental

#### 3.1.2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) based epoxy prepolymer (DER 332) with epoxide equivalent weight (EEW) of  $175 \text{ g}\cdot\text{mol}^{-1}$  was purchased from DOW Chemical Company. A conventional aromatic diamine, *i.e.* 4,4'-methylene bis(3-chloro-2,6-diethylaniline) denoted MCDEA was supplied by Lonzacure with Amine Hydrogen Equivalent Weight (AHEW) of  $95 \text{ g}\cdot\text{mol}^{-1}$ . Two types of ionic liquids: Trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl)phosphinate denoted IL-TMP and tributyl(ethyl)phosphonium diethyl-phosphate denoted IL-DEP were kindly provided by Cytec, Inc. Two types of Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) having different molar masses denoted PPE-1 and PPE-2 were considered. PPE-1 having the higher molar mass was supplied by Spolana Neratovice, Czech Republic. PPE-2 was purchased from Asahi Kasei Chemicals Corporation, Japan referred commercially as Xyron<sup>TM</sup> S201A. Molar masses of two PPE were measured by SEC in chloroform and were founded to be  $32,000 \text{ g}\cdot\text{mol}^{-1}$  and  $15,000 \text{ g}\cdot\text{mol}^{-1}$  for PPE-1 and PPE-2, respectively. All the chemical structures are shown in Table 3-1.

**Table 3-1** Chemical structure and some principal properties of DGEBA, MCDEA, phosphonium ILs and PPE thermoplastics.

Material	Chemical structure	$T_g$ (°C)	Degradation temperature		
			$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	$T_{dmaxDTGA}$ (°C)
DGEBA	—	-22	255	272	335

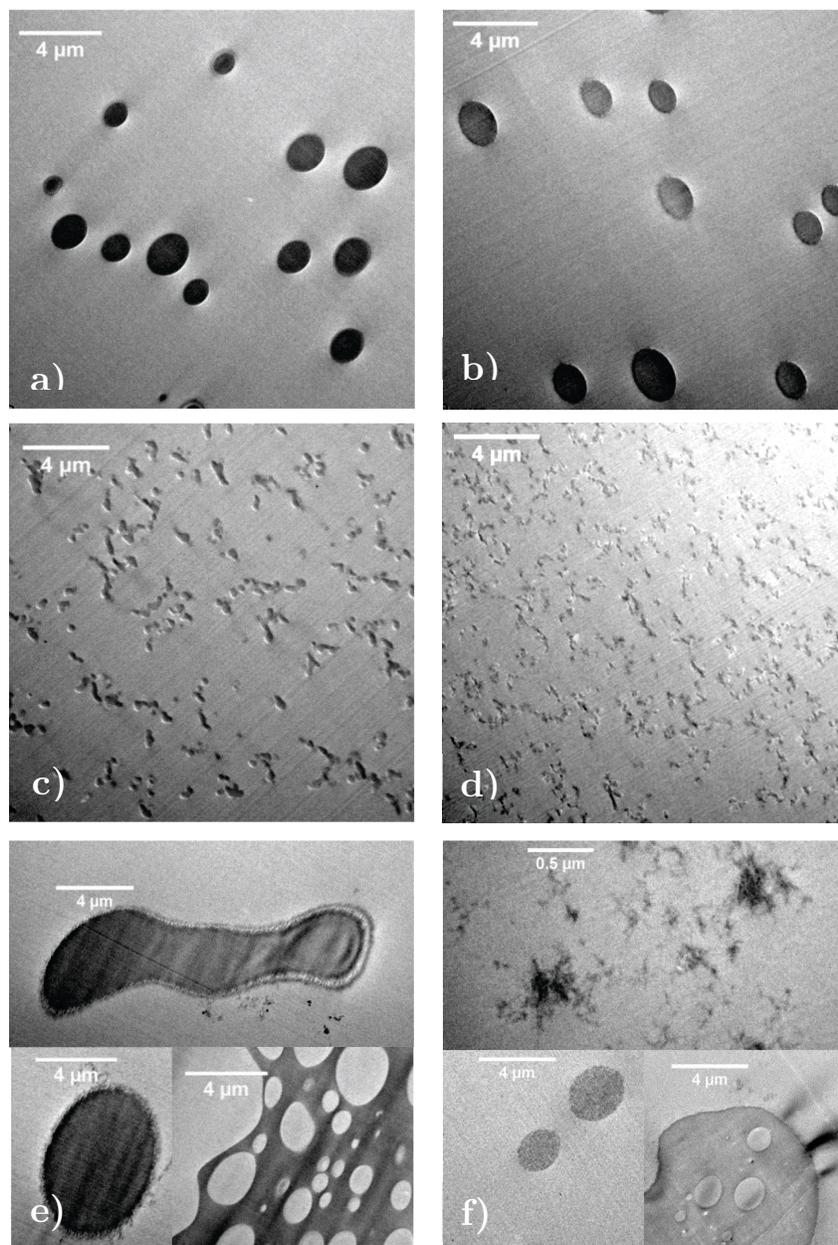
MCDEA		--	218	233	283
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IL-TMP

### 3.1.3. Results and discussion

#### 3.1.3.1. Morphology of PPE-modified epoxy networks

To reveal the different morphologies of PPE-modified epoxy systems, transmission electron microscopy was performed. TEM micrographs of thermoplastic-modified epoxy networks cured with aromatic amine (MCDEA) and ionic liquids (IL-TMP and IL-DEP) are shown in Figure 3-1.



**Figure 3-1** Morphology of different PPE-1 (a, c, e) and PPE-2 (b, d, f) modified epoxy/amine (a, b), epoxy/IL-TMP (c, d) and epoxy/IL-DEP (e, f) networks.

In the previous chapter, no phase separation was observed for neat epoxy networks cured with ILs denoted IL-DEP and IL-TMP or cured with MCDEA. In the opposite, the addition of PPE-1 or PPE-2 into epoxy networks leads to the formation of a second PPE-rich phase into epoxy matrix as a consequence of the reaction induced phase separation phenomenon (Figure 3-1). In addition, the structure and the size of this PPE-rich phase strongly depend on the chemical nature of the curing agents (amine or ILs) and the molar mass of the selected PPE.

In the case of DGEBA/MCDEA-based blends, the use of PPE-1 or PPE-2 induces the formation of spherical particles having diameter from 1 to 3  $\mu\text{m}$ . In addition, decreasing the molar mass of the PPE from 32,000  $\text{g}\cdot\text{mol}^{-1}$  to 15,000  $\text{g}\cdot\text{mol}^{-1}$  does not avoid the presence of large particles. These results are in agreement with previous studies.<sup>37,38,47</sup> In fact, Pearson *et al.* have obtained similar results when they used PPE with molar mass of 42,500  $\text{g}\cdot\text{mol}^{-1}$  and 32,000  $\text{g}\cdot\text{mol}^{-1}$  with dispersed PPE particles size of about 2  $\mu\text{m}$ .<sup>29</sup>

Concerning epoxy networks cured with IL-TMP, the incorporation of the high  $T_g$  thermoplastics (PPE-1 and PPE-2) in the epoxy networks induces a different morphology composed of PPE-rich particles and co-continuous phase. In fact, the PPE particle size in the DGEBA/IL-TMP network was found to be significantly smaller compared to that observed in the DGEBA/MCDEA based blend. Moreover, a pseudo-formation of an inter-connected PPE networks was observed. These two types of morphologies can be explained by the use of ILs which are well known as processing aids or as compatibilizers of several polymers such as thermoplastics or biopolymers (cellulose, starch, etc.).<sup>3-5</sup> Thus Yousfi *et al.* have demonstrated that the use of only 1 wt% of IL-TMP in PP/PA6 blends led to a reduction of the PA domain sizes from 27  $\mu\text{m}$  to 3  $\mu\text{m}$ .<sup>3</sup> Likewise, a finer morphology was observed with the lower molar mass such as PPE-2 for modifying DGEBA/IL-TMP networks. As expected, lowering the molar mass of thermoplastics increases their compatibility with ionic liquids and/or epoxy/ILs networks resulting in a decrease of dispersed phase size.<sup>29,50</sup> In addition, those morphologies may be explained by the mechanism of curing reaction between epoxy and ILs through chainwise polymerization (Chapter 2). In fact, such chemical paths, *i.e.* polymerization for the formation of the epoxy network lead to ternary diagrams of epoxy conversion and transformation which are different from the case of blends based on epoxy/amine networks issued from stepwise copolymerization of epoxy and amine comonomers.<sup>51</sup>

For blends based on IL-DEP, different morphologies were observed from spherical and non-spherical PPE-rich particles in the epoxy matrix to inversed-phase dispersion of epoxy-rich particles in heterogeneous PPE particles. The complex morphologies can also be explained by the chainwise mechanism of curing reaction between IL-DEP and epoxy prepolymer (Chapter 2).

Compared to epoxy matrices cured with IL-TMP, the addition of PPE in the IL-DEP cured epoxy networks leads to even more complicated morphology with dispersed PPE-rich phase with particles having a considerable bigger sizes. In fact, IL-DEP was reported in previous works to have lower reactivity towards epoxy prepolymer than IL-TMP or MCDEA (Chapter 2). Thus, compared to other systems, phase separation could take profit of a longer time in the case of DGEBA/IL-DEP systems due to lower polymerization rate.<sup>51</sup> As a consequence, phase separation could lead to higher particle sizes of the thermoplastic-rich phase<sup>37</sup> and at some point induce phase inversion. In addition, the influence of PPE molar mass was also emphasized for PPE-modified DGEBA/IL-DEP networks. As expected, compared to PPE-1, the low molar mass of PPE-2 leads to a finer distribution of thermoplastics in the DGEBA/IL-DEP networks including smaller particles as well as phase inversion.

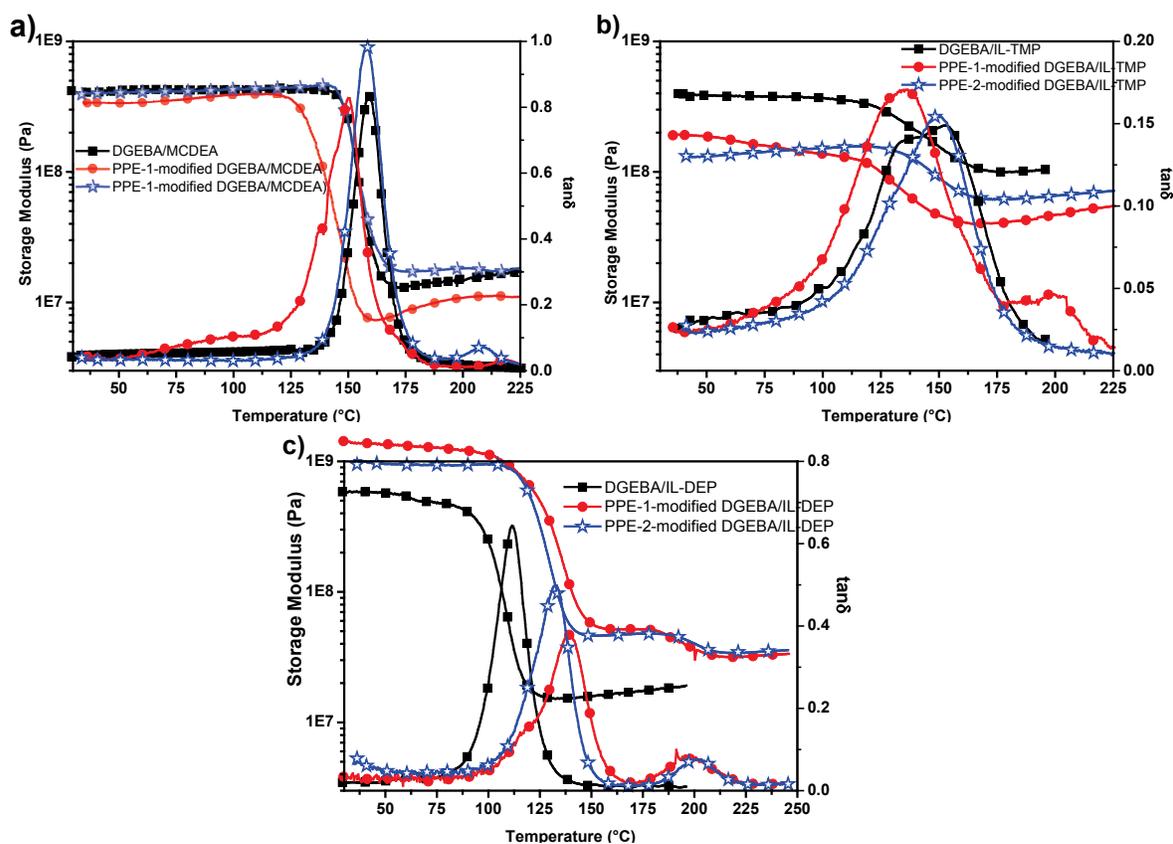
Besides, the morphologies of PPE-modified epoxy/IL networks also show an interface between PPE and epoxy phase, especially in the case of PPE-1 modified DGEBA/IL-DEP system (Figure 3-1e), which can be attributed to the existence of a thin layer of ionic liquids. Regarding the interaction between ILs and thermoplastics, we can suppose that in this case, ILs also acted as interfacial agents, which contributed to decrease interfacial surface tension and modify the ternary phase diagram resulting in the formation of co-continuous and phase inverted morphologies.

Generally, the addition of thermoplastics into epoxy networks generates a phase separation which is governed by the thermodynamics of the chemical system controlled by the nature of the initial components (nature of the comonomers and thermoplastic architecture and molar mass) and reaction kinetics (temperature, presence of catalyst) as the governing mechanism is the entropy changes during reaction.<sup>52-55</sup> In addition, the nature of reactive epoxy systems can influence the reaction between phenolic end groups of PPE and epoxide functions.<sup>43</sup> In fact, such PPE chain ends reaction could generate species, which modify the interfacial tension between phases, *i.e.* lead to the formation of different morphologies in the case of the IL. In the case of PPE-modified DGEBA/IL systems, the reaction kinetics is not the same as for the one of the DGEBA and MCDEA copolymerization. In the later, according to the low reactivity of MCDEA, the reaction kinetics is quite slow compared to the one of DGEBA/IL-based systems.<sup>22,56</sup> A noticeable difference between the two types of reactive systems, *i.e.* MCDEA- or IL-based systems, is the glass transition temperature value of the resulting epoxy networks. In fact, as for the IL-based networks the  $T_g$  is about 20 to 30 K lower than for DGEBA-MCDEA networks which means that the phase separation faces a longer time before vitrification. As an additional phenomenon, one can suppose that the ionic liquids could also act as interfacial agents in order to contribute to decrease interfacial surface

tension, *i.e.* modify the ternary phase diagram leading to a decrease of the PPE particle size and/or to the generation of co-continuous morphologies.

### 3.1.3.2. Thermomechanical properties of PPE-modified epoxy networks

Thermomechanical properties of PPE-modified epoxy/amine and epoxy/IL networks were characterized using Differential Scanning Calorimetry DSC and Dynamic Mechanical Analysis DMA, respectively. Viscoelastic spectra of unmodified and PPE-modified epoxy/amine and epoxy/ILs networks are illustrated in Figure 3-2. Glass transition temperature,  $T_g$ , taken at the inflection point of  $\Delta C_p$  change as well as the temperatures of  $\alpha$ -mechanical relaxations, determined from the maximum of  $\tan\delta$  ( $T_{\alpha 1}$  and  $T_{\alpha 2}$ ) associated with the glass transition phenomena of the epoxy networks and PPE, are given in Table 3-3.



**Figure 3-2** DMA analysis of (■) unmodified, (●) PPE-1-modified and (☆) PPE-2-modified epoxy networked cured by a) MCDEA, b) IL-TMP and c) IL-DEP.

In all the cases, the glass transition temperature and  $\alpha$ -relaxation temperatures of unmodified epoxy networks denoted DGEBA/MCDEA, DGEBA/IL-TMP and DGEABA/IL-DEP are in agreement with the values reported in the previous chapter.

For all PPE-modified and unmodified epoxy/amine and epoxy/IL networks, DSC thermograms of cured epoxy prove the completion of the curing reaction according to the complete disappearance of the exothermic peak corresponding to the reaction of the epoxy groups. A single glass transition temperature relates to the glass transition of epoxy/amine or epoxy/IL network was observed by DSC due to the measurement sensitivity. The incorporation of PPE in the epoxy networks leads to a slight decrease of the glass transition temperatures of 3 K and 10 K for DGEBA/MCDEA and DGEBA/IL-TMP networks, respectively. On the opposite, the addition of PPE in the DGEBA/IL-DEP network leads to an increase of the glass transition temperature (+ 10 K). This difference may be explained by the phase inversion observed in the Figure 3-1 and the composition of the epoxy and PPE rich phases.

**Table 3-3** Thermal and viscoelastic properties of neat PPE, unmodified and PPE-modified epoxy networks.

Material	DSC	DMA	
	T <sub>g</sub> (°C)	T <sub>α1</sub> (°C)	T <sub>α2</sub> (°C)
PPE-1	250	-	225
PPE-2	210	-	210
DGEBA/MCDEA	148	160	-
PPE-1-modified DGEBA/MCDEA	145	150	210
PPE-2-modified DGEBA/MCDEA	145	158	208
DGEBA/IL-TMP	130	150	-
PPE-1-modified DGEBA/IL-TMP	120	136	200
PPE-2-modified DGEBA/IL-TMP	128	149	-
DGEBA/IL-DEP	110	112	-
PPE-1-modified DGEBA/IL-DEP	129	133	195
PPE-2-modified DGEBA/IL-DEP	127	138	203

In addition, the phase-separated morphology of the PPE-modified epoxy/amine and epoxy/IL networks is observed using Dynamic Mechanical Analysis (Figure 3-2). In fact, two relaxation peaks corresponding to the T<sub>α</sub> of epoxy-rich and thermoplastics-rich phases<sup>35,37,57,43,47</sup> are evidenced confirming the phase separation of PPE phase in the epoxy networks observed by TEM (Figure 3-1). Moreover, the relaxation temperatures of each phase in the modified epoxy networks vary from those of unmodified ones due to the fact that the phases are not pure, *i.e.* a part of the PPE thermoplastic remains dissolved in the epoxy-rich phase (matrix network).<sup>43</sup> In details, the incorporation of PPE-1 and PPE-2 in the epoxy/amine networks results in a decrease of both relaxation temperatures corresponding to epoxy-rich phase and PPE-rich phase. The decrease of epoxy-rich phase T<sub>α</sub> can be attributed to the reduction of final conversion due to the epoxy and amine comonomers which stood in the thermoplastic rich phase and/or the reaction of PPE

phenolic chain ends with the glycidyl of epoxy group as the two phenomena lead to a modification of the stoichiometric ratio between DGEBA and curing agent.<sup>35,45,58</sup> As expected, the second  $\alpha$ -relaxation temperature which is associated to the PPE phase in the epoxy networks is lower than that of the neat PPE thermoplastics due to the incorporation of unreacted epoxy in the PPE phase.<sup>37,47</sup> The difference of relaxation temperatures between modified and unmodified epoxy/amine networks also depends on the PPE molar mass.  $T_\alpha$  decreases from 160 °C for neat DGEBA/MCDEA network to 150 °C and 158 °C for epoxy-rich phase in the PPE-1 and PPE-2 modified DGEBA/MCDEA networks, respectively. The relaxation temperatures of PPE-1 and PPE-2-rich phases in the modified epoxy/amine networks are 210 °C and 208 °C compared to the glass transition temperatures of neat PPE-1 and PPE-2 of 225 °C and 210 °C, respectively. Obviously, the use of lower molar mass of PPE-2 leads to lower difference in relaxation temperature than the case of PPE-1 which can be explained by the higher compatibility of PPE-2 with epoxy phase and *vice versa*.

For DGEBA/IL-TMP systems, interpenetration between epoxy and thermoplastics phase leads to similar variations of the  $\alpha$ -relaxation temperatures compared to those of the epoxy/amine networks. A decrease of  $T_\alpha$  of both epoxy-rich and PPE-rich phases is observed for PPE modified DGEBA/IL-TMP networks due to the change of the DGEBA-to-IL stoichiometric ratio in the epoxy/IL network phase. In fact, this result demonstrates that no PPE chains remain dissolved in the epoxy-rich phase compared to DGEBA which stays in a large amount in the PPE-rich phase. As evidence by TEM, the IL-TMP seems to be localized at the interface between the two phases, *i.e.* a large amount of ionic liquid cannot participate to the epoxy network formation. Compared to epoxy/amine networks, the addition of PPE to DGEBA/IL-TMP systems leads to large changes of  $\alpha$ -relaxation temperatures. Concerning the effect of PPE molar mass, the incorporation of PPE-2 does not lower the  $T_\alpha$  of the epoxy-rich phase compared to the non-modified networks. In addition, the second relaxation peak corresponding to PPE-2  $\alpha$ -relaxation cannot be observed by Dynamic Mechanical Analysis. As a phase separated morphology is evidenced by TEM, it means that the two relaxation peaks of both phases are superimposed, *i.e.* the glass transition temperature of the PPE-rich phase is close to the one of the epoxy matrix. This effect could be attributed to an increase of the miscibility between the two components.

Regarding DGEBA/IL-DEP systems, the  $\alpha$ -relaxation temperature corresponding to the PPE-rich phase in the PPE-modified network is lower than the one of the neat thermoplastic while the  $\alpha$ -relaxation peak corresponding to epoxy-rich phase are shifted to higher temperature, *i.e.* from 112 °C to 133 °C and 138 °C considering PPE-1 and PPE-2, respectively. This effect is clearly associated to the fact that PPE chains remain dissolved in the epoxy-rich phase leading to an

increase of its  $T_g$  and that epoxy/IL components are present in the PPE-rich phase contributing to decrease the  $T_g$  of this phase. The difference with PPE-modified DGEBA/IL-TMP systems is the lower reactivity of the DGEBA/IL-DEP leading to a different balance in the competition between reaction kinetics and phase separation phenomenon.  $\alpha$ -relaxation peaks corresponding to PPE-1 and PPE-2 rich phase in the PPE-modified DGEBA/IL-DEP networks are located at 195 °C and 203 °C, *i.e.* much lower than for systems based on MCDEA and IL-TMP.

### 3.1.3.3. Thermal stability of PPE-modified epoxy networks

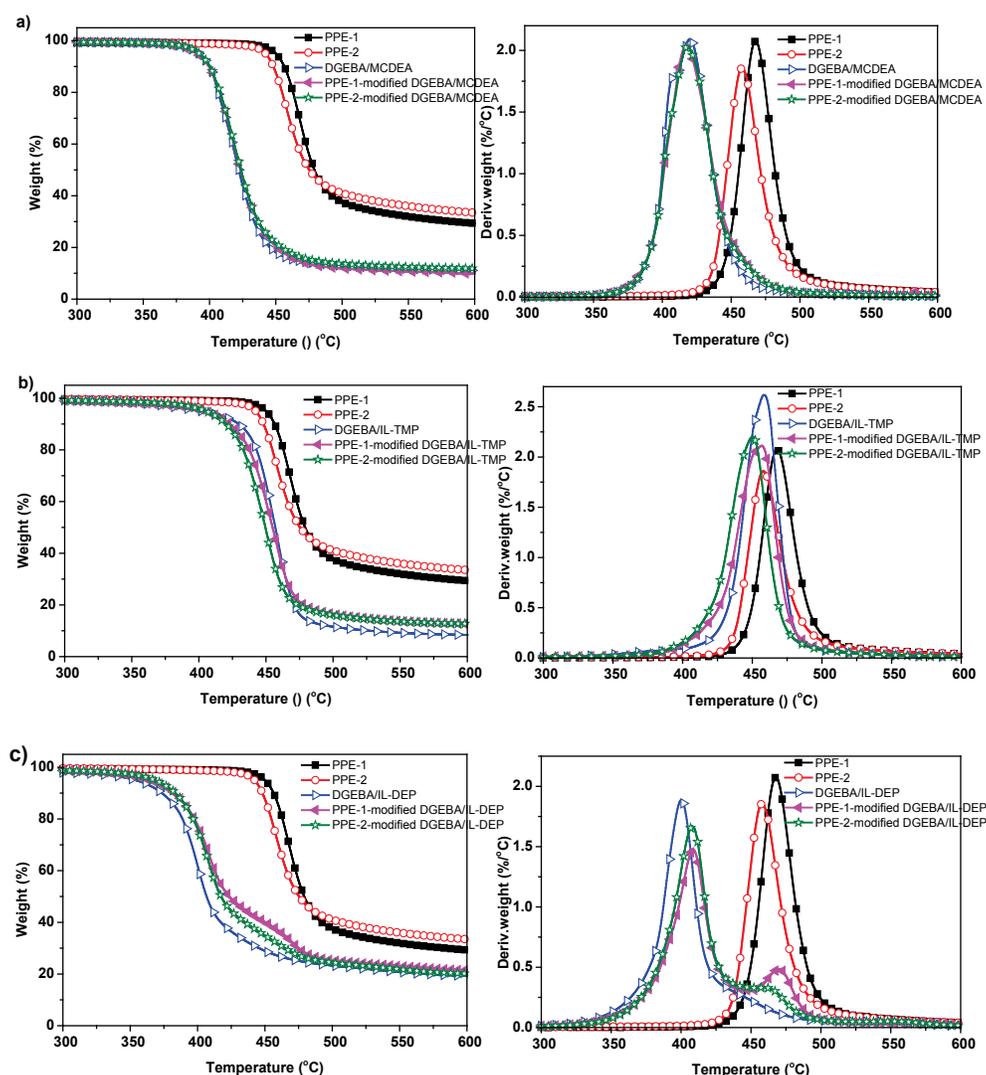
The influence of PPE on the thermal stability of epoxy networks cured by aromatic amine (MCDEA) and phosphonium ILs (IL-TMP, IL-DEP) was investigated by thermogravimetric analysis (TGA) under  $N_2$  atmosphere. The changes of the weight loss as well as the derivative weight loss as a function of the temperature of neat PPE, unmodified and all PPE-modified epoxy/amine and epoxy/ILs networks are presented in Figure 3-3. In addition, the degradation temperatures at which 5 % and 10 % of weight loss are reached, temperatures at which the degradation is achieved, and the amount of residus at 600 °C are listed in Table 3-4.

**Table 3-4** Thermal stability of neat PPE, unmodified and PPE-modified epoxy networks.

Material	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	$T_{dmax}$ (°C)	$T_{d\ 2nd\ peak}$ (°C)	Residue (%)
PPE-1	441	450	466	-	31.5
PPE-2	450	456	466	-	31.4
DGEBA/MCDEA	392	400	420	-	1.8
PPE-1-modified DGEBA/MCDEA	390	399	418	-	9.9
PPE-2-modified DGEBA/MCDEA	392	400	418	-	11.2
DGEBA/IL-TMP	399	430	458	-	8.4
PPE-1-modified DGEBA/IL-TMP	404	422	457	-	12.6
PPE-2-modified DGEBA/IL-TMP	405	420	450	-	12.6
DGEBA/IL-DEP	354	373	400	-	19.2
PPE-1-modified DGEBA/IL-DEP	364	382	408	470	21.4
PPE-2-modified DGEBA/IL-DEP	368	383	408	464	20.2

In all the cases, an excellent thermal stability of the unmodified and PPE modified-epoxy networks could be highlighted as degradation temperatures are higher than 400 °C. In agreement with the results reported in the literature as similar results were observed on epoxy/thermoplastic networks.<sup>59</sup> The addition of PPE-1 and PPE-2 in epoxy/amine reactive system does not affect the thermal stability of these materials, which have similar degradation temperatures, *i.e.* close to 420 °C. The same behavior was also observed for PPE modified epoxy/IL networks, which include IL-

TMP having a higher thermal stability, *i.e.* leading to degradation temperatures 40K higher than epoxy/amine networks. These results have already been demonstrated in the previous chapter where IL-TMP acts as flame retardant for epoxy networks. In the case of PPE-modified epoxy networks cured with IL-DEP, a slight increase of the thermal degradation was observed as well as the appearance of a second degradation peak at a higher temperature (465-470 °C) which could be associated to the degradation temperature of the PPE thermoplastic.<sup>47</sup> These results confirm very clearly the phase-inverted morphology obtained in Figure 3-1 where a portion of the epoxy domains is included into PPE matrix.



**Figure 3-3** Weight loss as a function of temperature of neat PPE-1 (■), PPE-2 (○), unmodified epoxy networks (▷) and PPE-modified considering the addition of PPE-1 (◄) and PPE-2 (☆) cured by a) MCDEA, b) IL-TMP and c) IL-DEP.

PPE and phosphonium ILs are known for their non-flammability.<sup>36,60,61</sup> In fact, the use of IL-DEP as curing agents leads to epoxy networks possessing high flame retardancy with the formation of carbonaceous floccules as protective layer.<sup>62</sup> These results can be explained by the chemical nature of the phosphonium ILs and by the presence of phosphorous element. In fact, as reported in the literature, different phosphorous based systems have been used as flame retardancy agent including phosphinate and phosphate compounds.<sup>63</sup> As a conclusion, PPE-modified epoxy/IL networks are promising candidates for applications requiring flame resistance

### 3.1.3.4. Surface energy of PPE-modified epoxy networks

The surface energy of unmodified and PPE modified epoxy networks were characterized from sessile drop method. From the contact angles with water and diiodomethane, non-dispersive and dispersive components were determined according to the Owens-Wendt model and are presented in Table 3-5.

**Table 3-5** Surface energy of neat PPE, unmodified and PPE-modified epoxy/amine and epoxy/IL networks.

Material	$\Theta_{\text{water}}$ (°)	$\Theta_{\text{CH}_2\text{I}_2}$ (°)	$\gamma_{\text{non-dispersive}}$ (mJ.m <sup>-2</sup> )	$\gamma_{\text{dispersive}}$ (mJ.m <sup>-2</sup> )	$\gamma_{\text{total}}$ (mJ.m <sup>-2</sup> )
PPE-1	102	50	0.1	34.7	34.8
PPE-2	95	49	0.6	35.1	35.1
DGEBA/MCDEA	81	50	4.5	29.8	34.3
PPE-1-modified DGEBA/MCDEA	89	52	1.5	31.0	32.5
PPE-2-modified DGEBA/MCDEA	90	51	1.1	32.5	33.6
DGEBA/IL-TMP	91	44	1.0	37.3	38.3
PPE-1-modified DGEBA/IL-TMP	101	79	1.6	16.4	18.0
PPE-2-modified DGEBA/IL-TMP	105	71	0.2	22.3	22.5
DGEBA/IL-DEP	96	67	1.5	24.8	26.4
PPE-1-modified DGEBA/IL-DEP	99	73	1.3	19.6	20.9
PPE-2-modified DGEBA/IL-DEP	100	71	1.0	21.2	22.2

According to chapter 2, the use of phosphonium ionic liquids denoted IL-TMP and IL-DEP as hardeners of the epoxy prepolymer, denoted DGEBA, leads to a more hydrophobic character compared to epoxy/amine systems. In fact, the hydrophobic nature of ILs having a surface energy from 29 to 33 mJ.m<sup>-2</sup> induces a decrease of the non-dispersive component for DGEBA/IL-TMP and DGEBA/IL-DEP, respectively.

In all the cases, the addition of PPE-1 or PPE-2 in epoxy/amine or epoxy/IL networks leads to a reduction of the non-dispersive components due to the chemical nature of PPE. Nevertheless, different behaviors are observed depending on the chemical nature of the curing agents. In the case of unmodified and modified epoxy/amine networks, the surface energies are very close to each other with the almost identical non-dispersive and dispersive components. When IL-TMP or IL-DEP is considered as hardeners, significant decreases of surface energies of PPE (1 or 2) modified epoxy/IL networks are observed as values from 18 to 23 mJ.m<sup>-2</sup>. Such values of the surface energies, which are similar to those of polyolefin surfaces, lead to the conclusion that the ionic liquids bearing alkyl chains are present at the surface. In fact, according to the surface energies of the ILs compared to the surface tension of initial reactive epoxy systems and growing network,<sup>64,65</sup> their low surface tension is the driving force for migration of the ionic liquid species to the network surface.

As a summary, the combination of ILs and PPE thermoplastic with reactive epoxy systems leads to an increase of the hydrophobic character of the resulting epoxy networks.

### 3.1.3.5. Mechanical properties of PPE-modified epoxy networks

The influence of the two PPE thermoplastics on the flexural properties as well as on the fracture toughness,  $K_{Ic}$ , of epoxy-based material was studied. The values of the flexural modulus, flexural strength and the critical stress intensity factor,  $K_{Ic}$ , of epoxy/amine, epoxy/IL, and PPE-modified epoxy networks are presented in Table 3-6.

**Table 3-6** Mechanical properties of unmodified and PPE-modified epoxy/amine and epoxy/IL networks.

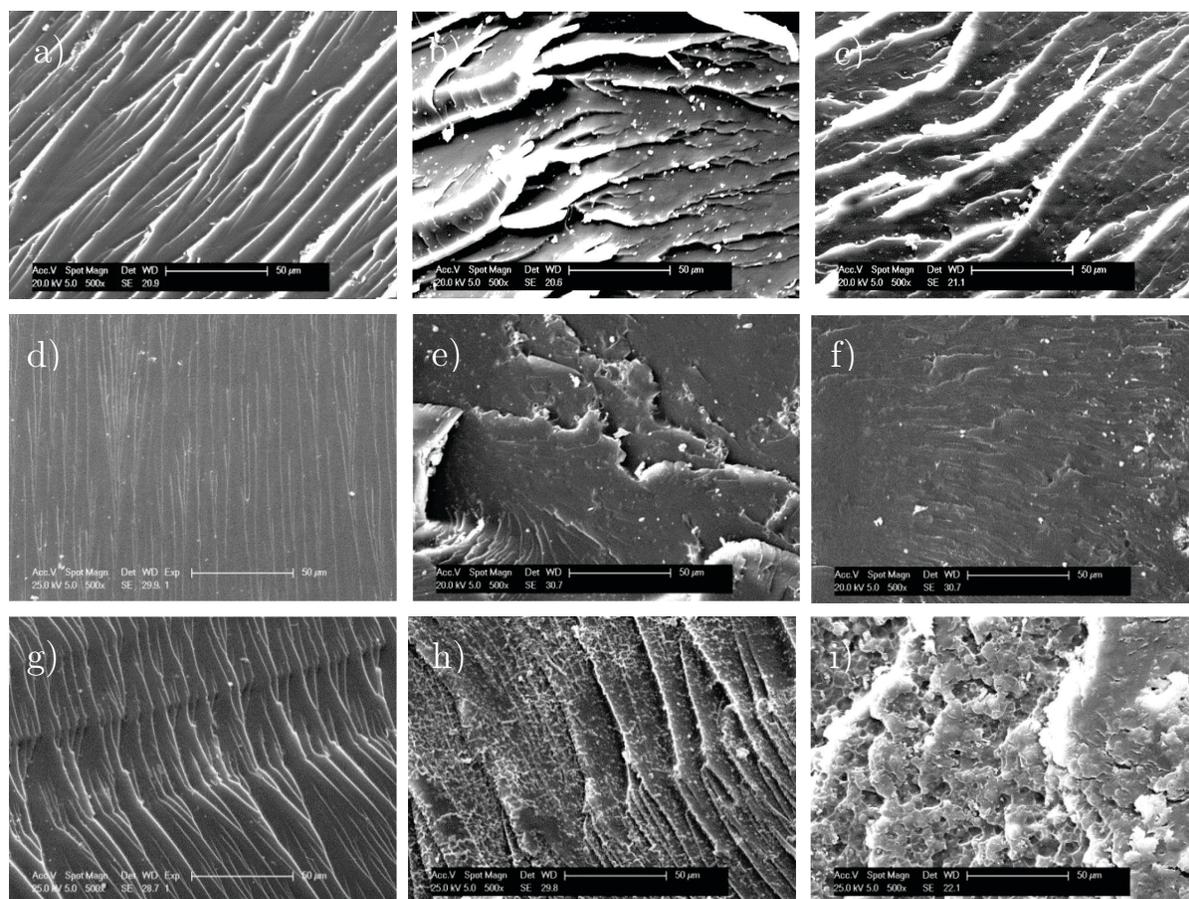
Material	Flexural modulus (GPa) $\pm 0.1$	Flexural strength (MPa) $\pm 4$	$K_{Ic}$ (MPa.m <sup>1/2</sup> ) $\pm 0.05$
DGEBA/MCDEA	2.3	77	0.56
PPE-1-modified DGEBA/MCDEA	2.4	115	0.69
PPE-2-modified DGEBA/MCDEA	2.3	77	0.64
DGEBA/IL-TMP	1.6	25	0.39
PPE-1-modified DGEBA/IL-TMP	1.8	52	0.99
PPE-2-modified DGEBA/IL-TMP	2.4	49	0.46
DGEBA/IL-DEP	2.6	73	0.55
PPE-1-modified DGEBA/IL-DEP	2.4	45	1.67
PPE-2-modified DGEBA/IL-DEP	2.5	96	1.56

For epoxy/amine and epoxy/IL networks denoted DGEBA/MCDEA, DGEBA/IL-TMP or DGEBA/IL-DEP, the flexural modulus as well as the flexural strength are in agreement with the data reported in the literature.<sup>66</sup> Then, the addition of PPE thermoplastics whatever their molar

mass in the epoxy/amine system has no influence on the flexural moduli as at room temperature both the PPE thermoplastic and the epoxy network are in the glassy state. However, differences could be observed in terms of flexural strength, especially for the PPE-1 modified DGEBA/MCDEA network where a 50 % increase is obtained. This result can be explained by the higher molar mass of PPE-1 compared to PPE-2 (32,000 g.mol<sup>-1</sup> versus 15,000 g.mol<sup>-1</sup>). In the case of epoxy/IL networks denoted DGEBA/IL-TMP where a lower value of flexural modulus (1.6 GPa) was observed for the neat networks, the addition of thermoplastics leads to significant increases in flexural moduli (+ 12 % for PPE-1, + 50 % for PPE-2) due to the fact that the modulus of PPE is higher than the one of the neat epoxy matrix, *i.e.* 2.45 GPa at 23 °C.<sup>43,57,67</sup> In the opposite, the flexural strength depends on the type of the morphologies (Figure 3-1). For example, the flexural strength of the PPE-modified epoxy/IL-TMP networks is two times higher than for neat epoxy network both from the addition of PPE-1 and PPE-2. These results are explained by the co-continuous morphologies shown in Figure 3-1 with a finer dispersion of PPE particles combined with the formation of an interconnected PPE network is observed.<sup>68</sup> As the molar mass of the PPE thermoplastic strongly influences the morphology of PPE-modified epoxy/IL-DEP blends, the flexural strength is also strongly dependent on the type of PPE. The coarser morphology, *i.e.* the one of the PPE-1-based blend, displays the lower flexural strength compared to PPE-2-based blend. This difference could be easily attributed to the large particle sizes, which act as defects with stress concentration effects with PPE-1, compared to PPE-2-based blend having a phase-inverted morphology, which is known to be efficient for improving ultimate mechanical properties (Figure 3-1).

According to the literature, the use of thermoplastics as toughening agents of epoxy networks has a significant influence on the fracture toughness.<sup>30,35,47,57</sup> In fact,  $K_{Ic}$  values are very dependent on as the morphologies of the thermoset/thermoplastic blends, resulting from chemical nature of the components of the reactive thermosetting systems and the molar mass of the given thermoplastics.<sup>30,35,47,57</sup> Fracture toughnesses,  $K_{Ic}$ , of the various neat epoxy networks and PPE-modified blends are reported in Table 3-6 and SEM micrographs of the fracture surfaces are shown in Figure 3-4.

The fracture toughness of unmodified epoxy networks are in agreement with the literature. In fact, our previous study has shown that DGEBA/IL-DEP networks with lower crosslinking density have similar fracture toughness to epoxy networks cured with aromatic amine MCDEA. On the other hand, the use of IL-TMP leads to a high crosslinked networks and a lower  $K_{Ic}$  of 0.39 MPa.m<sup>1/2</sup>.



**Figure 3-4** Fracture surface of unmodified (a, d, g), modified by PPE-1 (b, e, h) and PPE-2 (c, f, i) modified epoxy/amine (a, b,c), epoxy/IL-TMP (d, e, f) and epoxy/IL-DEP (g, h,i) networks observed by SEM.

Then, the addition of PPE into the epoxy networks improved the fracture toughness. In the case of epoxy networks cured with MCDEA, the values of the fracture toughness are similar to those reported in the literature.<sup>69,70</sup> For such blends, only a slight increase of the fracture toughness is evidenced. Indeed, many authors have demonstrated that morphologies highlighting the presence of thermoplastic particles having micrometer size have no significant toughening impact compared to a co-continuous or phase-inverted morphology.<sup>28,59,71,72</sup> In addition, SEM micrographs of the fracture surfaces of unmodified and PPE-modified epoxy/amine networks are very similar and are very smooth as mirror-like fracture surfaces corresponding to the fracture surfaces of brittle materials. In the opposite, the incorporation of PPE in epoxy/IL systems has a significant influence on the fracture toughness with differences related to the chemical nature of the phosphonium ILs. When IL-DEP is used as curing agent of epoxy-PPE systems, significant increases of the fracture toughness are observed. In fact, the fracture toughness is about 3 times higher than for the neat

network, which displays almost the same fracture properties as the brittle epoxy/amine network. These results could be associated with the morphologies of the PPE-modified epoxy/IL-DEP materials (see Figure 3-1) for which the coexistence of co-continuous and phase-inverted morphologies combined with the presence of thermoplastic particles induces an efficient toughening mechanism which is evidenced by the very rough fracture (Figure 3-4).<sup>73</sup> Thus, the crack propagation was slowed down by the ductile thermoplastic domains. In the case of PPE modified-epoxy/IL networks based on IL-TMP, two different behaviors are observed. In a first case, the addition of PPE-1 leads to an increase of the fracture toughness from  $0.39 \text{ MPa}\cdot\text{m}^{1/2}$  to  $0.99 \text{ MPa}\cdot\text{m}^{1/2}$ . This increase can be explained by the presence of the interconnected PPE particles forming a pseudo-network and the fracture toughness enhancement is evidenced by the rough fracture surface observed by SEM. Moreover, it is well known that the toughening effect of the thermoplastics is very dependent on the crosslinking density of the epoxy network.<sup>28</sup> In fact, when the crosslinking density is high, the effect of the thermoplastic material used is more important.<sup>28</sup> In the previous chapter, we have demonstrated that DGEBA/IL-TMP have a higher crosslinking density compared to DGEBA/MCDEA. In the case of PPE-2-modified epoxy/IL-TMP and despite the presence of the same thermoset network, a decrease of the fracture toughness is observed. This difference could be attributed to the lower molar mass of PPE-2 as well as the decrease in the PPE particle size leading to a morphology, which does not display interconnected PPE particles as for PPE-1. As expected, such blend displays fracture surfaces which are very smooth as DGEBA/IL-TMP based blends.<sup>28,37,71</sup>

In conclusion, the use of ILs to replace amine in the formation of epoxy networks changed the morphology of the modified epoxy networks leading to more significant improvements of mechanical properties. Besides, the mechanical properties of the PPE-modified epoxy/IL networks are clearly dependent on the chemical nature of the phosphonium ionic liquids (phosphate versus phosphinate) which are used as reactants with epoxy prepolymer to form the epoxy networks. The molar mass of the PPE thermoplastics could also be considered to a slightly lesser extent as a parameter for tailoring mechanical properties of the PPE-epoxy blends. With the results reported in this part, we demonstrated for the first time that epoxy-thermoplastic blends having enhanced mechanical performances can be designed by using IL as curing agents.

### 3.1.4. Conclusion

In this part, new epoxy-thermoplastic networks using phosphonium ILs denoted IL-TMP and IL-DEP as curing agents have been developed. In addition, the influence of the chemical nature of the ILs (phosphinate versus phosphate counter anions) as well as the molar mass of PPE

thermoplastics on the morphology and the final properties was investigated. Thus, we have demonstrated that the addition of PPE in epoxy/IL thermoplastics leads to the formation of co-continuous or phase-inverted morphologies compared to epoxy/amine networks where the presence of PPE particles of 1-3  $\mu\text{m}$  is observed. These different morphologies obtained, especially when PPE-1 was used as toughening agent of epoxy network involves significant increases of fracture toughness, a more hydrophobic character as well as an excellent thermal stability. In conclusion, these results highlight that ILs act as not only curing agent of epoxy prepolymer but also as dispersing and modifier agents of TP in the epoxy networks. This new discovery can open a new route for toughening epoxy networks as well as for the formation of new nanostructured thermosets. Nevertheless, further studies are required to fully understand the role of ionic liquids in thermoplastics-modified thermosetting materials and also the toughening mechanism of new networks. Other researches are in progress on other epoxy-thermoplastic systems.

## **3.2. Dual functions of IL in the core-shell particle reinforced epoxy networks: curing agent *vs* dispersion aids**

### **3.2.1. Introduction**

The epoxy networks are one of the most important thermosetting polymers thanks to their excellent properties.<sup>74</sup> The brittleness of epoxy networks that reduces their range of applications can be improved by several modifications such as the addition of rubbers,<sup>26</sup> or thermoplastics.<sup>28</sup> However, while the use of rubbers reduces the elastic modulus of epoxy networks, the processing difficulties and the complex relationship between curing cycles, generated morphologies and phase compositions are the major disadvantages of thermoplastics modified epoxy networks.<sup>51</sup>

Then, core-shell rubber particles (CSR) with a soft rubber core and hard shell appear to be a great solution allowing the control of size and of composition of dispersed phase. In fact, the presence of CSR increases the fracture toughness without affecting the glass transition temperature of epoxy networks. The idea of using preformed core-shell particles has been reported since 1990s with several kinds of CSR employed in the epoxy matrix. Usually, the material used for the shell is poly (methyl methacrylate) (PMMA) which is compatible with the epoxy matrix.<sup>26</sup> The most common rubbers used as the soft core of the CSR particles include poly (butyl acrylate) (PBA),<sup>75-87</sup> poly (styrene-co-butadiene) (SBR),<sup>80,86-93</sup> and polysiloxane (PDMS).<sup>87,94-96</sup> In order to improve the dispersion of CSR particles as well as the fracture toughness of epoxy networks, several modifications were conducted on CSR particles such as crosslinking or functionality. In fact, the shell of CSR particles can be crosslinked through the polymerization of methyl methacrylate with

a small amount of glycidyl methacrylate (GMA) leading to higher toughening effect.<sup>81,84</sup> Moreover, PMMA shell was also functionalized with carboxyl group which can react with oxirane and hydroxyl groups of epoxy prepolymer in order to improve the interfacial adhesion of CSR with epoxy matrix.<sup>78,80,83,93</sup> In fact, a better dispersion of functionalized CSR in the epoxy matrix than the non-functional ones led to a significant improvement of fracture toughness compared to neat epoxy networks. Among the soft inner core composition, PDMS has lately gained the attention thanks to their heat resistant. Giannakopoulos *et al.*,<sup>87</sup> Chen *et al.*,<sup>95</sup> and Roy *et al.*<sup>96</sup> have investigated the employment of PDMS based core-shell particles in the epoxy networks and have discovered the effective toughening effect even at low temperature *i.e.* -100 °C. Also, Wacker Silicones company has introduced a commercial type of silicone CSR particles under name of Genioperl that were modified to facilitate their dispersion leading to excellent toughening improvements.<sup>94</sup>

Overall, it has to be noted that the dispersion of CSR is the most important factor governing the properties of modified epoxy networks. Recently, a new method to disperse fillers in the epoxy networks was developed using ionic liquids (ILs) thanks to their multifunctional effect in the nanocomposites.<sup>97</sup> In details, the existence of ILs in the epoxy/amine networks improve the dispersion of fillers such as the exfoliation of clays,<sup>98</sup> or the clustering of silica particles.<sup>99</sup> Not only acting as dispersion aid for fillers, the existence of small amount of ILs can also modify the properties of epoxy/amine networks such as thermomechanical behavior,<sup>8,9</sup> ionic conductivity,<sup>10</sup> and scratch resistance.<sup>11,12</sup> Also, ILs has proven their potential as alternatives to conventional curing agents. In the literature, many papers reported the formation of epoxy networks cured by imidazolium and phosphonium based ILs. The advantages of using ILs to replace conventional curing agents include the low loading of ILs and their tunable structure aiming to different applications. In fact, high reactivity of ILs towards epoxy prepolymer requires low curing temperature.<sup>22,23</sup> Epoxy/IL networks provide outstanding thermal and mechanical properties,<sup>22,23</sup> which can be tuned as a function of ionic liquids structure including the glass transition temperature, thermal stability and nanostructuration. Hence, very recently, a viable process to produce epoxy nanocomposites was reported by Throckmoton *et al.*,<sup>100</sup> and Maka *et al.*<sup>24,25,101</sup> in which single-phase dispersion and cure were both provided by ILs. A uniform dispersion of silica, and carbon nanofillers was obtained for epoxy nanocomposites leading to excellent mechanical and electrical properties as well as flame retardancy.

This work describes the effect of ILs on the dispersion of commercial CSR particles – Genioperl in epoxy networks in comparison with a conventional system based on aromatic amine. The morphology-properties relationship will be demonstrated, which should highlight the important role of ILs in designing nanostructured materials.

### 3.2.2. Experimental

#### 3.2.2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) based epoxy prepolymer (DER 332) with epoxide equivalent weight (EEW) of 175 g.mol<sup>-1</sup> was purchased from DOW Chemical Company. Conventional aromatic amine, 4,4'-methylene bis(3-chloro-2,6-diethylaniline) denoted MCDEA was supplied by Lonzacure with Amine Hydrogen Equivalent Weight (AHEW) of 95 g.mol<sup>-1</sup>. Then different ionic liquids: trihexyl (tetradecyl) phosphonium bis-2,4,4-(trimethyl pentyl) phosphinate denoted IL-TMP and tributyl (ethyl) phosphonium (diethyl) phosphate denoted IL-DEP were kindly provided by Cytec. Genioperl P52 (CSR), which is a core-shell particle with two glass transition temperatures observed by DSC at -134 °C and 130 °C corresponding respectively to the silicone core and methacrylate based shell, was purchased from Wacker Chemie AG. In addition, the primary particles size of CSR is around 200 nm.

#### 3.2.2.2. Samples preparation

In order to prepare epoxy/CSR samples, Genioperl (10 and 20 phr) was dispersed in DGEBA at 60 °C during one hour with the stirring velocity of 200 rpm. Then, the mixture was sonicated for 15 minutes in order to totally disperse the CSR in DGEBA (amplitude 60mW). After, a stoichiometry ratio of MCDEA and 10 phr of IL-TMP and IL-DEP were added and were mixed until a homogenous blend is obtained. The mixture was then poured into silicone molds and cured in oven with the same curing protocol as unmodified DGEBA/curing agents systems (Table 3-7).

**Table 3-7** Curing protocol for CSR-modified epoxy networks.

Curing agent	Curing	Post-curing
MCDEA	1h@150 + 2h@180	1h@200
IL-TMP	2h@80 + 3h@120	1h@200
IL-DEP	2h@80 + 3h@160	3h@200

### 3.2.3. Results and discussions

#### 3.2.3.1. Curing behavior of CSR-modified epoxy blends

The effect of CSR particles on the curing of epoxy/amine and epoxy/IL mixtures was investigated by DSC and FTIR techniques. DSC thermograms obtained under dynamical mode in the exothermal region are presented in the Supporting Information – Figure S3-2 with the

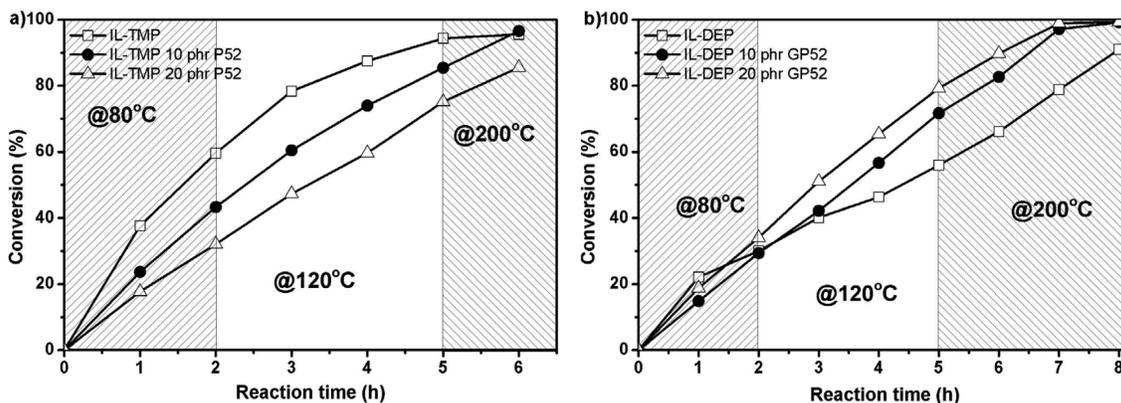
exothermal peak temperatures reported in Table 3-8. The evolution of the conversion of epoxide group as a function of the reaction time was calculated from FTIR (Figure S3-3), especially from the relation between two adsorption peaks at 914 and 1184  $\text{cm}^{-1}$  as described in the previous chapter and was presented in Figure 3-5.

**Table 3-8** Exothermal peak temperature of G52-modified epoxy networks measured by DSC.

Curing agent	CSR particles (phr)	T <sub>1st exothermal peak</sub> (°C)	T <sub>2nd exothermal peak</sub> (°C)
MCDEA	0	268	--
	10	266	--
	20	267	--
IL-TMP	0	142	--
	10	145	172
	20	151	173
IL-DEP	0	344	--
	10	325	--
	20	322	--

The influence of the aromatic amine as well as ILs was investigated (Table 3-8, see DSC curves in the Supporting Information – Figure S3-2). Firstly, based on our previous chapter, exothermal peak temperatures of 142 °C, 268 °C and 344 °C were obtained for epoxy cured with IL-TMP, MCDEA and IL-DEP, respectively. Thus, we have demonstrated that IL-TMP and IL-DEP acted as crosslinking initiator of the anionic polymerization. However, the two phosphonium ionic liquids have a different reactivity due to the basicity of their counteranions which explains the difference in exothermal peak temperatures. In all cases, the incorporation of CSR particles including their functionalization has an influence on the formation of epoxy/IL networks compared to epoxy/amine networks where no change was observed in the DSC curves. Indeed, it is possible to see that an increase of the CSR particles led to an increase of the exothermal peak temperature of about 30 °C for epoxy initiated with IL-TMP highlighting a lower reactivity in the presence of CSR. These results can be explained by the appearance of a shoulder peak (see DSC curves) at higher temperatures (around 170 °C) which had a tendency to increase as a function of CSR particles. We have attributed this new peak by the presence of side reactions between epoxy and CSR particles due to the functionality on CSR shell.<sup>94</sup> In fact, it is well known that the reactive groups on PMMA shell can react with epoxy prepolymer to form an interfacial adhesion between

CSR and epoxy matrix.<sup>78,80,83,93</sup> In the opposite, the introduction of 10 or 20 phr of CSR particles in epoxy initiated by IL-DEP led to a decrease of the exothermal peak temperatures of about 20 °C which can be explained by a lower reactivity of IL-DEP. However, these results are attributed to the combination of the IL with the CSR particles.



**Figure 3-5** Epoxide group conversion as a function of curing time of epoxy/IL networks (□) modified by 10 phr (●) and 20 phr (△) CSR and cured with a) IL-TMP and b) IL-DEP.

In order to quantify the epoxide group conversion during the curing process, FTIR analysis was used to follow the evolution of the absorption peak corresponding to the epoxide groups as a function of the reaction time. The epoxide group conversion was calculated from the evolution of the absorption peaks of the epoxy and ether groups at respectively  $914\text{ cm}^{-1}$  and  $1184\text{ cm}^{-1}$  using the following equation:  $X = (A_o - A_t) / A_t$ , where  $A_o$  and  $A_t$  are the area ratios of the peaks at  $914\text{ cm}^{-1}$  and  $1184\text{ cm}^{-1}$  at reaction times  $t_o$  and  $t$ , respectively.<sup>102</sup> Thus, Figure 3-5 shows the epoxy conversions versus curing time of modified and unmodified epoxy networks cured with IL-TMP and IL-DEP, respectively.

As evidenced in Figure 3-5, a conversion of about 90 % for all the epoxy/IL networks is obtained. These results are consistent with Chapter 2. Moreover, the evolution of epoxide group conversion as a function of the curing time is influenced by the addition of CSR. An increase of the final epoxy conversion is also highlighted for CSR-modified epoxy systems cured with IL-DEP. In fact, an increase of the final epoxy conversion was also highlighted for CSR-modified epoxy systems cured with IL-DEP. As demonstrated by DSC results, the introduction of CSR particles resulted in a decrease in the exothermal peak temperatures and their functionalization can react on the epoxy prepolymer. Thus, the combination of these two phenomena led to a final conversion higher than neat DGEBA/IL-DEP networks, *i.e.* over 99 % and 91 % of epoxy conversion were obtained for modified and unmodified DGEBA/IL-DEP networks, respectively. In the opposite, the presence of CSR particles in the DGEBA/IL-TMP networks led to a considerable reduction in

epoxide group conversion of modified DGEBA/IL-TMP networks increases with the CSR amount *i.e.* the final conversion of DGEBA/IL-TMP networks containing 20 phr CSR is only 85 % instead of 96 % for unmodified networks. These results can be explained by the reduction of system reactivity due to an increase of the amount of CSR particles (see DSC curves and Table 3-8). In addition, IL-TMP may have a better affinity with PMMA matrix. Indeed, several studies have shown that ionic liquids can be excellent plasticizers of PMMA revealing their great affinity towards this polymer.<sup>103-105</sup> Thus, a partial migration of the ionic liquid in the PMMA leads to a reduction in the quantity of initiators of the anionic polymerization inducing a decrease of the final epoxy conversion.

Overall, the effect of Genioperl depends strongly on the chemical nature of used curing agent and initiator (amine and IL, respectively) and the amount of CSR particles introduced. The curing behavior of epoxy blends is influenced by the side reactions between epoxy prepolymer and CSR as well as the affinity between polymer and ILs.

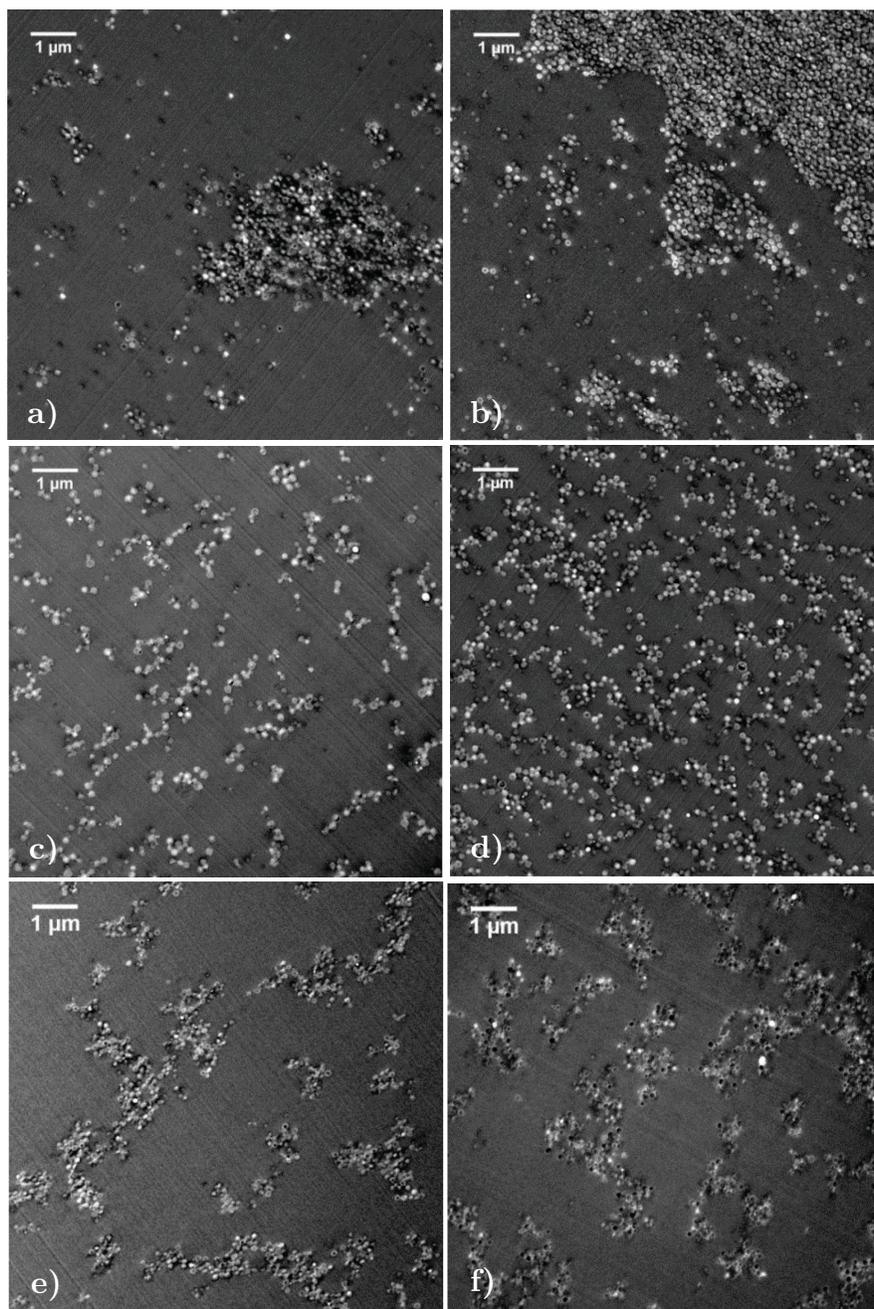
### ***3.2.3.2. Effect of IL on the morphology of CSR-modified epoxy networks***

The effect of curing agents on the dispersion of CSR particles in the epoxy networks was demonstrated using transmission electron microscopy (TEM). TEM micrographs of all epoxy networks are displayed in Figure 3-6. It should be noted that the same dispersion method was applied for all systems.

In the case of epoxy/amine systems, a poor dispersion of CSR particles is observed with many aggregates of 5 – 20  $\mu\text{m}$ . This indicates that the dispersion method is not efficient for CSR-modified DGEBA/MCDEA because homogenous morphologies have been reported in the literature when Genioperl<sup>94</sup> or other core-shell rubber particles<sup>79,84,86</sup> were incorporated in the epoxy/amine networks.

On the other hand, a better dispersion of CSR particles (10 and 20 phr) is achieved in the epoxy/IL networks compared to epoxy/amine systems. The use of IL-TMP and IL-DEP involves the formation of inter-connected groups of particles uniformly distributed throughout the epoxy matrix without the presence of big agglomerates. In fact, ILs have shown their ability as plasticizers<sup>103,104</sup> or compatibilizers for PMMA.<sup>106</sup> Thus, in the case of epoxy/IL networks, both ILs and epoxy prepolymer can interact with CSR particles leading to a finer and more homogenous morphology than epoxy/amine systems. Recently, ILs have been reported by Throckmorton *et al.* and Maka *et al.* to serve as both curing agent for epoxy prepolymer and dispersion aids for silica and carbon nanofillers in order to prepare epoxy nanocomposites.<sup>24,25,100,101</sup> Moreover, the morphology of CSR-modified epoxy/IL networks depends clearly on the chemical structure of ILs.

Various interconnecting agglomerates of 1  $\mu\text{m}$  are observed for CSR-modified DGEBA/IL-DEP networks while CSR particles are dispersed as finer interconnecting and individual particles in the DGEBA/IL-TMP networks. The dispersion effect is evidently less significant in the case of IL-DEP due to its shorter alkyl chain on cation and anion, which reduces the interaction with CSR. In addition, no difference in the morphology was discovered with the increase of CSR amount (10 to 20 phr) for epoxy/IL networks cured with IL-TMP or IL-DEP.



**Figure 3-6** TEM image of epoxy networks modified by 10 (a, c, e) and 20 phr (b, d, f) of CSR using MCDEA (a, b), IL-TMP (c, d) and IL-DEP (e, f).

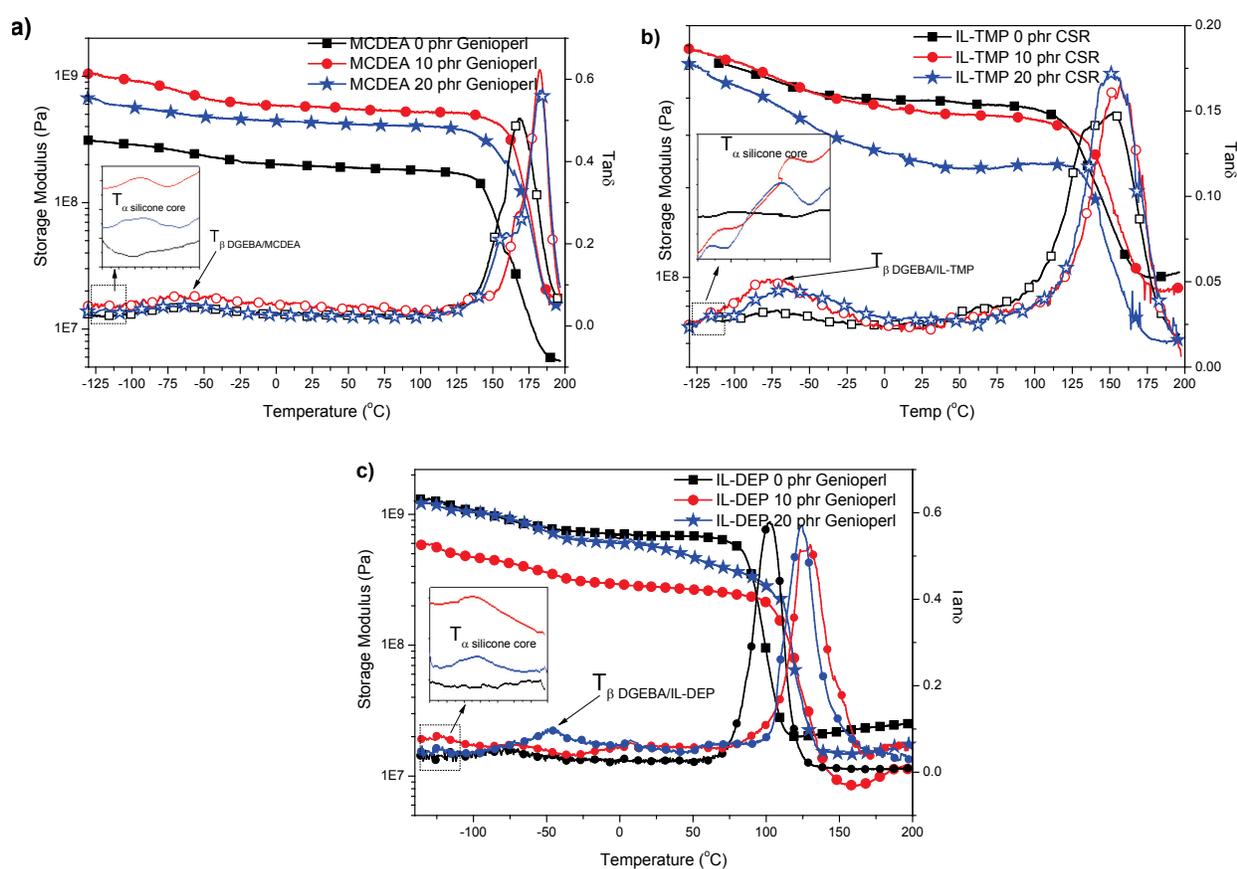
In conclusion, ILs play a key role on the dispersion of CSR in the epoxy networks compared to conventional epoxy/amine networks. In fact, the chemical nature of ILs but also the affinity of ILs with CSR particles has an influence on the shape and size of rubbery dispersed phase.

### 3.2.3.3. Properties of CSR-modified epoxy/IL networks

The properties of CSR-modified epoxy/IL networks were investigated in terms of thermomechanical properties (DMA), thermal stability (TGA), surface energy (sessile drop) and mechanical properties (flexural test and fracture toughness test).

#### 3.2.3.3.1. Thermomechanical properties of CSR-modified epoxy/IL networks

The thermomechanical properties of epoxy networks were measured by DMA with relaxation temperatures presented in Table 3-9 and the DMA curves in Figure 3-7.



**Figure 3-7** DMA curves of epoxy networks modified by CSR using MCDEA (a), IL-TMP (b) and IL-DEP (c).

**Table 3-9** Relaxation temperatures of unmodified and CSR-modified epoxy networks.

Curing agent	CSR (phr)	$T_{\alpha \text{ core}}$ ( $^{\circ}\text{C}$ )	$T_{\alpha \text{ matrix}}$ ( $^{\circ}\text{C}$ )
MCDEA	0	--	160
	10	-119	172
	20	-120	170
IL-TMP	0	--	150
	10	-116	149
	20	-118	151
IL-DEP	0	--	112
	10	-122	124
	20	-124	124

For all unmodified epoxy systems, DMA curves display only one relaxation peak ( $T_{\alpha}$ ) of epoxy networks *i.e.* 160  $^{\circ}\text{C}$ , 150  $^{\circ}\text{C}$  and 112  $^{\circ}\text{C}$  for DGEBA/MCDEA, DGEBA/IL-TMP and DGEBA/IL-DEP networks, respectively. Then, the addition of CSR leads to the appearance of a relaxation temperature at around -120  $^{\circ}\text{C}$  corresponding to  $T_{\alpha}$  of the silicone core of CSR particles (see Figure 3-7). The relaxation peak  $T_{\alpha}$  of methacrylate shell is not observed by DMA as it is overlapped by the  $\alpha$ -relaxation peak of epoxy networks.<sup>80</sup> The relaxation temperature of CSR core is not remarkably influenced by the dispersion in the epoxy networks. *Vice versa*,  $\alpha$ -relaxation temperature of epoxy networks does not change considerably with the presence of CSR, which is in agreement with other works on the modification of conventional epoxy networks by CSR particles.<sup>79,80,84,85,87,89,92,95,96</sup> In the study of Chen *et al.*, the use of polysiloxane based CSR up to 20 wt% has no influence on the glass transition temperature of epoxy/anhydride networks.<sup>95</sup> The relaxation temperatures of IL-TMP based systems remained stable with the addition of CSR while an increase 10  $^{\circ}\text{C}$  in  $T_{\alpha}$  was revealed for modified DGEBA/MCDEA and DGEBA/IL-DEP networks compared to the neat ones. These results can be explained by a modification of architecture of network that displays a better final epoxy conversion (Figure 3-5). Above all,  $T_{\alpha}$  values were not significantly influenced by the increase of CSR content up to 20 phr. In addition, in the case of epoxy initiated by IL-TMP and whatever the amount of CSR particles, the presence of the broad peaks extending over a wide temperature range was observed indicating a greater heterogeneity of the epoxy networks. In the opposite, the use of IL-DEP and MCDEA as initiator and curing agents led to the formation of more homogeneous epoxy networks. Moreover, the observed temperatures between -70  $^{\circ}\text{C}$  and -80  $^{\circ}\text{C}$  have attributed to the  $\beta$ -relaxation ( $T_{\beta}$ ) *i.e.* to the movement of the hydroxy ether units into epoxy networks.<sup>107,108</sup>

3.2.3.3.2. Thermal stability of CSR-modified epoxy/IL networks

The thermal stability of CSR, unmodified and CSR-modified epoxy networks was followed by Thermogravimetric analysis (TGA) and the degradation temperatures at 5 % and 10 % weight loss and at the maximum of DTGA curve are summarized in Table 3-10. Thermogravimetric curves of Genioperl, unmodified and modified epoxy networks are presented in the supporting information (Figure S3-4).

**Table 3-10** Degradation temperature of CSR, neat epoxy networks and CSR-modified epoxy networks from TGA.

Material	CSR (phr)	TGA		
		T <sub>d5%</sub> (°C)	T <sub>d10%</sub> (°C)	T <sub>dmax</sub> (°C)
CSR	100	296	342	387
MCDEA	0	392	400	420
	10	383	396	418
	20	378	394	411
IL-TMP	0	399	430	458
	10	412	428	453
	20	401	422	449
IL-DEP	0	354	373	400
	10	367	383	409
	20	365	383	411

Overall, all unmodified and CSR-modified epoxy networks exhibit an excellent thermal stability with a degradation temperature of about 400°C. The addition of CSR has no significant influence on the thermal stability of epoxy networks. Indeed, the same effect was observed by Roy *et al.* when incorporating polysiloxane based CSR in the epoxy networks.<sup>96</sup> In details, the degradation temperatures of modified epoxy/amine networks are very slightly reduced by the lower thermal stability of CSR (T<sub>dmax</sub> = 387 °C). In fact, the degradation temperatures at 420 °C, 418 °C and 411 °C are obtained for DGEBA/MCDEA networks containing 0, 10 and 20 phr CSR, respectively. Similarly, the degradation temperatures decreased of 5 °C and 10 °C for DGEBA/IL-TMP containing 10 phr and 20 phr of CSR, respectively. On the other hand, the degradation temperatures of DGEBA/IL-DEP networks are enhanced by adding 10 phr and 20 phr CSR probably due to the increase of final epoxide group conversion with an increase of 9 °C and 11 °C for the maximal degradation temperature, respectively.

In conclusion, the degradation temperatures of epoxy networks are slightly influenced by the addition of CSR particles. Above all, the highest thermal stability is observed for systems cured by IL-TMP independently of the amount of CSR particles.

### 3.2.3.3.3. Surface energy of CSR-modified epoxy/IL networks

The surface energy of epoxy networks including dispersive and non-dispersive components shown in Table 3-11 were measured from sessile drop method.

**Table 3-11** Surface energy of neat epoxy networks and epoxy networks modified by CSR.

Curing agent	CSR (phr)	$\Theta_{\text{water}}$ (°)	$\Theta_{\text{CH}_2\text{I}_2}$ (°)	$\gamma_{\text{non-dispersive}}$ (mJ.m <sup>-2</sup> )	$\gamma_{\text{dispersive}}$ (mJ.m <sup>-2</sup> )	$\gamma_{\text{total}}$ (mJ.m <sup>-2</sup> )
MCDEA	0	81	50	4.5	29.8	34.3
	10	80	48	4.5	31.1	35.6
	20	85	68	6.1	19.8	25.9
IL-TMP	0	91	44	1.0	37.3	38.3
	10	101	70	0.5	22.4	22.9
	20	102	71	0.7	21.4	22.1
IL-DEP	0	96	67	1.5	24.8	26.4
	10	96	74	2.5	18.3	20.8
	20	97	67	1.2	23.3	24.5

For unmodified systems *i.e.* epoxy/amine and epoxy/IL networks, the results presented in Table 3-11 are in agreement with Chapter 2 where epoxy/IL networks using phosphonium ionic liquids denoted IL-TMP and IL-DEP as curing agents are more hydrophobic than conventional epoxy/amine systems. In addition to this, the presence of CSR in epoxy networks increases the hydrophobicity of samples compared to the unmodified systems. It should be noted that PMMA has high surface tension of around 41.2 mJ.m<sup>-2</sup>,<sup>109</sup> the reduction in surface energy can be explained by the presence of silicone cores having a very low surface tension of 20 – 23 mJ.m<sup>-2</sup>.<sup>110</sup> It is also evident that the hydrophobicity of epoxy networks is improved by the increase of CSR particles amount. Thus, all systems containing 20 phr of CSR have lowered the surface energies to 25 mJ.m<sup>-2</sup>. Compared to neat epoxy networks, a reduction of 24.5 %, 42.3 % and 7.1 % in surface energy was obtained by using 20 phr of CSR for epoxy networks cured with MCDEA, IL-TMP and IL-DEP, respectively. In addition, the highest improvement was obtained for system based on IL-TMP, which can be explained by the better dispersion of CSR throughout the epoxy matrix (Figure 3-6).

In conclusion, the incorporation of CSR particles improves the hydrophobicity of the epoxy networks, which is promising for composites and coating applications.

3.2.3.3.4. Mechanical properties of CSR-modified epoxy/IL networks

The mechanical properties of modified epoxy networks were investigated by flexural tests and fracture toughness presented in Table 3-12. Overall, flexural modulus, flexural strength and fracture toughness of unmodified epoxy/amine and epoxy/IL networks are in agreement with the previous chapter.

**Table 3-12** Mechanical behavior (Determined at room temperature) of epoxy networks modified by CSR.

Curing agent	CSR (phr)	Flexural modulus (GPa) $\pm 0.1$	Flexural strength (MPa) $\pm 4$	$K_{Ic}$ (MPa.m <sup>1/2</sup> ) $\pm 0.05$
MCDEA	0	2.3	77	0.56
	10	2.1	93	0.61
	20	1.9	80	0.71
IL-TMP	0	1.6	25	0.39
	10	2.1	55	0.40
	20	1.9	56	0.51
IL-DEP	0	2.6	73	0.55
	10	2.0	86	0.74
	20	1.9	61	0.85

*a. Flexural Properties*

Concerning the flexural properties, the incorporation of CSR induces a decrease of flexural moduli of all epoxy networks except for the systems based on IL-TMP. For MCDEA based systems, flexural modulus decreases from 2.3 GPa for glassy epoxy networks to 2.08 GPa and 1.93 GPa when 10 and 20 phr of CSR is added, respectively. Similar results are reported by other groups on flexural modulus<sup>92</sup> as well as tensile modulus<sup>77,84-89,95,111</sup> using CSR particles in conventional epoxy networks. In fact, Sue *et al.* have observed a decrease of flexural modulus epoxy systems from 3.25 GPa to 3.05 GPa when 5 wt% of CSR was used. Regarding epoxy/IL systems, DGEBA/IL-DEP networks have the same behavior as MCDEA based networks with a 20 % and 26 % decrease in flexural modulus by using 10 and 20 phr CSR, respectively. In the opposite, the flexural modulus of modified IL-TMP based systems increases from 1.6 GPa to 1.9-2.1 GPa with the addition of CSR. In fact, the improvement in flexural modulus of DGEBA/IL-TMP networks can be explained

by the fine dispersion of CSR particles throughout the epoxy matrix (Figure 3-6). Nevertheless, the flexural strength of modified epoxy networks is also influenced by the presence of CSR. In all the cases, the flexural strength increases considerably when 10 phr of CSR is added, especially in the case of DGEBA/IL-TMP where an improvement of 120 % is obtained. Obviously, the ductility of silicone core of CSR reduces the stiffness of epoxy networks resulting in a growth of flexural strength for all systems containing 10 phr of CSR.<sup>112</sup> The most significant improvement is discovered for CSR-modified DGEBA/IL-TMP systems where a fine and uniform dispersion of CSR is observed (Figure 3-6). However, when the fillers concentration is too high *i.e.* 20 phr, the flexural strength tends to reduce due to the stress concentration effect of the particles.<sup>87,95</sup> In fact, Chen *et al.* have discovered the diminution of tensile strength linearly with the amount of silicone based CSR particles incorporated into the epoxy networks.<sup>95</sup>

In conclusion, the addition of CSR in the epoxy networks induces to a slight decreasing effect of the flexural moduli as well as an increase of the flexural strength due to the ductility of CSR particles. Moreover, the dispersion of CSR governed by the used curing agent plays a significant role on the flexural properties of CSR-modified epoxy networks

#### *b. Fracture toughness*

In terms of fracture toughness, the use of CSR results in toughness improvements of epoxy networks in particular for  $K_{Ic}$  values. In fact, a proportional increase of  $K_{Ic}$  with CSR amount is revealed, which is similar to other studies on epoxy networks modified with core-shell particles.<sup>77,95</sup> However, the toughening extent depends on the nature of epoxy networks and CSR amount. For all epoxy systems, the fracture toughness increases proportionally with CSR content *i.e.* highest  $K_{Ic}$  values are obtained when using 20 phr CSR. Thus,  $K_{Ic}$  values are improved of 27 %, 31 % and 55 % for systems based on MCDEA, IL-TMP and IL-DEP, respectively. It is evident that CSR have lower effect on DGEBA/MCDEA systems than other reported works in the literature<sup>77,84,87,88,92,94,95</sup> due to its poor dispersion in the epoxy matrix. Noted that the dispersion of fillers depends directly on the interaction between the matrix and particles, the difference between epoxy/amine systems such as nature of prepolymer, amine and used dispersion method plays an important role in the final morphology and properties. Indeed, Qian *et al.* have investigated the effect of mixing method on the dispersion state of CSR particles and have found an improvement of CSR distribution with a higher speed of mechanical stirring.<sup>88</sup> Concerning epoxy/IL networks, a more significant toughening effect of core-shell particles was discovered due to the homogenous dispersion of CSR particles (Figure 3-6).<sup>83,88</sup> The  $K_{Ic}$  increment in case of DGEBA/IL-DEP systems is comparative to other previous studies using core-shell particles as toughening agents for epoxy

networks.<sup>85,96</sup> However, toughening effect of CSR is less pronounced in the case of IL-TMP despite its finest dispersion observed in Figure 3-6. It may be explained by the great difference of fracture toughness between DGEBA/IL-TMP systems and core-shell particles, which results in low interface bonding. In fact, the same phenomenon was observed by Lu *et al.* when using the same CSR particles to toughen two different epoxy/amine systems.<sup>113</sup> They have shown that the debonding mechanism is more dominant than cavitation mechanism in the case of more brittle epoxy systems, which reduces the toughening effect.<sup>95,114</sup> In this case, although the high interaction between IL-TMP and CSR led to a better dispersion of CSR particles, the high crosslinking density of DGEBA/IL-TMP networks (Chapter 2) results in the failure of interface between particles and matrix leading to a lower improvement of  $K_{Ic}$ .

In conclusion, the properties of the CSR-modified epoxy networks are clearly dependent on their morphology, which is in turn controlled by the chemical nature of the curing agent: amine or phosphonium ionic liquids (phosphate versus phosphinate). Thus, in the case of epoxy-amine network, a good compromise between mechanical properties and a poor dispersion of CSR was observed. Whereas for the epoxy cured with ILs, the chemical nature of the phosphonium ILs plays a key role on the dispersion of CSR particles as well as the mechanical performances, especially the fracture toughness.

### 3.2.4. Conclusion

This work provides an investigation on the effect of ILs on the dispersion of core-shell particles as well as the final properties of epoxy networks. Thus, we have demonstrated that the chemical nature of the phosphonium ionic liquids plays a key role on the dispersion of CSR particles in the epoxy matrix. In fact, IL-TMP and IL-DEP have a dual function *i.e.* as curing agent of epoxy prepolymer but also as dispersion aids of CSR particles in the network. Moreover, the final properties of modified epoxy networks are consequently tunable as a function of the used curing agent where a more significant toughening effect is highlighted with phosphonium ILs. However, toughening mechanism is depending on the interaction between the epoxy matrix and core-shell particles, which in turn is controlled by the chemical structure of curing agent. Other works are required with other ILs in order to achieve a better understanding on the relationship between ILs chemical nature and their effect on the dispersion of fillers as well as on the final properties of epoxy networks.

### 3.3. Conclusion of chapter 3

In chapter 3, epoxy/IL networks were modified by two different methods using RIPS thermoplastics and preformed core-shell silicone particles. Properties and morphology of modified epoxy/IL networks have been compared to those of conventional epoxy/amine network, which illustrates the effect of ILs.

In the first part, with the same amount of thermoplastics, the use of ILs leads to different morphologies from co-continuous to inversed phase instead of nodulus dispersion of thermoplastics in the modified epoxy/amine networks. Form and size of dispersed PPE in the epoxy networks depend on the type of IL and the type of used PPE. High fracture toughness was achieved in case of PPE modified epoxy/IL networks with 154 – 200 % higher than neat epoxy/IL networks.

In the second part, the dispersion of CSR particles was facilitated by the introduction of ILs. In fact, ILs act as both curing agent for epoxy prepolymer and dispersion aids for CSR particles. In comparison to epoxy/MCDEA networks, a more uniform morphology was obtained without agglomeration. Thus, a higher improvement in the properties of epoxy networks *i.e.* fracture toughness was discovered for the case of CSR modified epoxy/IL.

In both cases, the morphology and properties of modified epoxy networks depend on the interactions between modifier and ILs, *i.e.* the chemical nature of ILs.

## References of chapter 3

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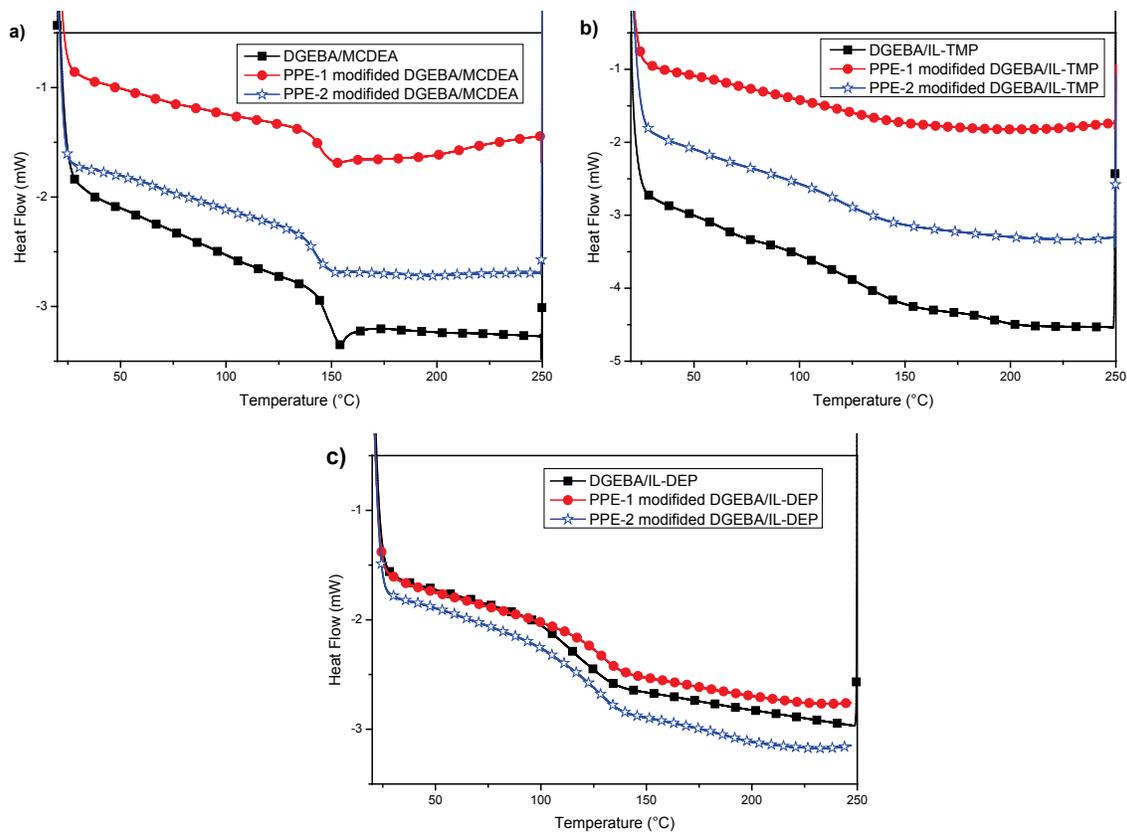
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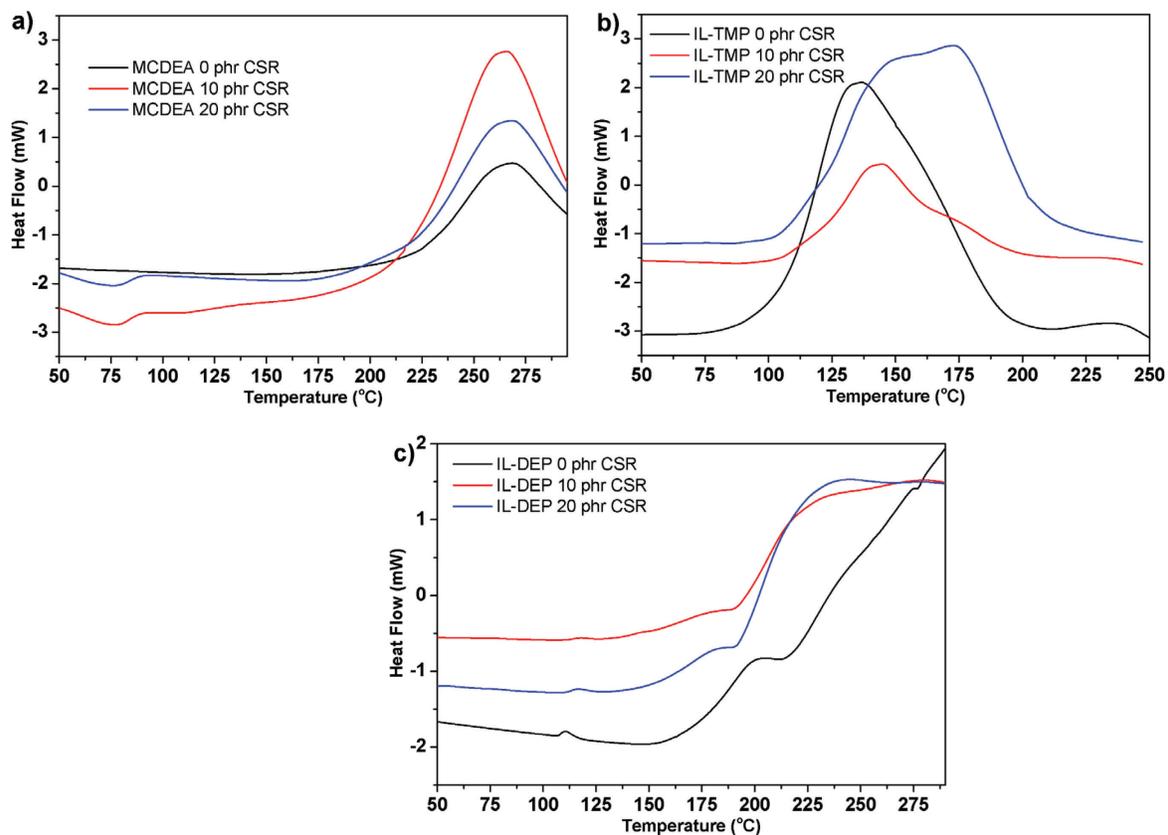
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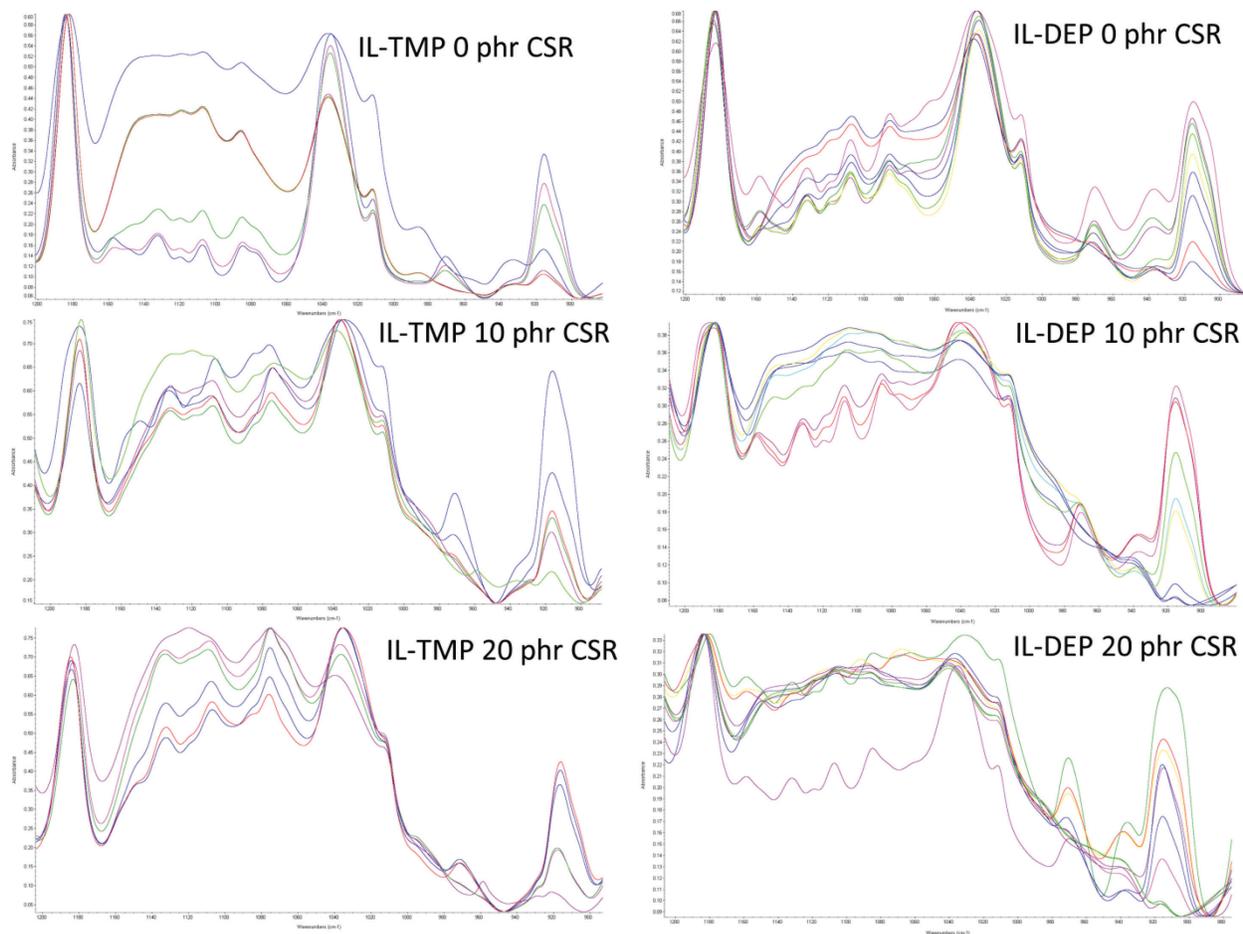
## Supporting Information of chapter 3



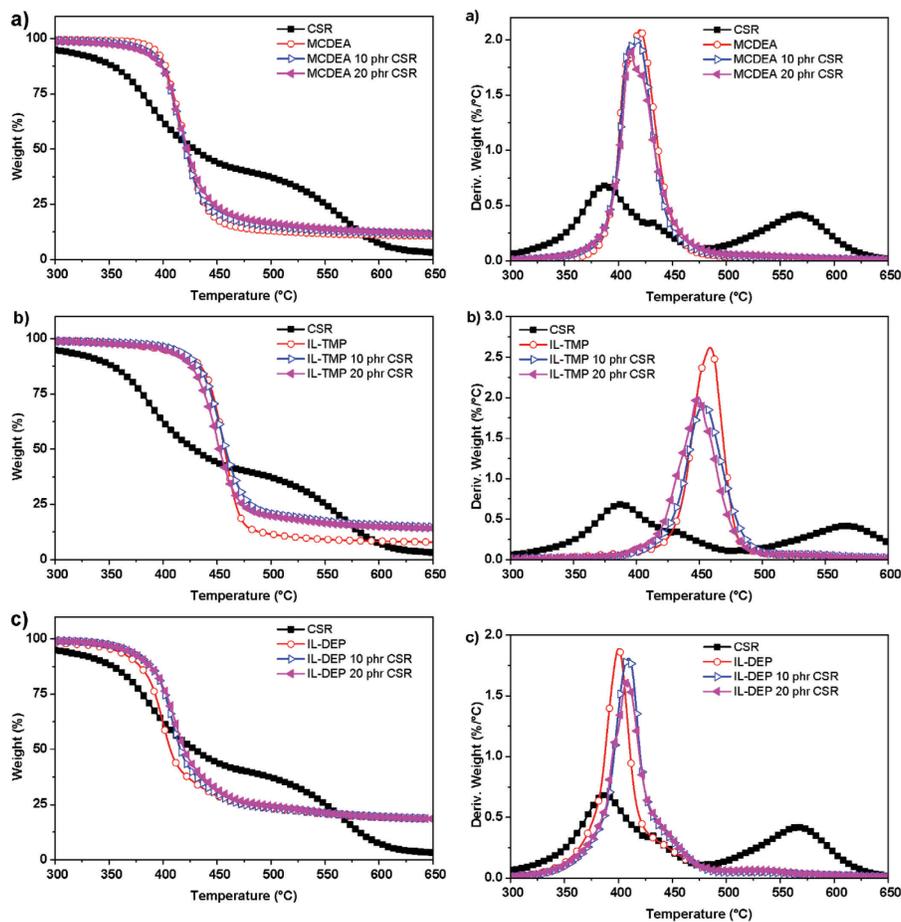
**Figure S3-1** DSC thermograph of (■) unmodified, (●) PPE-1-modified and (☆) PPE-2-modified epoxy networked cured by a) MCDEA, b) IL-TMP and c) IL-DEP.



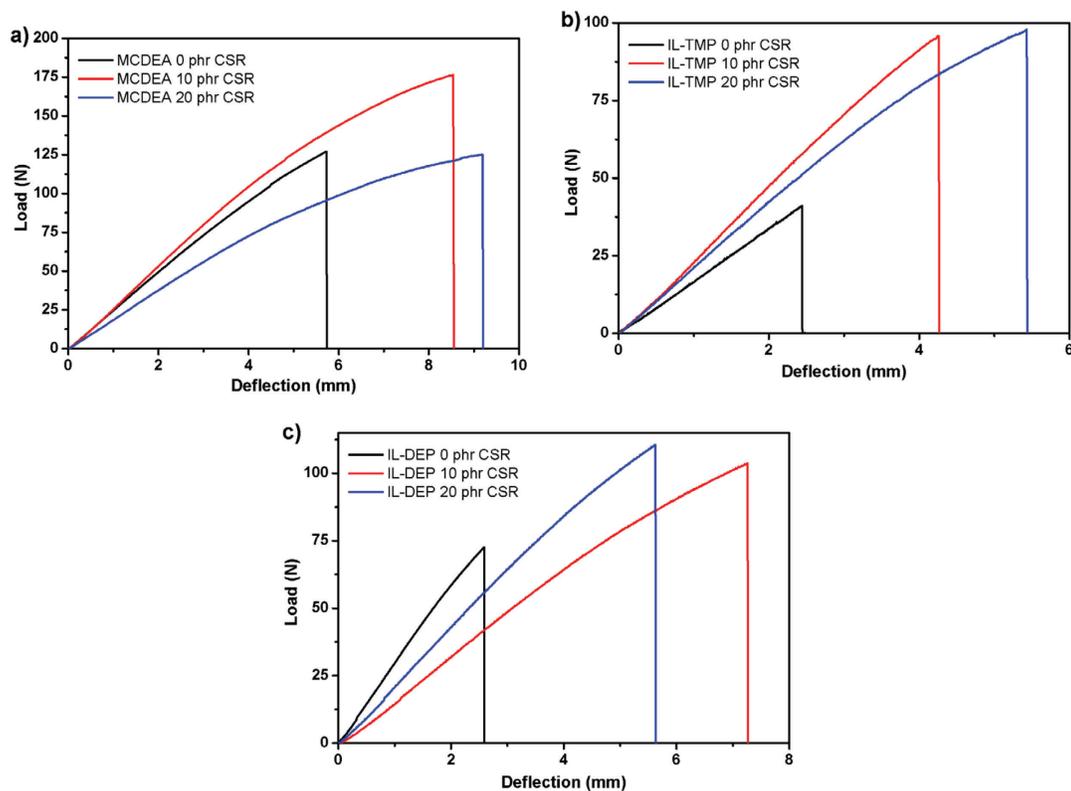
**Figure S3-2** DSC thermograms for dynamic scanning of epoxy networks modified by CSR using MCDEA (a), IL-TMP (b) and IL-DEP (c).



**Figure S3-3** Evolution of FTIR spectra with curing time of epoxy networks modified by CSR using IL-TMP (left) and IL-DEP (right).



**Figure S3-4** Thermogravimetric curves (TGA, DTGA) of CSR particles, unmodified and modified epoxy networks cured with a) MCDEA, b) IL-TMP and c) IL-DEP.



**Figure S2-5** Load-deflection curves of epoxy networks modified by CSR using a) MCDEA, b) IL-TMP and c) IL-DEP (2 mm.min<sup>-1</sup>).

## **Chapter 4:**

# **Bio-based Epoxy/IL networks**

In this chapter, phosphonium based ionic liquids combined with dicyanamide and phosphinate counter anions were used to develop new bio-based epoxy networks. The effect of IL structure (anion type) and amount on the reactivity towards epoxy prepolymer as well as on the thermal and thermomechanical properties and surface performance of bio-based epoxy/IL networks were investigated. In addition, bio-based epoxy prepolymers also served as partial or total substitution for epoxy/IL networks in order to improve their properties in particular the fracture toughness.

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## Table of contents

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<b>4.1. Introduction .....</b>	<b>194</b>
<b>4.2. Experimental.....</b>	<b>195</b>
4.2.1. Materials.....	195
4.2.2. Samples preparation.....	196
4.2.2.1.Preparation of bio-based epoxy/IL (CA/IL) networks .....	196
4.2.2.2.Preparation of CA-modified Epoxy/IL networks.....	196
<b>4.3. Results and discussions.....</b>	<b>196</b>
4.3.1. Bio based epoxy/IL (CA/IL) networks.....	196
4.3.1.1.Reactivity of CA/IL systems .....	196
4.3.1.2.FTIR Analysis on CA/IL blends.....	198
4.3.1.3.Surface energy of CA/IL networks .....	199
4.3.1.4.Thermal behavior of CA/IL networks .....	200
4.3.1.5.Dynamical Mechanical properties of CA/IL networks.....	202
4.3.2. Influence of Cardolite on the properties of DGEBA/ILs systems.....	204
4.3.2.1.Curing behavior of CA-modified epoxy/IL blends.....	204
4.3.2.2.FTIR analysis of CA-modified epoxy/IL blends during the curing process.....	205
4.3.2.3.Morphologies of CA-modified epoxy/IL networks .....	207
4.3.2.4.Dynamic mechanical properties of CA-modified epoxy/IL networks .....	208
4.3.2.5.Thermal properties of CA-modified epoxy/IL networks .....	210
4.3.2.6.Surface energy of CA-modified epoxy/IL networks .....	212
4.3.2.7.Fracture toughness of CA-modified epoxy/IL networks .....	213
<b>4.4. Conclusion of chapter 4 .....</b>	<b>215</b>
<b>References of chapter 4 .....</b>	<b>216</b>

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## 4.1. Introduction

Epoxy networks play an important role in the thermosetting polymer fields with a wide range of applications due to their excellent chemical and mechanical properties.<sup>1</sup> Nowadays, the most popular epoxy prepolymer currently used in the epoxy applications is diglycidyl ether of bisphenol A (DGEBA) derived from petroleum products.<sup>1</sup> However, the use of bisphenol A (BPA) in the polymers has recently raised concerns due to its toxicity.<sup>2</sup> Moreover, the increase of oil prices and the environmental problems also require the development of bio-based epoxy systems derived from sustainable resources. Among all the available bio-based epoxy systems, those derived from cashew nut shell liquid commercially named cardanol based epoxy compounds appear to be great candidates to substitute DGEBA due to their commercial availability.<sup>2,3</sup> In fact, the chemical structure of cardanol containing both aromatic rings and long aliphatic chains provides exceptional combination of properties.<sup>4</sup> Cardanol based compounds can be served as modifiers for conventional epoxy networks in order to improve their processability,<sup>5,6</sup> their flexibility<sup>7-10</sup> (impact resistance and fracture toughness), as well as their chemical and water resistance.<sup>11-13</sup> In addition, cardanol based epoxy comonomers (epoxy prepolymers<sup>14-19</sup> or curing agents<sup>20-24</sup>) have been developed by several authors to combine with conventional comonomers of epoxy networks resulting in epoxy networks with excellent properties. Then, the combination of both cardanol based epoxy prepolymers and curing agent<sup>23</sup> provides fully bio-based epoxy networks suggesting a new way to develop environmentally friendly materials.

Ionic liquids (ILs) possessing an excellent thermal stability, good ionic conductivity, low saturated vapor pressure and non-flammability have recently become as new target of academic and industrial research as additives within epoxy networks to develop new polymer electrolytes, anti-corrosive coatings or for composite applications.<sup>25,26</sup> In fact, the incorporation of small amount of ILs can efficiently improve the properties of conventional epoxy networks such as thermo-mechanical properties,<sup>27-29</sup> wear and scratch resistance<sup>30</sup> and ion conductivity.<sup>31,32</sup> Self-healing properties of ILs were also revealed on the surface of epoxy/amine system after multiple scratch tests.<sup>33,34</sup> Besides, the potential of ILs as reactive additives to replace conventional curing agents for epoxy prepolymers has already been demonstrated.<sup>35,36</sup> These new epoxy/IL systems require low content of curing agents thanks to the high reactivity of ILs towards epoxy prepolymers. The obtained epoxy/IL networks have excellent thermal and mechanical properties combined with outperformed hydrophobic properties.<sup>35,36</sup> Indeed, the strong dependence of the nanostructuration and properties of epoxy/IL networks on the chemical nature of ILs (Chapter 2) makes them tunable for a wide range of applications. Nevertheless, due to the solvent effect of ILs, epoxy/IL networks

are also excellent hosts of nanoparticles and particles in the preparation of composites or nanocomposites.<sup>37,38</sup>

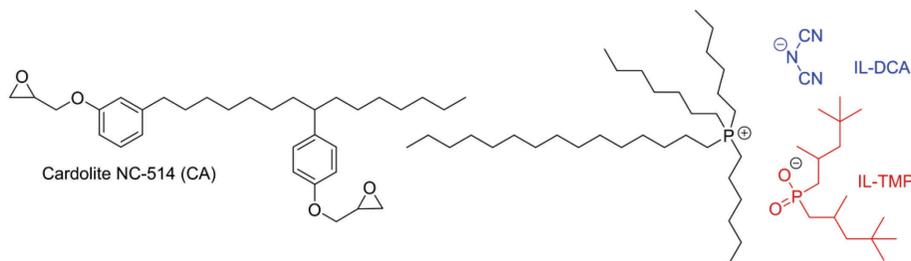
Hence, the combination between ionic liquids and bio-based materials in particular cardanol based epoxy prepolymers can provide a new way to design and develop sustainable and environmentally friendly high-performed materials. Thus, this work will describe the preparation of cardanol based epoxy/IL networks. In fact, a commercial cardanol based epoxy prepolymer from Cardolite® will be used to partially and totally substitute DGEBA in the epoxy/IL networks. Also, the effect of IL structure will be demonstrated through the incorporation of two phosphonium ionic liquids combined with dicyanamide and phosphinate counter anions as reactive components of epoxy systems. Moreover, the polymerization kinetics (DSC, FTIR) of epoxy/IL mixtures, thermal (ATG, DSC) and thermomechanical properties (DMA) as well as the morphology and surface properties of cardanol based epoxy/IL networks will be investigated. In addition, the influence of the presence of cardanol based epoxy prepolymer with long alkyl chain on the fracture toughness of epoxy/IL networks will be highlighted.

## 4.2. Experimental

### 4.2.1. Materials

Bio-based epoxy prepolymer derived from Cardanol under the reference of Cardolite NC-514 (CA) was purchased from Cardolite®, USA. Two kinds of ionic liquids - trihexyl(tetradecyl)phosphonium dicyanamide - denoted IL-DCA and trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethyl pentyl) phosphinate - denoted IL-TMP were kindly provided by Cytec. Chemical structures of Cardolite and ionic liquids are presented in

Figure 4-1. Also, conventional epoxy prepolymer - Diglycidyl ether of bisphenol A (DGEBA) based epoxy prepolymer (DER 332) with epoxide equivalent weight (EEW) of 175 g.mol<sup>-1</sup> was purchased from DOW Chemical Company.



**Figure 4-1** Chemical structures of Cardolite® cardanol derived epoxy prepolymer and phosphonium ILs.

The choice of ionic liquids was based on their commercial availability. Only IL-TMP, IL-DEP and IL-DCA are available at the industrial scale, which are possible for conducting the experiments. However, knowing the low reactivity of IL-DEP towards DGEBA (Chapter 2) and the lower reactivity of Cardolite than DGEBA (presented later), IL-DCA was chosen in this Chapter.

## 4.2.2. Samples preparation

### 4.2.2.1. Preparation of bio-based epoxy/IL (CA/IL) networks

To prepare bio-based epoxy/IL networks, Cardolite (CA) was mixed with ionic liquid (IL-DCA or IL-TMP) at different ratio of 10, 20 and 30 phr until homogeneous mixture. The mixtures were degassed at room temperature during 1 hour before being poured into silicone molds. The curing protocol was chosen for all systems as 2 hours at 120 °C, 2 hours at 140 °C and 1.5 hours at 210 °C in order to complete the curing reaction. Cardolite/IL samples will be presented as CA/IL type-IL concentration.

### 4.2.2.2. Preparation of CA-modified Epoxy/IL networks

In order to study the effect of CA incorporation in the properties of epoxy/IL networks, CA-modified epoxy/IL systems were prepared by mixing 10 phr of IL (IL-DCA or IL-TMP) and 10, 20 and 30 phr of Cardolite in DGEBA at room temperature in order to obtain a homogenous mixture. The mixture was then poured into silicone molds and cured in oven. The curing protocol for CA-modified Epoxy/IL networks was 2 hours at 80 °C, 3 hours at 120 °C and 3 hours at 160 °C. Then CA-modified Epoxy/IL will be presented as DGEBA/IL type/CA-CA concentration. Noted that DGEBA/IL-TMP samples containing 30 phr of CA cannot form a solid cured network with the used protocol, the properties of this system will not be investigated.

## 4.3. Results and discussions

### 4.3.1. Bio based epoxy/IL (CA/IL) networks

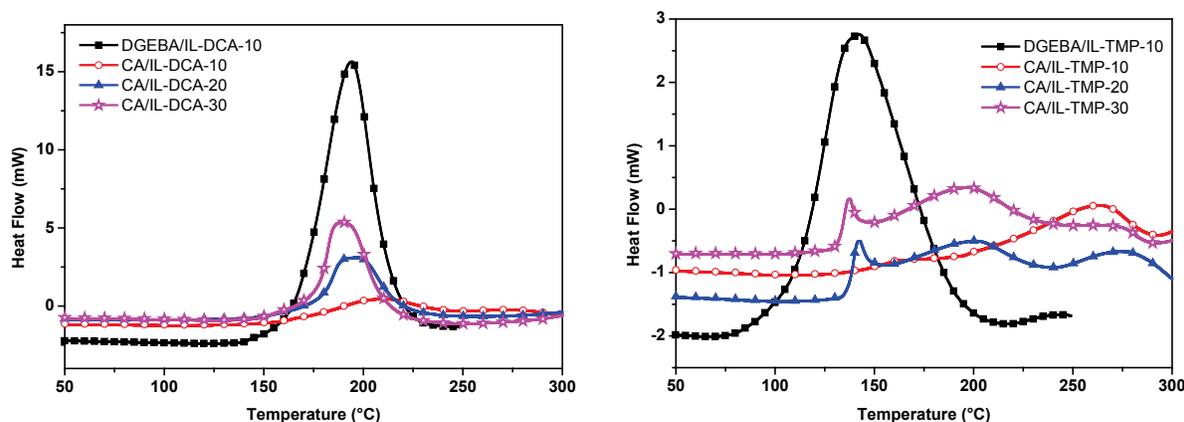
#### 4.3.1.1. Reactivity of CA/IL systems

The reactivity of cardanol based epoxy/IL reactive systems was investigated using DSC from the reaction enthalpy peak. Thus, DSC curves of different IL cured epoxy (DGEBA or CA) systems were illustrated in Figure 4-2 with the reaction enthalpy peak temperature presented in Table 4-1.

**Table 4-1** Reaction enthalpy peak temperature (DSC, 10 K.min<sup>-1</sup>) of different epoxy/IL reactive systems.

Samples	1 <sup>st</sup> peak (°C)	2 <sup>nd</sup> peak (°C)	3 <sup>rd</sup> peak (°C)
DGEBA/IL-DCA-10	194	--	--
CA/IL-DCA-10	210	--	--
CA/IL-DCA-20	197	--	--
CA/IL-DCA-30	190	--	--
DGEBA/IL-TMP-10	140	--	--
CA/IL-TMP-10	163	263	344
CA/IL-TMP-20	142	200	279
CA/IL-TMP-30	137	197	273

At first, for DGEBA based epoxy systems cured with ILs, the exothermic peak occurs at the same temperature as that reported previously *i.e.* 140 °C for DGEBA/IL-TMP. IL-DCA also exhibited high reactivity towards DGEBA with the exothermic peak at 194 °C for system containing 10 phr of IL-DCA. Then, DSC curves performed on the bio-based epoxy/IL blends (IL-TMP or IL-DCA) highlight exothermic peaks suggesting the existence of curing reactions between ILs and cardanol based epoxy prepolymer (CA).

**Figure 4-2** DSC curves (10 K.min<sup>-1</sup>, under nitrogen) of different epoxy/IL reactive systems containing IL-DCA (left) and IL-TMP (right).

Concerning CA/IL-DCA systems, DSC curves display only one exothermic peak, which is shifted to higher temperature indicating the reduction of the system reactivity due to the substitution of DGEBA by cardanol based epoxy prepolymer. In details, using the same amount of IL of 10 phr, the exothermic peak of epoxy systems cured by IL-DCA are shifted from 194 °C for DGEBA based system to 210 °C for CA based system, respectively. Regarding the reaction mechanism between epoxy prepolymer and ILs proposed previously in Chapter 2, the chemical

structure containing soft segments of Cardolite NC-514 is the major reason for the reduction of reactivity. In fact, ILs act as initiators to open the epoxide ring of epoxy prepolymer to form an anionic reactive center (O<sup>-</sup>). This reactive center will be responsible to react with the others epoxide group in order to form the epoxy networks. In the case of CA/IL system, the steric hindrance effect of CA-based reactive center due to the presence of long alkyl chain between two epoxide groups results in a decrease of the system reactivity.

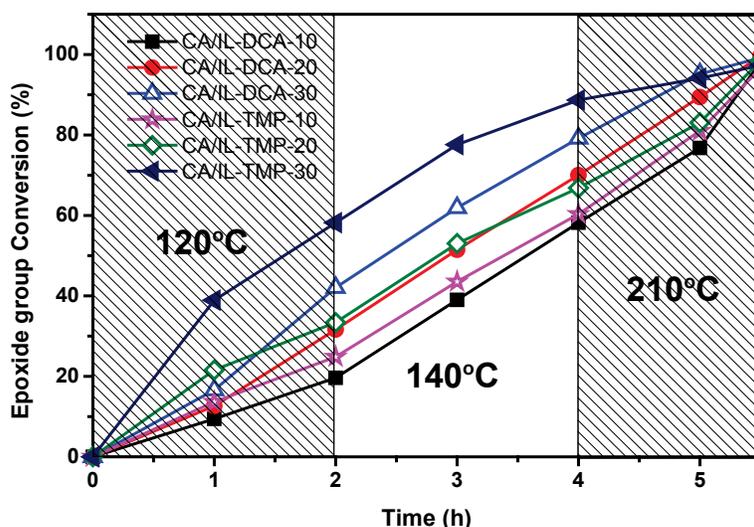
On the other hand, DSC curve of CA/IL-TMP displays three peaks suggesting a more complicated curing mechanism. Indeed, Chrysanthos *et al.* have studied CA prepolymer with size exclusion chromatography and have found a complex structure of this epoxy prepolymer with the existence of various oligomers.<sup>16</sup> Noted that IL-TMP is more reactive than IL-DCA with lower exothermic peak temperature,<sup>36</sup> the ability of IL-TMP to react with all the components in the CA epoxy prepolymers leads to a complex enthalpy profile. In addition, the lowest value of exothermic peak temperature of CA systems with 10 phr of IL-TMP is 163 °C compared to 140 °C of DGEBA/IL-TMP blends suggesting also a decrease of the system reactivity similarly to IL-DCA based systems.

Concerning the effect of IL amount, for both IL-TMP and IL-DCA based systems, the increase of IL amount induces a decrease of the exothermic peaks, which is in agreement with Chapter 2. Especially, in the case of IL-TMP, all the three peaks are shifted to lower temperature indicating the increase of the system reactivity.

In conclusion, ILs (IL-DCA or IL-TMP) have an ability to react with cardanol based epoxy prepolymer. The reactivity of epoxy/IL systems depends mainly on the chemical structure of monomers (epoxy prepolymer or ILs) and the IL amount.

#### **4.3.1.2. FTIR Analysis on CA/IL blends**

In order to examine the effectiveness of the applied curing protocol on the curing reaction of ILs with cardanol based epoxy prepolymer, FTIR analysis was used to follow the reaction between cardanol based epoxy prepolymer (CA) and ILs. Thus, FTIR spectra of each system were recorded at different reaction times during curing and the epoxide group conversion of different epoxy/IL systems was calculated according to Equation 4-1 and was presented in Figure 4-3 as a function of curing time.



**Figure 4-3** Conversion of epoxide groups versus reaction time of different CA/ILs systems.

In fact, our previous works have shown that the applied curing schedule for DGEBA/IL-DCA and DGEBA/IL-TMP systems allowed to reach the epoxy conversion of higher than 90 %.<sup>36</sup> Thus, as expected, a decrease of absorption peak at  $914\text{ cm}^{-1}$  corresponding to epoxide group was observed on the FTIR spectra of CA/IL mixtures (IL-DCA or IL-TMP) justifying the opening of epoxide ring during curing process.<sup>25,36</sup> At the end of the curing protocol, this absorption peak was nearly disappeared with a conversion of over 95 % for all the CA/IL blends (Figure 4-3). Also, the reactivity of CA/IL blends investigated by FTIR is in agreement with DSC results that showed the higher reactivity of IL-TMP compared to IL-DCA. After the same curing time (1h at  $120\text{ }^{\circ}\text{C}$ ), CA epoxy systems based on IL-DCA and IL-TMP (10 phr) have exhibited the conversion of epoxide groups of 9 % and 14 %, respectively. Likewise, the increase of the amount of IL (IL-DCA or IL-TMP) leads to an improvement of the conversion rate.

In conclusion, FTIR results confirm that ionic liquids are able to cure prepolymer derived from cardanol with high conversion of epoxide group after full curing process.

#### 4.3.1.3. Surface energy of CA/IL networks

The surface energy of epoxy/IL networks (CA or DGEBA) were determined by sessile drop method. Table 4-2 summarizes the non-dispersive and dispersive components of the epoxy networks calculated by using Owens-Wendt method from the contact angles with water and diiodomethane.

**Table 4-2** Contact angles and surface energy of epoxy networks measured by sessile drop method.

Samples	$\Theta_{\text{water}}$	$\Theta_{\text{diiodomethane}}$	$\gamma_{\text{non-dispersive}}$ (mJ.m <sup>-2</sup> )	$\gamma_{\text{dispersive}}$ (mJ.m <sup>-2</sup> )	$\gamma_{\text{total}}$ (mJ.m <sup>-2</sup> )
DGEBA/IL-DCA-10	102	63	0.5	27.2	27.6
CA/IL-DCA-10	103	66	0.7	24.3	25.0
CA/IL-DCA-20	103	80	1.1	16.3	17.4
CA/IL-DCA-30	105	82	1.1	15.0	16.1
DGEBA/IL-TMP-10	91	44	1.0	37.3	38.3
CA/IL-TMP-10	95	61	0.9	26.7	27.6
CA/IL-TMP-20	103	70	0.3	22.7	23.0
CA/IL-TMP-30	106	68	0.1	24.6	24.7

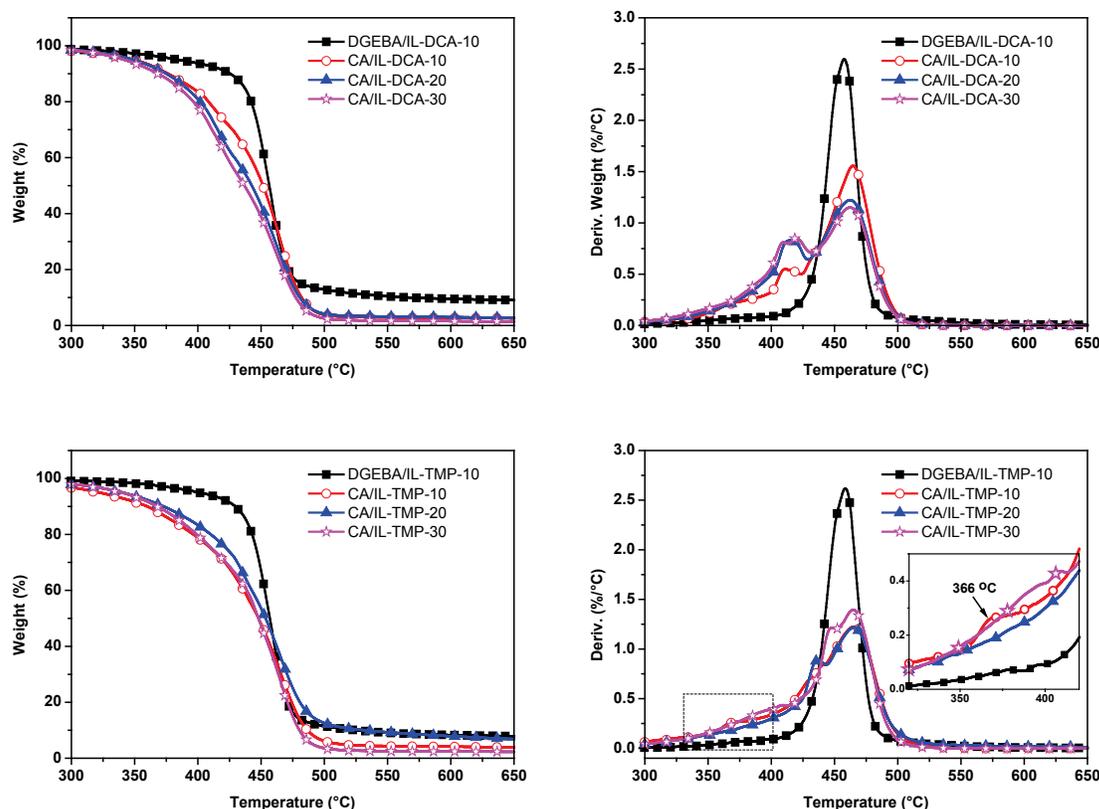
In fact, the use of ILs as hardeners for the epoxy prepolymer (DGEBA) was discovered to induce a more significant hydrophobic behavior thanks to the hydrophobic nature of ionic liquids compared to conventional epoxy/amine networks (Chapter 2). As can be seen in Table 4-2, DGEBA networks cured with 10 phr of ILs (both IL-DCA and IL-TMP) display low non-dispersive component and surface energy. Then, the replacement of conventional epoxy prepolymer by one derived from cardanol generates a significant reduction of the surface energy for all epoxy/IL networks. With the same amount of ILs (IL-DCA or IL-TMP) of 10 phr, CA/IL networks present lower surface energy than DGEBA/IL networks (25.0 mJ.m<sup>-2</sup> for CA/IL-DCA-10 and 27.6 mJ.m<sup>-2</sup> for CA/IL-TMP-10). In fact, the chemical structure of Cardanol affords excellent water resistance compared to DGEBA thanks to a long aliphatic pending chain.<sup>4</sup> In fact, many authors have used Cardanol based epoxy prepolymer as modifiers for epoxy coatings.<sup>13,18</sup> Moreover, the addition of 20 and 30 phr of IL results in an even lower surface energy, which are in agreement with the Chapter 2 in which the hydrophobicity of epoxy/IL increases with the IL amount. In particular, bio-based epoxy/IL systems cured by 30 phr IL-DCA have surface energy of only 16.1 mJ.m<sup>-2</sup> with a non-dispersive component of 1.1 mJ.m<sup>-2</sup>.

In conclusion, the combination of two hydrophobic components: ionic liquids and cardanol based epoxy prepolymer leads to outperformed hydrophobic systems suggesting new perspectives for coatings applications.

#### 4.3.1.4. Thermal behavior of CA/IL networks

The thermal stability of CA/IL networks was investigated by thermogravimetric analysis (TGA) with the evolution of the weight loss (TGA, DTGA) as a function of the temperature of all the CA/IL networks and DGEBA/IL networks presented in Figure 4-4. The degradation

temperatures at 5 %, 10% of weight loss and at maximum of DTGA curves are summarized in Table 4-3.



**Figure 4-4** Weight loss as a function of temperature (TGA, DTGA) of epoxy/IL networks cured with IL-DCA (up) and IL-TMP (down): at left, evolution of weight and at right, derivative of weight loss as a function of temperature.

Overall, both DGEBA/IL and CA/IL networks exhibit an excellent thermal behavior with a maximal degradation temperature at around 450-460 °C. In fact, the degradation temperatures of DGEBA prepolymer cured with 10 phr IL-DCA and IL-TMP are both at 458 °C. Concerning the cardanol based epoxy/IL networks, the degradation temperatures determined at the maximum of the DTGA peaks are over 460 °C, slightly higher than epoxy/IL networks based on DGEBA. This slight difference can be explained by the better intrinsic stability of cardanol based epoxy prepolymer characterized by a higher DTGA peak temperature of 454 °C compared to 335 °C of DGEBA (Table 4-3). However, the oligomers contained in CA prepolymers result in a lower degradation temperature at 5 % and 10 % of CA/IL networks compared to DGEBA based networks. In addition, all CA/IL networks display two peaks of degradation, which is consistent with the studies about cardanol based epoxy networks cured with amines.<sup>17,23</sup> Obviously, this

multistep decomposition can be explained by the complex profile of cardanol based epoxy prepolymer with the existence of several oligomers. Moreover, it is evident from Figure 4-4 that the second degradation temperature becomes more important with the increase of IL amount from 10 to 30 phr, which is attributed to the increase of system reactivity. In details, in the case of CA cured with IL-TMP, the second peak is shifted from 366 °C (10 phr) corresponding to CA prepolymers (Table 4-3) to 445 °C (30 phr) corresponding to CA/IL-TMP networks. Nevertheless, compared to the literature, the use of ILs as curing agent of Cardanol based epoxy networks also leads to a higher thermal stability than that reported for cardanol based epoxy/amine networks.<sup>17,23</sup> In fact, Darroman *et al.* have found a degradation temperature at 30 % of weight loss of 360 °C for Cardanol based epoxy/amine networks. By using IL, we have obtained an increase of the degradation temperature of 40 °C *i.e.* around 410–420 °C at 30 % weight loss.

**Table 4-3** Degradation temperatures used epoxy prepolymers and formed epoxy/IL networks

Samples	T <sub>d5%</sub> (°C)	T <sub>d10%</sub> (°C)	T <sub>d max DTGA</sub> (°C)	T <sub>d 2<sup>nd</sup> peak</sub> (°C)
CA	247	296	454	365
DGEBA	256	272	335	--
DGEBA/IL-DCA-10	384	426	458	--
CA/IL-DCA-10	349	376	465	410
CA/IL-DCA-20	349	375	462	414
CA/IL-DCA-30	342	369	462	420
DGEBA/IL-TMP-10	401	430	458	--
CA/IL-TMP-10	322	360	466	366
CA/IL-TMP-20	340	373	465	436
CA/IL-TMP-30	339	368	465	445

In conclusion, phosphonium ionic liquids can be considered as curing agent for bio-based epoxy prepolymer derived from cardanol. In fact, these new epoxy/IL networks have a similar thermal stability as that of systems based on conventional epoxy prepolymer (DGEBA) and higher than the epoxy/amine systems reported in the literature.

#### 4.3.1.5. Dynamical Mechanical properties of CA/IL networks

The influence of the chemical nature of epoxy prepolymer (DGEBA *versus* CA) on the dynamical mechanical properties of epoxy/IL networks was studied by DMA. The  $\alpha$ -relaxation temperature T <sub>$\alpha$</sub>  from the maximum of tan $\delta$  as well as the storage modulus, E', in the rubbery state (E'<sub>R</sub>) of epoxy/IL networks are listed in Table 4-4.

**Table 4-4** Relaxation temperature  $T_{\alpha}$ , storage modulus in the rubbery state ( $E'_R$ ) of epoxy/IL networks.

Samples	$T_{\alpha}$ (°C)	$E'_R$ (MPa)
DGEBA/IL-DCA-10	126	31.2
CA/IL-DCA-10	31	2.6
CA/IL-DCA-20	36	6.1
CA/IL-DCA-30	28	6.2
DGEBA/IL-TMP-10	150	104.0
CA/IL-TMP-10	20	1.1
CA/IL-TMP-20	25	3.8
CA/IL-TMP-30	22	5.7

For all epoxy/IL systems, DMA spectra display only one relaxation peak suggesting the homogeneity of epoxy networks. The relaxation temperatures ( $T_{\alpha}$ ) of the DGEBA/IL systems (IL-DCA or IL-TMP) are consistent with the data of literature.<sup>36</sup>

Regarding CA/IL networks, all systems display a low glass transition region included between 20-36 °C, which are in the same magnitude order of the relaxation temperatures of cardanol based epoxy prepolymer cured by different amines such as isophorone diamine,<sup>16,18,19,41</sup> Jeffamine D400<sup>17</sup> and T403,<sup>18,19</sup> and bio-based curing agents.<sup>23,42</sup> In fact, the long aliphatic chain of cardanol based epoxy prepolymer softens the epoxy/IL networks generating lower relaxation temperatures compared to those of DGEBA epoxy based networks.<sup>16</sup> In addition, the storage moduli in the rubbery state of CA/IL networks are considerably lower than those of DGEBA/IL systems. In fact, the storage modulus in the rubbery state is representative for crosslinking density of epoxy network suggesting a lower crosslinking density of CA/IL networks. Indeed, the long aliphatic chain between two epoxide functional group of cardanol based epoxy prepolymer decreases the crosslinking density of related epoxy networks.<sup>16,17</sup> Concerning the influence of IL amount on the properties of CA/IL networks (both IL-DCA and IL-TMP), higher  $T_{\alpha}$  and  $E'_R$  are obtained when IL content increases from 10 phr to 20 phr, which is in accordance with DGEBA/IL networks (Chapter 2). A slight plasticizing effect was also observed when 30 phr of IL was introduced in epoxy prepolymer with a decrease of relaxation temperature. In fact, for epoxy/IL networks, there is a critical concentration of IL above which free ILs will be taken place in the epoxy matrix acting as plasticizing agent.

Overall, the flexible structure of cardanol based epoxy prepolymer results in epoxy/IL networks with low glass transition temperature and crosslinking density. In addition, the plasticizing effect of IL was also observed for high amount of IL (30 phr) in the cardanol based epoxy/IL networks.

### 4.3.2. Influence of Cardolite on the properties of DGEBA/ILs systems

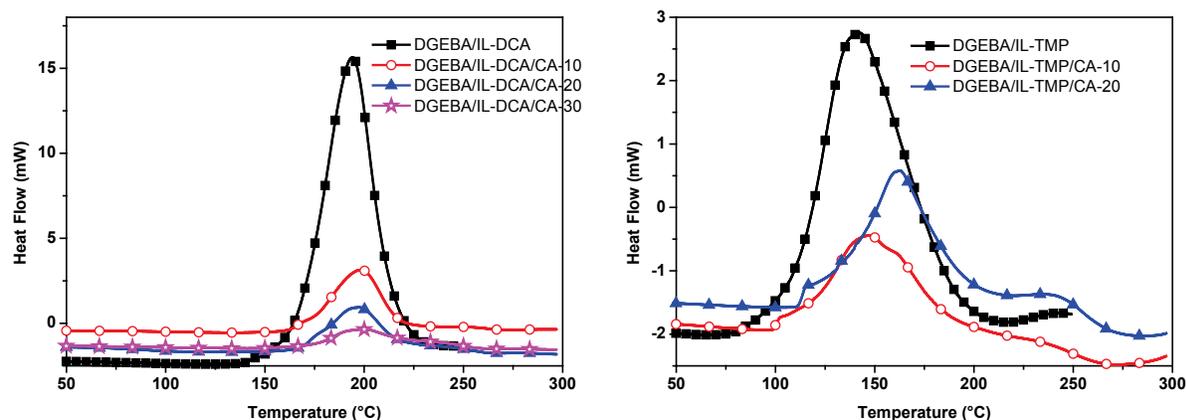
Although ILs are able to form epoxy networks with bio-based epoxy prepolymers, it is evident from the previous part that the properties of CA/ILs systems are not competitive to those based on DGEBA. The partial replacement of DGEBA by Cardolite appears to be a new way to introduce bio-based materials into conventional systems while keeping their properties. Thus, this part is dedicated to investigate the influence of the addition of Cardolite on the properties of DGEBA/ILs systems.

#### 4.3.2.1. Curing behavior of CA-modified epoxy/IL blends

The effect of cardanol based epoxy prepolymer on the curing behavior of epoxy/IL blends was also investigated by non-isothermal DSC. DSC thermograms obtained under dynamic mode in the exothermic region of CA-modified epoxy/IL blends are illustrated in Figure 4-5 with the exothermic peak temperature presented in Table 4-5.

**Table 4-5** Exothermic peak temperature of CA-modified epoxy/IL networks measured by DSC.

Samples	Reaction peak (°C)
DGEBA/IL-DCA	191
DGEBA/IL-DCA/CA-10	199
DGEBA/IL-DCA/CA-20	198
DGEBA/IL-DCA/CA-30	200
DGEBA/IL-TMP	140
DGEBA/IL-TMP/CA-10	148
DGEBA/IL-TMP/CA-20	163



**Figure 4-5** DSC thermogram of CA-modified epoxy/IL networks.

In all the cases, DSC thermograms of epoxy/IL blends before the curing process show one exothermal peak corresponding to the reaction between epoxide groups of both DGEBA and CA with the ionic liquids (IL-DCA or IL-TMP). The exothermic peak temperatures of unmodified DGEBA/IL-DCA and DGEBA/IL-TMP blends are in agreement with our previous study and Chapter 2.<sup>36</sup>

Then, the use of cardanol based epoxy prepolymer in the DGEBA/IL-DCA blends shifts the exothermic peak temperatures to higher temperature. Exothermic peak is shifted from 190 °C for unmodified DGEBA/IL-DCA blends to around 200 °C in the case of using 10, 20 or 30 phr of CA. Similar reductions in epoxy/anhydride systems reactivity were observed in the literature and caused by the presence of bio-based epoxy prepolymer.<sup>5,43,44</sup> Obviously, CA epoxy prepolymer possesses a lower reactivity towards ionic liquids compared to DGEBA due to the flexible chemical structure of cardanol based epoxy prepolymer (Figure 4-2).

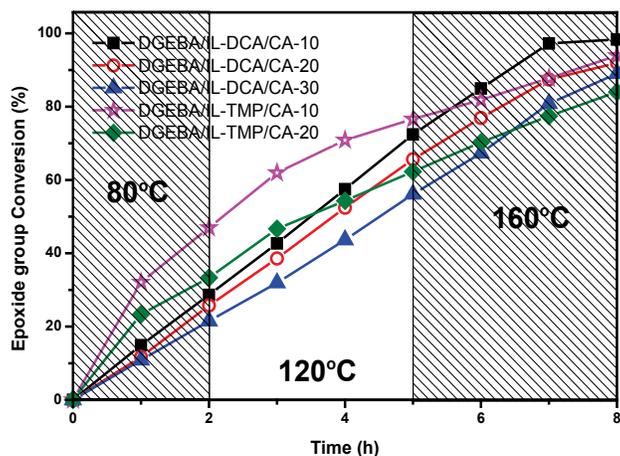
Concerning IL-TMP based system, remember that CA/IL-TMP blends exhibit a complex exothermic peak, the single exothermic peak evidenced in Figure 4-5 shows that the exothermic peak corresponding to the reaction between IL-TMP and CA is superimposed to that related to DGEBA/IL-TMP reaction due to low proportion of CA in the blends. In addition, a more significant increase of exothermic peak temperature is observed when CA is added to the DGEBA/IL-TMP blends especially the case of 20 phr CA (23 °C) due to the reaction between IL-TMP with CA prepolymer and its oligomers occurring at higher temperatures (Figure 4-2).

Overall, the presence of CA prepolymer decreases the reactivity of epoxy/IL blends resulting in an increase of the exothermic peak temperature.

#### ***4.3.2.2. FTIR analysis of CA-modified epoxy/IL blends during the curing process***

FTIR analysis was used to follow the curing process of CA-modified epoxy/IL blends based on the absorption peak corresponding to the epoxide groups. Then, the evolution of epoxide group conversion of CA-modified epoxy/IL blends as a function of curing time was shown in Figure 4-6.

As evidenced in Figure 4-6, after the curing process of 2 hours at 80 °C, 3 hours at 120 °C and 3 hours at 160 °C, a conversion of over 90 % is obtained for all CA-modified epoxy/IL networks except for the case of DGEBA/IL-TMP systems containing 20 phr of CA. In fact, at the end of the curing process, the absorption peak at 914 cm<sup>-1</sup> corresponding to epoxide group of both DGEBA and CA nearly disappeared indicating the incorporation of cardanol based epoxy prepolymer in the epoxy networks.<sup>10</sup> The evolution of this peak was affected by the amount of CA in the epoxy/IL blends and the type of ILs.



**Figure 4-6** Epoxide group conversion as a function of curing time of CA-modified epoxy/IL networks (IL-DCA or IL-TMP) with different amount of CA.

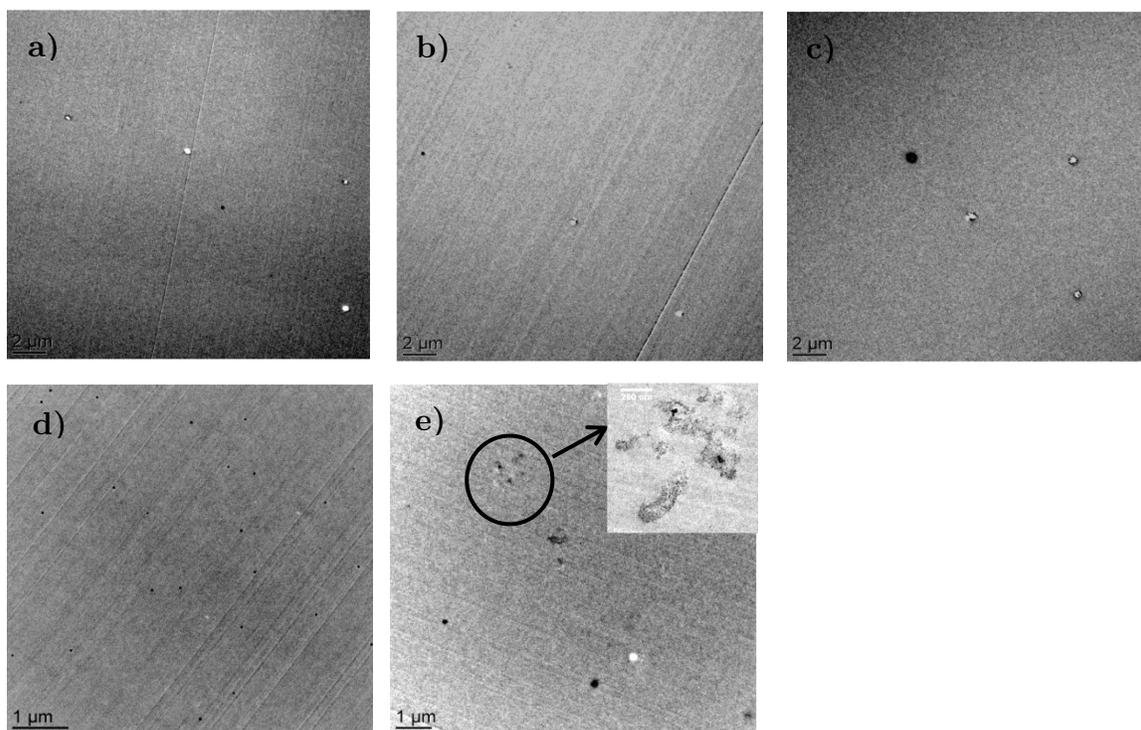
As expected, the increase of CA content decreases the reactivity of DGEBA/IL-DCA systems indicated by the decrease of the epoxide group conversion. In details, after 1 hour of curing at 80 °C, DGEBA/IL-DCA systems containing 10, 20, 30 phr of CA have exhibited an epoxide group conversion of 15 %, 12 % and 11 %, respectively. At the end of the curing process, all CA/IL-DCA display a final conversion of over 90 % indicating the completion of the curing reaction.

Similarly, the increase of CA amount from 10 phr to 20 phr in the DGEBA/IL-TMP networks induces a decrease of epoxide group conversion after 2 hours of curing at 80 °C from 61 % to 37 %. In addition, the final conversion of epoxy/IL systems was influenced by the presence of CA especially for DGEBA/IL-TMP blends with a final conversion of only 84 % for the system containing 20 phr of CA. These results can be explained by the exothermic peak corresponding to the reaction between CA and IL-TMP at high temperature of over 200 °C (Table 4-1). Thus, the applied curing protocol was unable to totally converse all the epoxide group of CA prepolymer. This also explains why the chosen curing protocol could not solidify the DGEBA/IL-TMP samples containing 30 phr of CA.

In conclusion, the incorporation of CA in the epoxy/IL blends leads to a reduction of epoxide group conversion. Moreover, the effect of CA depends on the CA amount and the type of IL (IL-DCA or IL-TMP).

### 4.3.2.3. Morphologies of CA-modified epoxy/IL networks

The morphologies of CA-modified epoxy/IL networks were studied by transmission electronic microscopy with TEM micrographs presented in Figure 4-7.



**Figure 4-7** TEM micrographs of CA-modified epoxy/IL networks cured with IL-DCA (a,b,c) and IL-TMP (d,e) containing cardanol based epoxy prepolymer of 10 phr (a,d), 20 phr (b,e) and 30 phr (c).

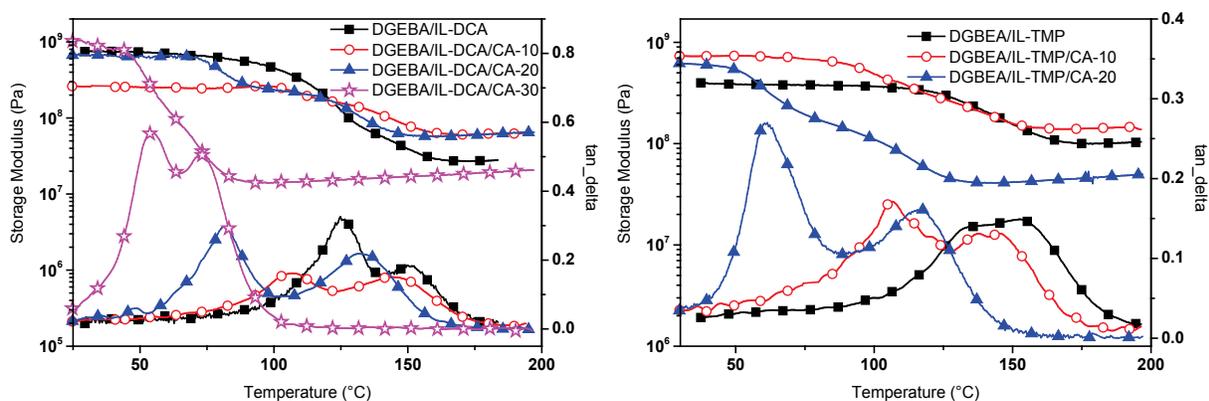
It was discovered from our previous works that the use of only 10 phr of IL (IL-DCA or IL-TMP) as comonomers to DGEBA led to no phase separation due to the good miscibility between epoxy and ILs.<sup>36</sup> Then, the addition of CA into epoxy networks results in the formation of a second phase which may be related to the dispersion of CA prepolymers or oligomers into epoxy matrix. In fact, in the literature, many authors have observed either one or two phases of epoxy networks modified with bio-based epoxy prepolymers depending on the compatibility between DGEBA and bio-based epoxy prepolymers.<sup>9,10,45,46</sup> For CA-modified DGEBA/IL-DCA systems, Figure 4-7 reveals that CA appears as a few small inclusions of 200-300 nm randomly dispersed in the epoxy matrix. The size and the density of these inclusions do not vary with the increase of CA amount. Concerning IL-TMP based systems, a better dispersion of CA was observed in the case of epoxy networks containing 10 phr of CA as small inclusions (< 100 nm) of a second phase homogeneously distributed in the epoxy matrix. The finer distribution of CA in case of IL-TMP may be explained

by the alkyl chain beared on the IL-TMP anion inducing a higher compatibility with cardanol based epoxy prepolymer. However, at higher CA content (20 phr), the morphology of CA-modified DGEBA/IL-TMP systems consists in both inclusion and co-continuous structures suggesting that a phase inversion may occur in the case of a high amount of CA (30 phr). Because the reaction between CA and IL-TMP system requires high temperature to occur, this is in agreement with the FTIR results explaining why the solid samples of DGEBA/IL-TMP modified by 30 phr of CA were not able to be formed.

Generally, the addition of cardanol based epoxy networks into epoxy/IL networks generates a nanophase separation, which varies as a function of the amount and type of used IL (IL-DCA or IL-TMP).

#### 4.3.2.4. Dynamic mechanical properties of CA-modified epoxy/IL networks

Thermomechanical properties of CA-modified epoxy/IL networks were evaluated by DMA. Then, the evolution of Storage modulus ( $E'$ ) and  $\tan\delta$  as a function of temperature of CA-modified epoxy/IL networks are presented in Figure 4-8 with the relaxation temperatures from maximum of  $\tan\delta$  listed in Table 4-6.



**Figure 4-8** DMA analysis of (■) unmodified, CA-modified epoxy networks containing 10 phr (○), 20 phr (▲), 30 phr of CA (☆) cured by IL-DCA (left) and IL-TMP (right).

For unmodified epoxy/IL networks, DGEBA/IL-TMP networks displayed a single relaxation peak at 150 °C (Chapter 2), while two relaxation peaks were observed for those based on IL-DCA at 126 °C and 150 °C, respectively. These two relaxation peaks are attributed to the formation of epoxy homopolymer and of DGEBA/IL-DCA network explained by the two competitive mechanisms proposed in Figure 2-13.

**Table 4-6** Thermomechanical behavior of CA-modified epoxy/IL networks (IL-DCA or IL-TMP).

Samples	1 <sup>st</sup> T <sub>α</sub> (°C)	2 <sup>nd</sup> T <sub>α</sub> (°C)
DGEBA/IL-DCA	126	150
DGEBA/IL-DCA/CA-10	107	147
DGEBA/IL-DCA/CA-20	82	132
DGEBA/IL-DCA/CA-30	55	71
DGEBA/IL-TMP	--	150
DGEBA/IL-TMP/CA-10	104	140
DGEBA/IL-TMP/CA-20	62	118

The use of cardanol based epoxy prepolymer in the epoxy/IL matrix induces a variation in their thermomechanical properties including the relaxation temperatures (Table 4-6). Both relaxation peaks of DGEBA/IL-DCA networks are shifted to lower temperatures due to the presence of flexible CA epoxy prepolymer. Thus, the relaxation temperatures of IL-DCA based epoxy networks decrease with the increase of CA content. For the DGEBA/IL-DCA networks containing 30 phr of CA, the two relaxation peaks are close to room temperature, *i.e.* at 55 °C and 71 °C, respectively. In fact, the reductions of T<sub>α</sub> have also been reported in the literature when bio based epoxy prepolymer or oligomers with flexible backbone and free alkyl chain are introduced into conventional epoxy networks due to a reduction of crosslinking density.<sup>9,10,13,44,46-51</sup> Regarding the mechanism of curing reaction between epoxy prepolymer and IL-DCA<sup>36</sup> and the close reactivity of IL-DCA towards both epoxy prepolymer (DGEBA or CA) (Table 4-1), the two curing reactions may happen at the same time leading to the formation of a heterogeneous epoxy network containing both CA and DGEBA backbone. However, the phase separation of CA in the DGEBA/IL-DCA networks observed by TEM (Figure 4-7) was not able to be checked by DMA.

On the other hand, DMA confirmed the phase separation in case of IL-TMP based systems in Figure 4-7 with the appearance of a second relaxation peak when CA was added to DGEBA/IL-TMP blends. In details, the addition of 10 phr of CA into DGEBA/IL-TMP involves two relaxation peaks at 104 °C and 140 °C, which may correspond to CA and DGEBA rich-phase, respectively. The temperature of these two relaxation peaks are included between one of the neat phases of 150 °C and around 20-25 °C for DGEBA/IL-TMP and CA/IL-TMP networks, respectively (Table 4-4). The decrease of T<sub>α</sub> corresponding to DGEBA/IL-TMP networks may be due to the existence of small amount of CA acting as plasticizers. Indeed, Altuna *et al.* have discovered the plasticizing effect of epoxidized soy bean oil in the continuous phase of DGEBA.<sup>46</sup> *Vice versa*, noted that the CA amount is only 10 phr, there must be a great amount of chemically bonded DGEBA in this second phase resulting in a much higher relaxation temperature compared to CA/IL-TMP networks. An interpenetrating effect occurs between the two phases of CA-modified DGEBA/IL-

TMP systems, which is similar to the case of using thermoplastics as modifiers for epoxy networks.<sup>52</sup> By increasing the CA amount in the DGEBA/IL-TMP systems, the two relaxation peaks are shifted to lower temperatures of 118°C and 62 °C, respectively. This can be explained by the increase of the concentration of flexible CA in each phase.

Overall, the incorporation of bio-based epoxy prepolymer induces a phase separation in the epoxy/IL networks witnessed by the two relaxation peaks. In addition, the interpenetration has occurred between the two polymers leading to the variation of glass transition temperatures depending on the type of ILs and the amount of CA.

#### 4.3.2.5. Thermal properties of CA-modified epoxy/IL networks

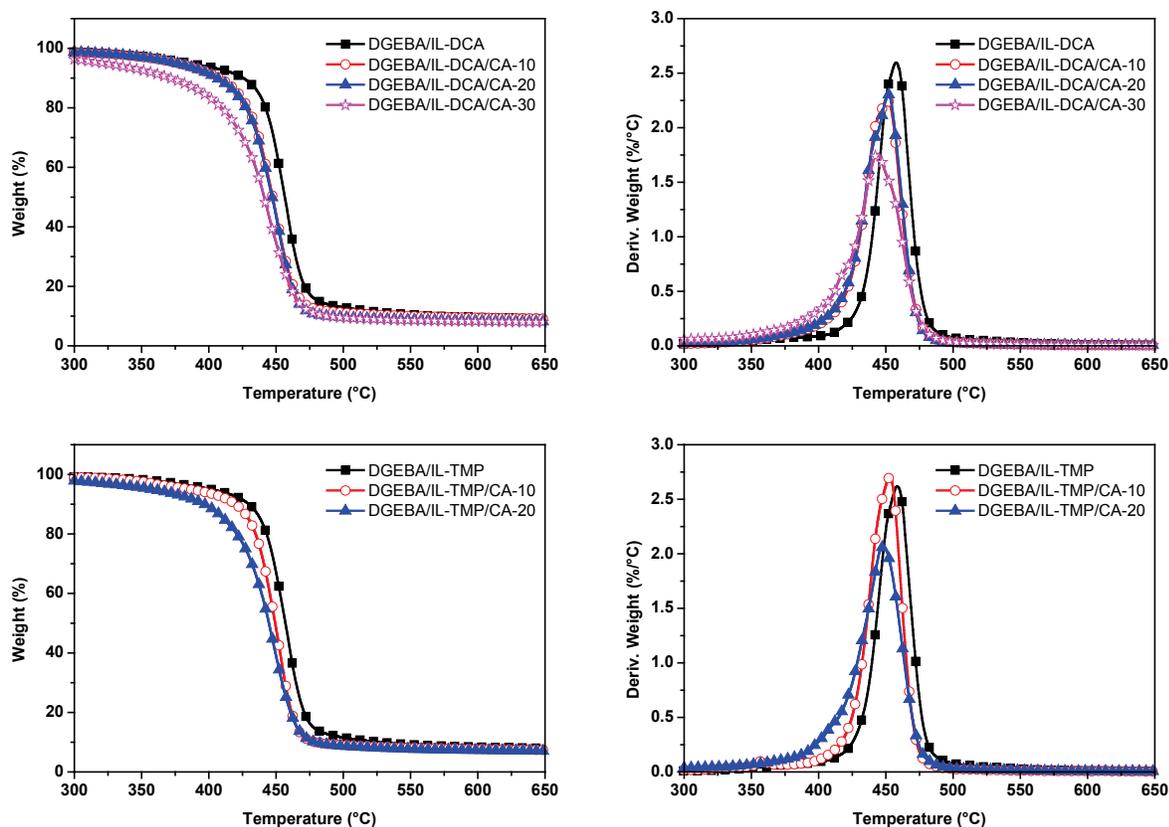
The thermal stability of CA-modified epoxy/IL networks was studied by thermogravimetric analysis (TGA). The evolution of the weight loss as a function of the temperature (TGA, DTGA) of unmodified and all CA-modified epoxy/IL are presented in Figure 4-9 and the degradation temperature at 5 %, 10 % of weight loss, the maximal degradation of DTGA curves are summarized in **Table 4-7**.

**Table 4-7** Thermal stability of neat CA, unmodified and CA-modified epoxy networks.

Samples	T <sub>d5%</sub> (°C)	T <sub>d10%</sub> (°C)	T <sub>d max DTGA</sub>
CA	247	296	454
DGEBA/IL-DCA	384	426	458
DGEBA/IL-DCA/CA-10	377	408	451
DGEBA/IL-DCA/CA-20	375	406	452
DGEBA/IL-DCA/CA-30	320	371	443
DGEBA/IL-TMP	401	430	458
DGEBA/IL-TMP/CA-10	384	420	452
DGEBA/IL-TMP/CA-20	356	396	448

In Figure 4-9, only one peak of degradation can be observed suggesting that the nanophase separation cannot be detected by TGA. All unmodified and modified epoxy/IL networks present an excellent thermal stability, which is highlighted by the degradation at maximum DTGA of over 450 °C. We already knew that both DGEBA/IL-DCA and DGEBA/IL-TMP networks showed high degradation temperatures.<sup>36</sup> In both cases, the modification of epoxy/IL networks (IL-DCA or IL-TMP) by cardanol based epoxy prepolymers does not vary much their T<sub>dmax</sub> since the CA also displays a high degradation temperature (454 °C). In the literature, the use of bio-based epoxy compounds as modifiers for epoxy networks was reported to have no considerable variation on degradation temperatures.<sup>9,10,48,49</sup> However, the degradation temperature at 5 % weight loss of

epoxy/IL networks was reduced by the presence of CA. This can be explained by the low temperature at 5 % weight loss of CA/IL networks and CA prepolymer (Table 4-3) due to the presence of small oligomers that undergo a quick degradation. In fact, the degradation temperature decreased with the increase of CA content. For examples, the  $T_{5\%}$  of DGEBA/IL-DCA networks decreases from 384 °C to 320 °C when 30 phr CA are added, lower than that of CA/IL networks (342 °C - Table 4-3) indicating the presence of non-reacted CA with a low  $T_{5\%}$  (247 °C) in the epoxy networks (Figure 4-7). Concerning DGEBA/IL-TMP systems, a dramatic decrease of  $T_{5\%}$  (45 °C) is observed when 20 phr CA are incorporated into the epoxy/IL networks. This can be related to the appearance of the co-continuous dispersed phase in the epoxy networks observed in Figure 4-7.



**Figure 4-9** Weight loss as a function of temperature (TGA, DTGA) (■) unmodified and CA-modified epoxy networks containing 10 phr (○), 20 phr (▲), 30 phr (☆) cured by IL-DCA (up) and IL-TMP (down).

Generally, the thermal properties of epoxy/IL networks are slightly influenced by the addition of cardanol based epoxy prepolymer but they are kept over 440 °C.

#### 4.3.2.6. Surface energy of CA-modified epoxy/IL networks

The surface energy of unmodified and CA-modified epoxy/IL networks are characterized by sessile drop method and the non-dispersive and dispersive components shown in Table 4-8.

**Table 4-8** Surface energy of neat epoxy/IL networks and epoxy/IL networks modified by CA.

Samples	$\Theta_{\text{water}}$ ( $^{\circ}$ )	$\Theta_{\text{diiodomethane}}$ ( $^{\circ}$ )	$\gamma_{\text{non-dispersive}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_{\text{dispersive}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	$\gamma_{\text{total}}$ ( $\text{mJ}\cdot\text{m}^{-2}$ )
DGEBA/IL-DCA	102	62.5	0.5	27.2	27.6
DGEBA/IL-DCA/CA-10	108	85.7	0.9	13.5	14.4
DGEBA/IL-DCA/CA-20	107	81.0	0.5	16.2	16.7
DGEBA/IL-DCA/CA-30	105	80.0	0.9	16.0	16.8
DGEBA/IL-TMP	91	44.4	1.0	37.3	38.3
DGEBA/IL-TMP/CA-10	103	90.1	3.1	10.3	13.4
DGEBA/IL-TMP/CA-20	107	85.6	1.1	13.4	14.5

The surface energy of unmodified epoxy/IL systems (IL-DCA or IL-TMP) in Table 4-8 are in agreement with Chapter 2 where epoxy/IL networks using phosphonium ionic liquids denoted IL-TMP and IL-DCA as curing agents exhibited an excellent hydrophobicity. However, the incorporation of CA into epoxy/IL networks reduces much more their surface energy indicating the formation of highly hydrophobic systems. In fact, all CA-modified epoxy/IL networks cured by IL-DCA or IL-TMP provide a surface energy lower than  $17 \text{ mJ}\cdot\text{m}^{-2}$ , similar to a Teflon surface. Apparently, the water resistance of cardanol based epoxy prepolymer is the major reason for the increase of the system hydrophobicity as previously observed for CA/IL networks compared to DGEBA/IL networks presented in Table 4-2.

In fact, many authors have demonstrated the use of cardanol based epoxy prepolymers as surface modifiers for epoxy systems.<sup>11-13</sup> Due to the chemical nature of cardanol based compounds, relevant properties for coating applications such as the water resistance, water vapor diffusion as well as the solvent resistance of modified epoxy networks were significantly improved. In addition, from Chapter 2, the substitution of conventional amines by ILs as curing agents for epoxy prepolymers provides systems with higher hydrophobicity. Thus, the results on the surface energy of CA-modified networks presented here suggest a great combination between ILs and cardanol based epoxy prepolymer leading to networks with emphasized hydrophobicity.

#### 4.3.2.7. Fracture toughness of CA-modified epoxy/IL networks

The fracture toughness of CA-modified epoxy/IL networks was studied using CT specimen and the values of critical stress intensity factor denoted  $K_{Ic}$  of unmodified and CA-modified epoxy/IL networks are presented in Table 4-9.

**Table 4-9** Fracture toughness ( $K_{Ic}$ ) of unmodified and CA-modified epoxy/IL networks.

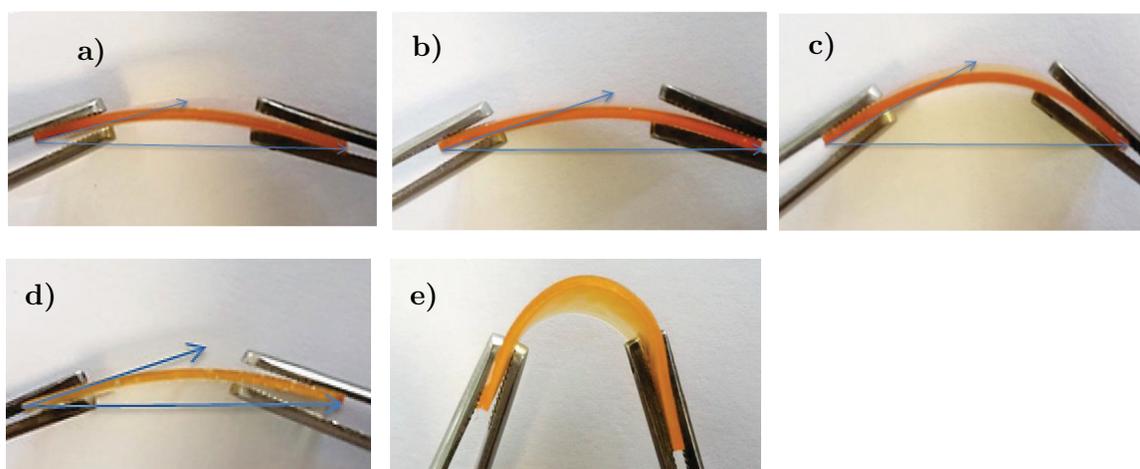
Samples	$K_{Ic}$ (MPa.m <sup>1/2</sup> ) $\pm$ 0.05
DGEBA/IL-DCA	0.41
DGEBA/IL-DCA/CA-10	0.33
DGEBA/IL-DCA/CA-20	0.38
DGEBA/IL-DCA/CA-30	0.41
DGEBA/IL-TMP	0.39
DGEBA/IL-TMP/CA-10	1.08
DGEBA/IL-TMP/CA-20	0.39

According to the literature, epoxy/IL networks cured by IL-DCA or IL-TMP have low fracture toughness of around 0.4 MPa.m<sup>1/2</sup> due to the high crosslinking density and high glass transition temperature of these networks (Table 4-6). Thus, the incorporation of cardanol based epoxy prepolymer with flexible chain is expected to improve the flexibility of these epoxy/IL networks. Besides, the relaxation temperature of epoxy/IL networks (IL-DCA and IL-TMP) in Table 4-6 clearly decreases suggesting the formation of more flexible networks. Moreover, the fracture toughness of CA-modified systems in Table 4-9 shows the dependence with the curing agent and the CA amount.

Concerning IL-DCA based systems, no fracture toughness improvement is obtained when CA is introduced into epoxy/IL networks despite the decrease of the relaxation temperature. It may be explained by the morphology of CA modified DGEBA/IL-DCA networks (Figure 4-7) with just a few randomly dispersed phase. Also, a flexibility test was conducted on CA-modified epoxy/IL samples showing little difference among systems containing different amounts of CA (Figure 4-10a, 4-10b, 4-10c). Indeed, in the studies of Miyagawa *et al.*, no change of fracture toughness of epoxy networks was obtained when epoxidized linseed oil was used as substitution for DGEBA.<sup>45,50</sup> The authors have explained the results by the lack of rubbery separated phase.

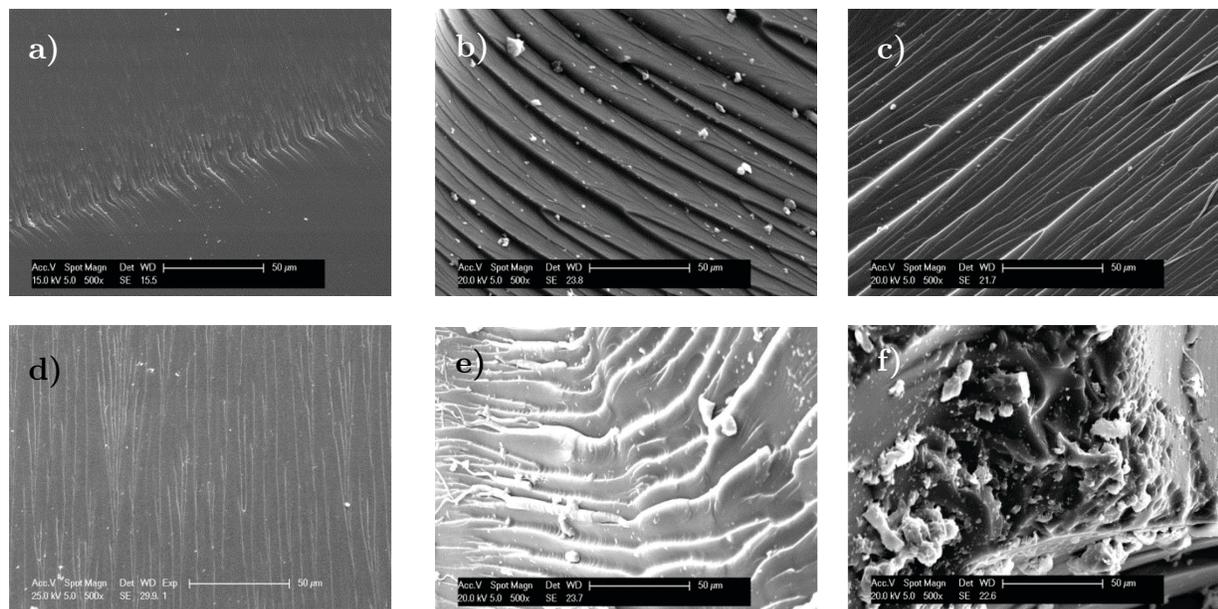
On the opposite, a significant increase of the fracture toughness was obtained when 10 phr of CA was incorporated into DGEBA/IL-TMP networks.  $K_{Ic}$  value of CA modified DGEBA/IL-TMP networks was 1.08 MPa.m<sup>1/2</sup>, *i.e.* a relative increase of 180 % compared to neat DGEBA/IL-TMP. Park *et al.*<sup>49</sup> and Shabeer *et al.*<sup>44</sup> have also observed an increase of the fracture toughness of epoxy

networks due to the presence of bio-based compounds and have explained their results by the decrease of crosslinking density. However, according to Maiorana *et al.*, a significant improvement can only be achieved with the existence of a phase separation.<sup>9</sup> In this case, a more homogeneously dispersed phase is observed when 10 phr CA are introduced into DGEBA/IL-TMP networks (Figure 4-7) than those cured with IL-DCA while the flexibility of cured samples by both ILs is nearly identical (Figure 4-10a, 4-10d). Thus, the rubbery dispersed phase is a decisive factor and has an influence on the toughening effect of CA-modified epoxy networks. However, when the CA amount increases, the fracture toughness decreases due to the formation of a ductile material (Figure 4-10c). In fact, Maiorana *et al.* also obtained a reduction of  $K_{Ic}$  with the increase of the concentration of cardanol based compound in the epoxy networks suggesting a critical concentration of tougheners.<sup>9</sup> In conclusion, an adjustment of the ratio between ductile and rigid matrix components is crucial in order to obtain the optimized fracture toughness of epoxy networks.<sup>9</sup>



**Figure 4-10** Flexibility test on CA-modified DGEBA/IL-DCA (a,b,c) and DGEBA/IL-TMP (d,e) networks containing 10 phr (a,d), 20 phr (b,e) and 30 phr (c) of CA.

SEM micrographs of fracture surface after fracture toughness test of CA-modified epoxy networks presented in Figure 4-11 are consistent with the obtained  $K_{Ic}$  values. Smooth and mirror-like fracture surfaces are obtained for neat epoxy/IL networks and CA-modified DGEBA/IL-DCA ones (Figures 4-11a, 4-11b, 4-11c, 4-11d). On the contrary, the CA-modified DGEBA/IL-TMP networks show a very rough fracture surface with ridges, river marks, and tortuous cracks (Figure 4-11e, 4-11f). In addition, a typical fracture surface of ductile materials is reached for DGEBA/IL-TMP networks containing 20 phr of CA, which is in agreement with the fracture toughness result.



**Figure 4-11** Fracture surface of unmodified (a,d) and CA-modified epoxy/IL networks containing 10 phr (b,e) and 20 phr (c,f) of CA cured with IL-DCA (a,b,c) and IL-TMP (d,e,f).

To conclude, the fracture toughness properties of the CA-modified epoxy/IL networks are clearly dependent on the chemical nature of ionic liquids (dicyanamide versus phosphinate). Thus, the use of ILs can lead to enhanced mechanical performances of epoxy networks with a very good toughness.

#### 4.4. Conclusion of chapter 4

In conclusion, phosphonium ionic liquids were investigated as curing agents for the development of bio-based epoxy systems. Epoxy/IL networks based on cardanol derived epoxy prepolymers and ILs are prepared with excellent thermal properties ( $> 460$  °C) combined with high hydrophobicity thanks to the unique structure of cardanol based epoxy prepolymer with aromatic rings, long backbone and alkyl pending chain. Then, this bio-based epoxy compound was applied as modifiers for epoxy/IL networks. Thus, we have demonstrated that the chemical nature of the phosphonium ionic liquids plays a key role on the properties of modified epoxy networks especially the fracture toughness. Also, the combination of hydrophobic phosphonium epoxy prepolymer and long alkyl chain cardanol based compound leads to a very low surface energy similar to fluorinated surface suggesting promising candidates for coating applications. Overall, this work opens a new way to develop “green materials” with outperformed properties and a new alternative to petroleum based materials. Further studies are required to reveal the relevancy between ILs structure and the properties of bio-based epoxy/IL networks.

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## Chapter 5:

# Conclusions and Perspectives

This research work aims to emphasize the role of ionic liquids in the preparation of high performance materials based on epoxy networks including comonomers to epoxy prepolymers and dispersion aids for modifiers to prepare epoxy networks. The combination of ILs and bio-based epoxy prepolymers also allows the formation of sustainable and environmentally friendly epoxy networks.

In the first part of this work, the use of different phosphonium ionic liquids combined with carboxylate, phosphate and phosphinate anion as sole comonomers of epoxy prepolymer was highlighted. Despite the small amount of ILs (10-20-30 phr), phosphonium ILs exhibit high reactivity towards conventional epoxy prepolymers and lead to the formation of poly-epoxy networks with epoxy group conversion higher than 90 %. The epoxy/IL networks provide excellent properties such as high glass transition temperature (90–140 °C), good thermal stability (350 °C) and hydrophobic behavior combined with comparative crosslinking density and mechanical properties of epoxy/amine networks. Moreover, the final properties of these networks are tunable as a function of the anion/cation combination or the amount of ILs suggesting new ways to easily design epoxy networks for different applications. In addition to this, a study was conducted on the reaction of epoxy compounds and ionic liquids in order to confirm the reaction mechanism of “anionic polymerization” in which ILs counter anions react to open the epoxy rings and to form the active center of O<sup>-</sup>. The reaction continues through this reactive center to form the entire networks. Thus, the reactivity of epoxy/ILs blends depends on the reactive center, which is in turn determined by the structure of ILs and epoxy prepolymers.

The second part of this work was dedicated to the incorporation of modifiers into epoxy/IL networks to improve their final properties. Firstly, two kinds of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) of different molar masses are introduced as toughening agents of epoxy/ionic liquid networks using phosphonium ionic liquids (ILs) combined with phosphinate and phosphate counter anions as curing agents of epoxy prepolymer. The effect of ILs on the morphology as well as the final properties of PPE-modified epoxy networks was investigated. For the same amount of thermoplastics (10 p.h.r), a morphology characterized by the presence of PPE particulates was observed in epoxy/amine networks whereas co-continuous or phase-inverted morphologies were

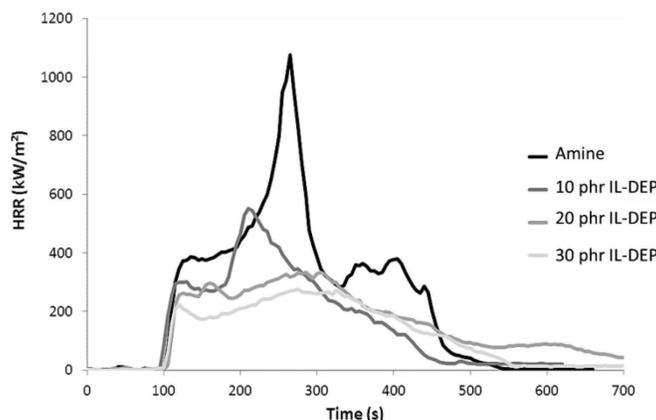
obtained in epoxy/IL networks. Thus, in comparison to PPE-modified epoxy/amine networks, a high hydrophobicity and an excellent thermal stability ( $> 400$  °C) were highlighted for PPE-modified epoxy/IL networks. In addition, IL-thermoplastic combination leads to significant increases in mechanical performances of epoxy networks especially in fracture toughness  $K_{Ic}$  (+ 150 % for IL-TMP and + 200 % for IL-DEP). The second route to modify epoxy/IL network was described using a commercial core-shell rubber particles (CSR) denoted Genioperl P52 (CSR). Epoxy networks containing 10 and 20 phr of CSR were prepared and the chemical nature of ILs play a key role on the morphology of modified epoxy networks resulting in a better dispersion of CSR compared to epoxy/amine networks. Thus, the CSR dispersion into epoxy/IL networks leads to an increase in fracture toughness *i.e.* 54 % higher of  $K_{Ic}$  for DGEBA/IL-DEP system modified by 20 phr of CSR particles.

The final part of this research work is focused on the development of new bio-based epoxy networks using phosphonium based ionic liquids combined with dicyanamide and phosphinate counter anions as curing agents of epoxy prepolymer. ILs display a high reactivity towards cardanol based epoxy prepolymer and the obtained bio-based epoxy/IL networks possess a glass transition temperature around 30 °C, an excellent thermal stability higher than 450 °C and a hydrophobic behavior close to that of PTFE. In addition, the use of cardanol based epoxy prepolymer as modifier of epoxy/IL networks was also reported leading to the improvements of the final properties of epoxy/IL networks especially their surface energy and fracture toughness (+180 %).

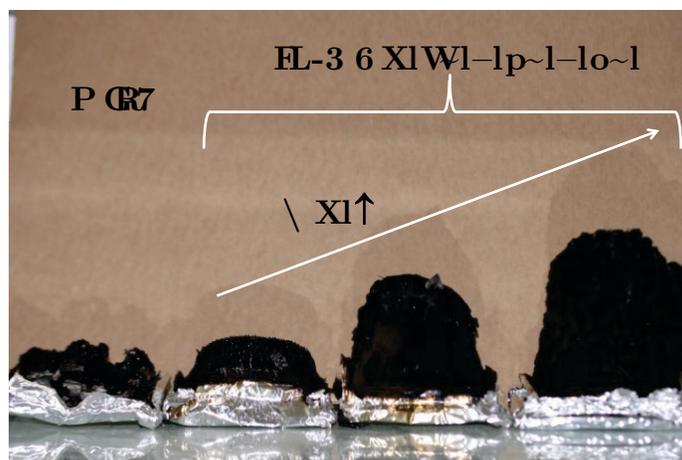
Overall, this work highlights the potential of ionic liquids in the epoxy systems. Indeed, the large choice of cation / anion combinations and the different possible functionalization of ionic liquids lead to design IL based epoxy networks for specific properties. Several routes can be carried out on the epoxy/IL networks:

- Being well known for their lack of flammability, the existence of ionic liquids in the epoxy networks can act as both curing agent and flame-retardants. Cone calorimetry tests conducted for epoxy networks cured with 10, 20, 30 phr of IL-DEP have revealed their efficiency in reducing the peak of heat release rate (pHRR) (Figure 5-1) and in forming a protective layer compared to an epoxy/amine system. (Figure 5-2). In fact, compared to epoxy/amine samples, the use of 30 phr of IL-DEP led to a significant decrease of the peak of heat release rate of 73 %. The residue content increases up to 39 % for 30 phr of IL-DEP. Nevertheless, the time-to-ignition remains stable around 100s for all samples thanks to high thermal stability of epoxy/IL networks. Moreover, it is obvious from Figure 5-2 that the presence of IL-DEP is the main reason for the expansion of samples residue after

cone calorimetry test. Overall, these results confirm the flame retardancy of epoxy/IL, which is advantageous for future applications.



**Figure 5-1** Heat release rate curves for epoxy resins in cone calorimeter test (heat flux 35 kW/m<sup>2</sup>).



**Figure 5-2** Residue after cone calorimetry test of epoxy/amine and epoxy/IL networks cured with 10, 20, 30 phr of IL-DEP.

- The excellent hydrophobic behavior of epoxy/IL networks is advantageous for coating applications. Corrosion test are in progress to evaluate the potential of ionic liquids as well as epoxy/IL systems as protective coatings for metallic materials under marine conditions.
- Curing reaction between epoxy prepolymer and ILs also requires more profound studies in order to obtain a complete understanding about the different mechanisms of the reaction as well as the relation between the reaction and the chemical nature of ILs.
- Thermoplastics modifications on epoxy/IL networks can also be conducted using different types of ILs and thermoplastics in order to obtain a more profound understanding about

the complex interactions among epoxy prepolymer, thermoplastic and ILs. Similarly, regarding the role of ionic liquids on the dispersion of nanofillers, other kinds of fillers can also be well-dispersed in the epoxy networks thanks to the interaction with ionic liquids suggesting the preparation of high performance nanocomposites.

- Finally, bio-based epoxy/IL networks also gained the interests as new method to prepare green materials. The combinations of other kind of bio-based epoxy prepolymers and ionic liquids can provide different properties aiming to different applications.

## FOLIO ADMINISTRATIF

### THESE DE L'UNIVERSITE DE LYON OPEREE AU SEIN DE L'INSA LYON

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DATE de SOUTENANCE : 25/11/2016

Prénom : Thi Khanh Ly

TITRE : New generation of epoxy networks based on ionic liquids: From structuration to final properties

NATURE : Doctorat

Numéro d'ordre : 2016LYSEI118

Ecole doctorale : Matériaux de Lyon

Spécialité : Matériaux polymères et Composites

#### RESUME

Les liquides ioniques (LIs), possédant d'excellentes propriétés intrinsèques et offrant une infinité de combinaisons possibles ouvrent de nouvelles perspectives dans le domaine des polymères, en particulier dans celui des réseaux époxyde. Ce travail de thèse présente la préparation, la caractérisation et la modification de réseaux époxy / liquides ioniques. Dans un premier temps, ce travail est dédié à étudier l'influence des LIs comme comonomères de prépolymère époxyde. Ainsi, la réactivité des LIs vers la DGEBA et leur rôle en tant qu'amorceurs et/ou durcisseurs de systèmes époxyde ont été étudiés. Ensuite, l'effet de la nature chimique des LIs sur les propriétés de réseaux époxy / LIs, y compris les propriétés thermomécaniques, la stabilité thermique, les propriétés de surface et les comportements mécaniques, a été démontré. En outre, le mécanisme de la réaction entre les prépolymères époxy et LIs a été révélé à l'aide de différentes méthodes (IRTF et RMN). Dans la deuxième partie, les agents modifiants (thermoplastiques et des particules cœur-coquille) ont été incorporés dans des réseaux époxy / LI en vue d'améliorer leurs performances mécaniques. Dans la dernière section, la combinaison des LIs et des réseaux époxyde biosourcés a été étudiée en tant que substituts partiels ou complets aux systèmes époxyde issus du pétrole afin de développer des matériaux à faible empreinte environnementale. Ainsi, l'utilisation des liquides ioniques a eu des effets bénéfiques sur la morphologie mais également sur les propriétés des réseaux. La relation entre la nature chimique des LIs, la morphologie et les propriétés obtenues a été soulignée.

**Mots clés** Réseaux époxydes ; liquides ioniques ; réseaux époxy / liquides ioniques; relation structure propriétés ; réactivité ; propriétés des réseaux ; mécanisme de la réaction; modifications ; mélange thermodurcissable / thermoplastique ; particules cœur-coquille; réseaux époxydes bio-sourcés.

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