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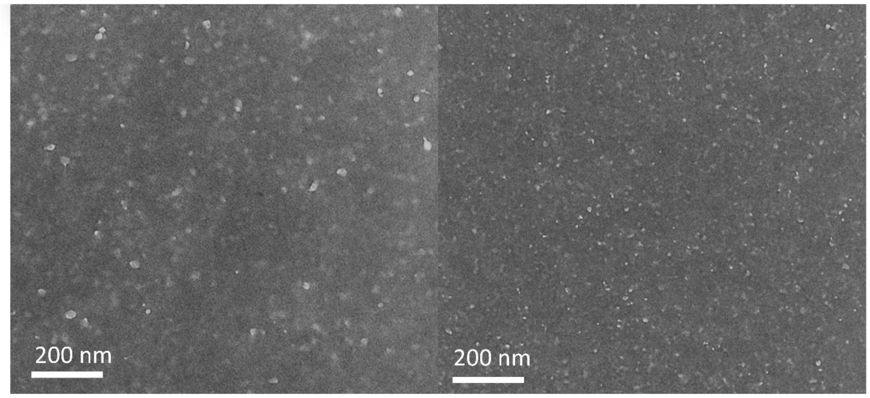
TEM micrographs of the epoxy-IL cured systems with 30 wt% of phosphonium ionic liquid.



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Abstract

Ionic liquids based on trihexyl(tetradecyl)phosphonium combined with dicyanamide counteranion were used for the first time as functional additives to achieve epoxy networked polymeric materials which display a structuration at nanoscale (20-30 nm) with dramatic mechanical properties and a higher thermal stability (> 400°C). In fact, the curing process was studied by FTIR, DSC highlighting an increase of the conversion epoxide groups in function of the IL amount (5-30 phr) and the morphology has been revealed by transmission electronic microscopy (TEM) and atomic force microscopy (AFM).

Keywords: Ionic liquids; Epoxy prepolymer; Structuration; Functional additives

1. Introduction

Nowadays, innovation in the materials field, particularly for polymer materials undoubtedly requires the control of their structure at nanoscale, especially in the field of polymer electrolytes where their key role in energy evokes a growing interest in academic and industrial research[1-4]. For such multicomponent systems, many challenges must be overcome such as the cost of materials, the lifetime of lithium ion cells, the safety of the installations and the mechanical performance of the electrolytes. In fact, it is necessary to optimize the preparation of polymer materials to achieve excellent mechanical properties, to avoid toxicity and volatility of conventional solvents as well as to create a structuration to the nanoscale within the polymer to enable the mobility of ions as lithium. Currently, most studies focuse on all electrolyte gels[5-8] which have the major drawback of a low mechanical strength. Recently various authors have also investigated all solid electrolytes[9-10]. Thus, the epoxy networks have emerged as important hosts for solvent or organic salts and especially epoxy-based networked polymers thanks to their versatility and easy preparation methods as well as their excellent thermo-mechanical properties, thermal stability and their adhesive properties. In addition, epoxy-prepolymers are commonly used by the industry in adhesive and composite applications[11-13]. Due to their unique properties such as their excellent thermal and chemical stability, high conductivity, wide electrochemical window and low vapour pressure, ionic liquids (ILs) so-called “green” solvents represent an alternative to conventional solvents and offer a real chance of success. In fact, ILs are increasingly used in the polymers as multifunctional agents of polymeric materials such as plasticizers, building blocks, processing aids, surfactant, particle dispersant of graphene or carbon nanotube particles but also as catalyst and/or curing agents of epoxy prepolymer[14-23].

Two routes are also investigated in the literature: *i)* ionic liquid can be covalently grafted on the network either by the cation or by anion depending on the reactive function that is carried by the IL monomer. This reactive function may be epoxy or amine groups to react towards epoxy-amine network. For example, Matsumoto et al have developed ion conductive networked polymers based on epoxy cured with tetraethylenepentamine[12]. *ii)* Ionic liquid is physically inserted within the epoxy system[21,24]. Thus, a phase separation leading to a nano versus micro scale structuration can be obtained. Different authors among which our group have highlighted that the ILs can act as a catalyst but also as a potential curing agent of epoxy-based reactive systems[21,24].

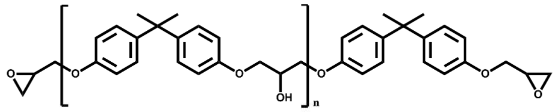
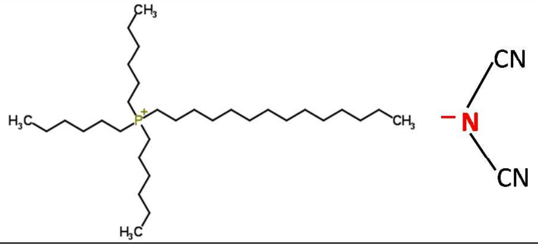
The objective of this work is to design ionic liquid containing networked polymers to be employed as new polymer electrolytes. The versatility of the ionic liquid due to the cation/anion combination is an excellent way to develop chemically cross-linked soft gel like materials. One condition must be respected through the design of epoxy-IL electrolyte: i) the creation of ionic channels within the polymer to ensure the conduction properties. For this reason, IL based on trihexyl(tetradecyl)phosphonium with dicyanamide anion has been used as functional additives (5-30 phr) to perform epoxy network with nanostructuration combined with good mechanical performance. Moreover, the structuration of IL in epoxy network has been highlighted for the first time by TEM and AFM.

2. Experimental

2.1. Materials and methods

Diglycidyleher of bisphenol A (DGEBA) – based epoxy pre polymer (EPON 828) (epoxy equivalent weight = 188 – 192; molar mass ≈ 377 $g.mol^{-1}$) was purchased from Shell Chemicals. The phosphonium ionic liquid (IL) denoted CYPHOS® IL105 and used as hardener was trihexyl(tetradecyl)phosphoniumdicyanamide (molar mass = 550.9 g/mol), and was kindly supplied by Cytec, Inc. Their chemical structures are presented in Table 1.

Table 1. Chemical structures of the epoxy prepolymer and the phosphonium ionic liquid

Name	**Structure**
DGEBA	
IL 105	

Different amounts, *i.e.* from 5 to 20 phr of the IL were dissolved with DGEBA under magnetic stirring at room temperature for 10 min. The solution was fully transparent even with 20 phr of IL; *i.e.* the phosphonium IL is miscible with epoxy prepolymer. The solution was then degassed in an ultrasound bath for 20 min and poured into a silicon rubber mold. The systems were polymerized under different conditions: 2h at 80°C and 3h at 140°C.

2.2. Characterization of epoxy-IL systems

Thermogravimetric analyses (TGA) of epoxy networks were performed on a Q500 thermogravimetricanalyzer (TA instruments). The samples were heated from 30 to 600 °C at a rate of 20 °C min^{-1} under nitrogen flow. The weight of the samples was included between 9-10 mg in all the cases.

DSC measurements were carried out by using Q20 (TA instruments) in the range of 25 °C to 200 °C. About 10 mg of sample was sealed into sealed aluminum pans and heated under nitrogen atmosphere. The heat evolved during the reaction (ΔH) was directly determined by integrating the exothermic peak.

Dynamic mechanical analyzer (Q-800, TA Scientific) was used for measuring dynamic mechanical properties of cured epoxy networks at a fixed frequency of 1 Hz with a heating rate of 3 °C.min^{-1}. A single cantilever clamp was used.

Fourier transformed Infrared spectra (FTIR) were recorded on a Nicolet Magna 550 spectrometer in a transmission mode (32 scans, resolution 4 cm^{-1}), in the wavelength range from 4,000 to 500 cm^{-1}.The DGEBA/IL mixtures were put between KBr pressed discs which were heated at fixed temperatures in an one stage oven. After each stage of heating at the corresponding temperature, the FTIR spectrum was recorded.

Transmission electron microscopy (TEM) was carried out at the Technical Center of Microstructures (University of Lyon) on a Phillips CM 120 microscope operating at 80 kV to characterize the structuration of ionic liquids in the epoxy network. The samples were cut using an ultramicrotome equipped with a diamond knife, to obtain 60-nm-thick ultrathin sections. Then, the sections were set on copper grids. ImageJ Software (U.S. National Institutes of Health) was used to estimate the average diameter of ionic domains.

Atomic Force Microscopy (AFM) was carried out on a picoscan SPM.The surface topography of the samples has been analyzed in tapping mode (75kHz) Atomic Force Microscopy [picoscan SPM] on 5x5µm^2 area with a resolution of 50 Angstrom. Raw data have been tuned and analyzed thank Gwyydion software[Gwyddion open source software (http://gwyddion.net/)] which allow to obtain a three dimensions surface topography pictures and a statistical characteristics of the sample surface like a rough mean square roughness, the amplitude distribution and the average size of ionic domains.

3. Results and discussion

3.1. Curing process of DGEBA/IL systems

By DSC and FTIR characterizations, the curing process of DGEBA/IL 105 systems has been studied. Thus, DSC thermograms of the DGEBA/IL 105 blends as a function of the IL concentration have been reported in Figure 1. In addition, the total reaction enthalpy and the maximum exothermic temperatures are summarized in Table 2.

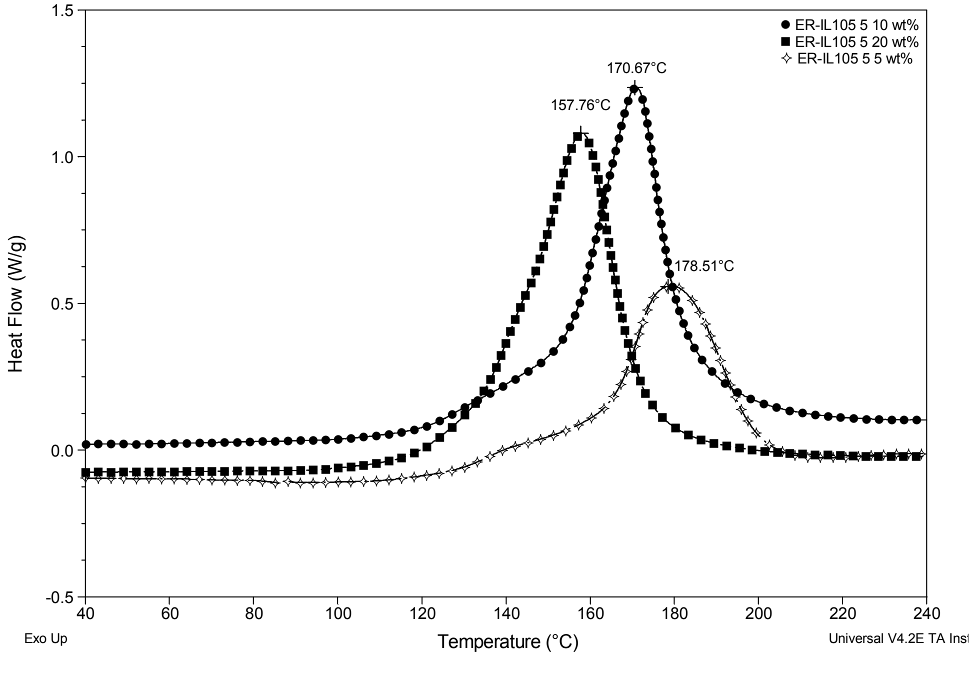


Figure 1. Dynamic DSC thermograms of Epoxy prepolymer-IL systems during heating at 10 °C.min^{-1} as a function of the IL concentration (ER-IL 105): (+) ER-IL 105 5 phr, (●) ER-IL 105 10 phr, (■) ER-IL 105 20 phr.

In all DGEBA/IL 105 systems (with 5, 10 and 20 phr of IL) an exothermic peak was observed which indicates the ability of the phosphonium ionic liquid to induce the polymerization of the epoxy prepolymer. These results have been confirmed in other studies that have used different cation/anion combinations of ionic liquids such as imidazolium salts or phosphonium salts combined with a phosphinate anion[21,24-25]. Compared to a previous study, the dicyanamide anion has a lower reactivity than the phosphinate anion[25]. In fact, 10 phr of IL 105 leads to a maximum curing temperature of 170 °C whereas a curing temperature of 128 °C is obtained when 10 phr of phosphonium ionic liquid combined with phosphinate anion is used[25]. Thus, the basicity of the two counter anions initiates the polymerization of the epoxy prepolymer as other bases such as imidazoles or tertiary amines[26-27] according to the mechanism proposed in Figure 2. In addition, the lower reactivity of the dicyanamide anion is due to its lower basicity compared to the phosphinate anion.

Table 2: Curing of DGEBA/IL systems from DSC

IL content (phr)	IL/epoxy (mol/ratio)	ΔH (J/g)	Maximum exotherm temperature (°C)
5	0.017	227	178
10	0.033	350	170
20	0.064	357	158

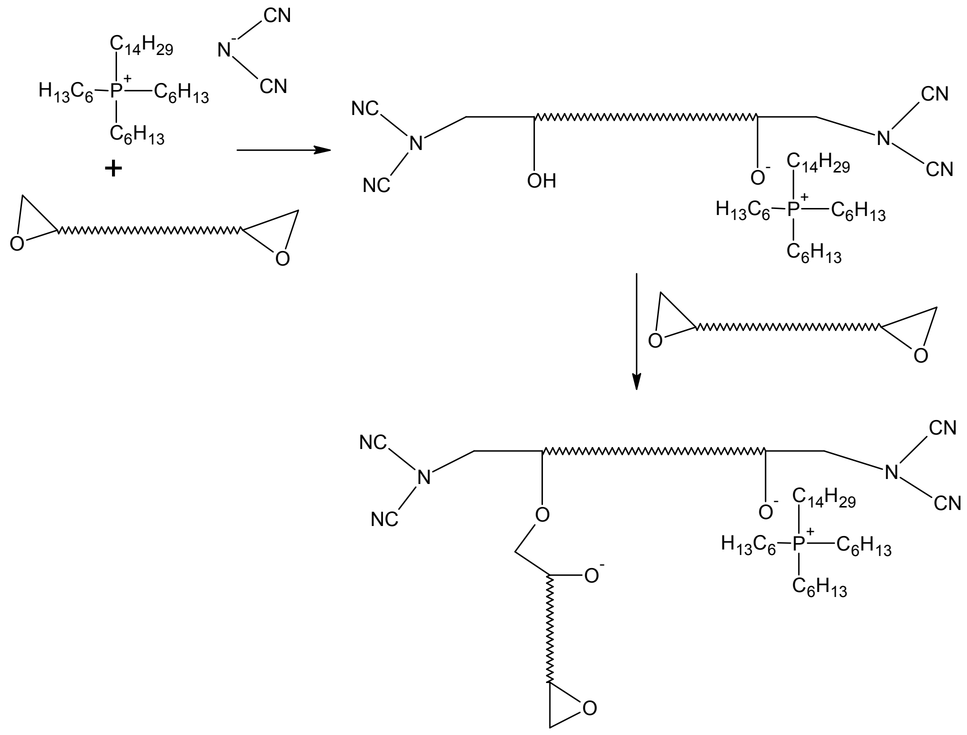


Figure 2. Proposed mechanism for the homopolymerization of epoxy prepolymer initiated by the dicyanamide anion.

Nevertheless, an amount of 5 phr of trihexyl(tetradecyl)phosphonium dicyanamide is sufficient to initiate polymerization. Moreover, a low IL 105/epoxy molar ratio is required to polymerize the epoxy prepolymer which highlights the role of ionic liquid as a catalytic curing agent.

To evaluate the catalytic ability of phosphonium ionic liquid for the epoxy prepolymer polymerization, the curing kinetics of the epoxy/IL blends were followed by FTIR technique. Thus, the spectra of pure IL 105, epoxy prepolymer DGEBA and the DGEBA/IL systems containing 10 phr of IL are presented in Figure 3.

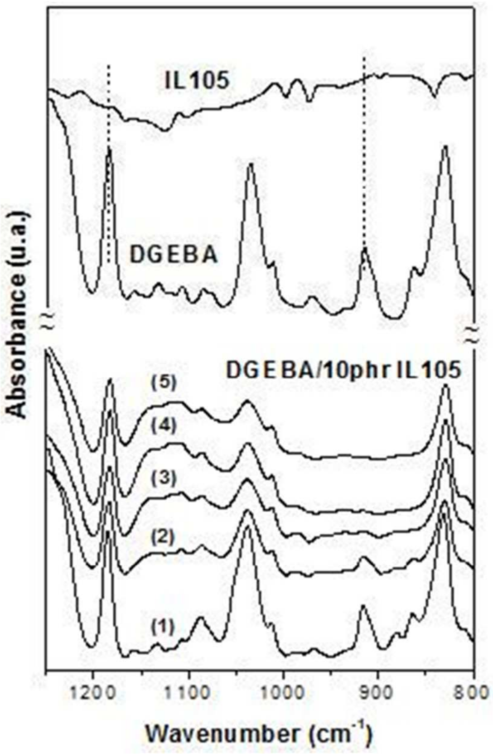


Figure 3. FTIR spectra of DGEBA, IL 105 and blends with 10 phr of IL 105 subjected to heating at 80°C during different times: (1) 0 min, (2) 30 min, (3) 60 min; and second heating stage at 140°C for (4) 60 min and (5) 120 min.

The evolution of the spectra of epoxy-ILs systems were recorded immediately at different times: (1) 0 min, (2) 30 min at 80 °C, (3) 60 min at 80 °C, (4) 60 min at 140 °C, (5) 120 min at 140 °C. The quantification of the polymerization process has been performed based on the decrease in the characteristic absorption band of epoxy functions at 918 cm^{-1} [28]. These results clearly demonstrate a reduction in the intensity of the absorption band at 918cm^{-1} for the system containing 10 wt% of phosphonium ionic liquid combined with dicyanamide counteranion only after 30min at 80 °C and then completely disappears after a post curing step at 120 °C for 3 hours. In addition, an increase of the absorption at about 1060-1200 cm^{-1} corresponds to the formation of C-O bonds which suggests that the dicyanamide anion acts also as a potential initiator of epoxy homopolymerization such as imidazoles, phosphinate or tertiary amines[27-28]. To highlight the influence of ionic liquid on the kinetic of the polymerization reaction, the conversion of epoxy groups was determined according to the equation described in the literature[26]: X% = $(A_0-A_t)/A_0)*100$ where A_0 and A_t represent the A_{918}/A_{1183} area ratio of the system at t = 0 an at a reaction time t, respectively. Figure 4 shows the epoxy conversion versus the polymerization time at 80 °C and 140 °C.

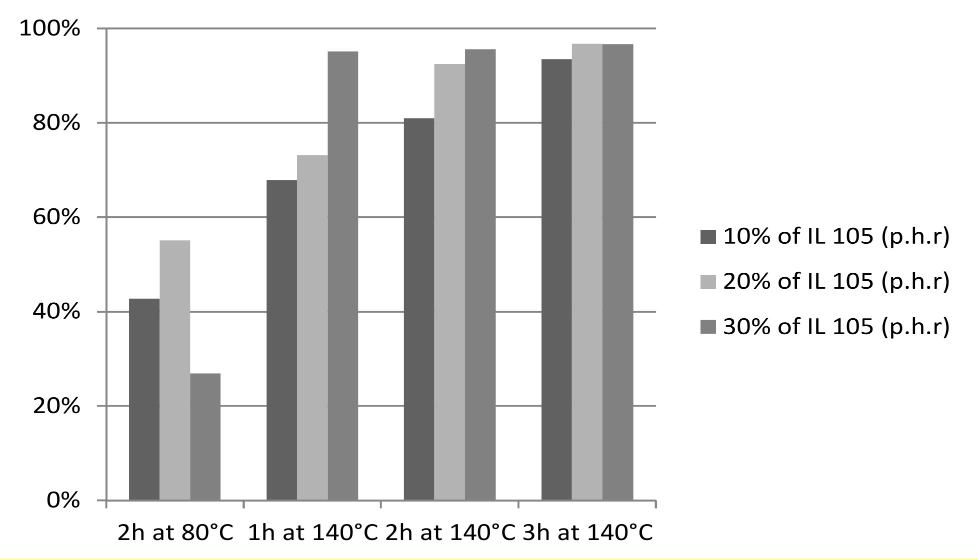


Figure 4.Conversion of epoxide groups versus reaction time at 80°C and 140°C of DGEBA-IL epoxy networks, as a function of the IL amount: (a) 10 phr, (b) 20 phr and (c) 30 phr.

In all cases, the conversion of the epoxy groups is dependent on the concentration of ionic liquid used (10-20-30 phr) but also of the reaction temperature. Moreover, the FTIR data confirm that there are unconverted epoxy groups left. Indeed, 30 phr of phosphonium ionic liquid leads to a conversion rate of 96% after1 hour of a post curing at 140 °C whereas the conversion rate is only 68% for 10 phr of IL used. However, a slight difference is observed after the first curing step at 80 °C. FTIR data clearly show that the addition of 30 phr of ionic liquid in the epoxy prepolymer induces a lower conversion rate (27% for 30 phr compared to 43% for 10 phr). This result can be explained by the miscibility of the ionic liquid in the epoxy prepolymer. In fact, the concentration limit was determined at 30 phr by different miscibility tests. From this value, the epoxy-IL mixture is cloudy while at a higher concentration of the phosphonium IL, one phase separation is observed. Then, when the temperature increases from 80 °C to 140 °C, the kinetics of the reaction as well as the miscibility of the phosphonium ionic liquid in the epoxy prepolymer are improved which explains the higher conversion of the epoxy groups.

3.2. Thermomechanical properties of epoxy networks

The influence of the IL amount (5, 10 and 20 phr) on the dynamical mechanical properties of the epoxy/IL cured systems was investigated by DMA. The dynamical mechanical spectrum (Figure 5) of the DGEBA/IL networks displays the storage moduli E’ and the main relaxation peak (Tα). The data of the storage moduli E’ as well as the Tα are summarized in Table 3.

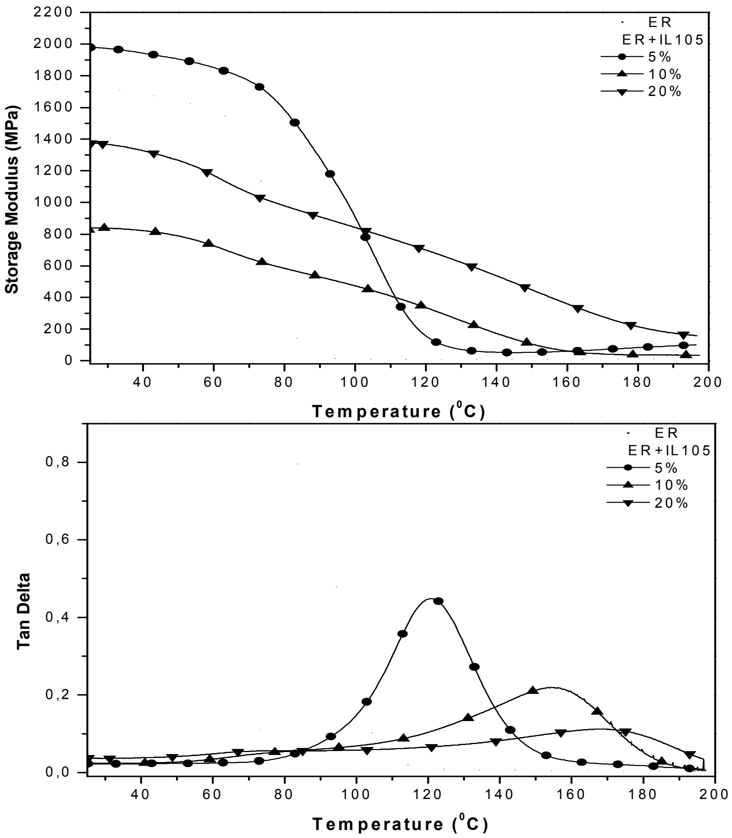


Figure 5. Dependence of storage modulus E’, and tan δ, with temperature at 1 Hz for the DGEBA/IL networks cured for 2 h at 80°C followed by 3h at 140°C as a function of the IL content: (●) 5 phr, (▲) 10 phr and (▼) 20 phr.

Table 3.Dynamical mechanical analysis of epoxy-IL networks: Storage moduli at glassy and rubbery states as well as the main relaxation peak (Tα).

IL amount (phr)	Main relaxation peak (Tα)	Glassy state E’ (GPa)	Rubbery state E’ (MPa)
5	121	1.9	83
10	154	0.8	164
20	180	1.4	41

The temperature corresponding to the main relaxation process (T_g) continuously increases as the amount of the phosphonium ionic liquid for the preparation of the epoxy networks increases (5 to 20 phr), Indeed, for the epoxy-IL system containing 20 phr of IL, a maximun glass transition temperature of 180°C was observed. By comparison with the Tα values reported in the literature for conventional epoxy networks cured by aliphatic amines such as jeffamine D230, D400, or triethylenetetramine (TETA), the values of the glass transition temperature (T_g) determined for epoxy-IL105 are quite similar [29-30]. In our previous work related to the use of phosphonium –based ionic liquid with phosphinate as the counteranion, a T_g value of about 140 °C[24] was obtained. Also Maka et al have highlighted T_g values in the temperature range of 75-170 °C when 1 to 9 wt% of imidazolium IL with dicyanamide anion was used[21]. In addition, the presence of a single peak for the epoxy-IL network containing 5 phr means a good crosslink density, suggesting a good dispersion of the IL inside the epoxy matrix. In the opposite, when 10 and 20 phr of phosphonium ionic liquid were incorporated in epoxy systems, broad peaks extending over a wide temperature range were obtained, especially for 20 phr. This broadening of the tan delta peak demonstrates poorer miscibility and/or dispersion of the IL 105 in the thermosetting matrix[29].

In the case of epoxy-IL network containing 20 phr of ionic liquid, a lower modulus in the rubbery state is observed in comparison with the epoxy systems filled with 5 and 10 wt% of IL (41 Mpa compared to 83 and 164 Mpa for 5 and 10 wt%). According to the rubber elasticity theory, the storage modulus above the main relaxation peak Tα related to the crosslink density. Thus, when the concentration of ionic liquid increases, an improvement of the crosslink density is obtained. This observation was confirmed for epoxy networks containing 5 and 10 phr of phosphonium ionic liquid.

Contrariwise, for an epoxy/IL network filled with 20 phr of IL 105, this low value of modulus at the rubbery plateau could be explained by the presence of the free ionic liquid that does not react with the epoxy prepolymer. Thus, there is a balance between the mobility of the chains within the network and the concentration of ionic liquid. In fact, if an excess of ionic liquid leads to the formation of ionic aggregates as is the case in some polymers such as polytetrafluoroethylene, the chain mobility would be increased resulting in a decrease in the rubbery modulus[17].

3.3. Thermal stability of epoxy networks

The degradation mechanisms and the influence of the ionic liquids on the thermal stability of DGEBA/IL 105 epoxy networks have been highlighted by thermogravimetric analysis (TGA). The evolution of the weight loss as a function of a temperature performed on IL 105 and DGEBA/IL 105 containing 5, 10 and 20 wt% are presented in Figure 6.

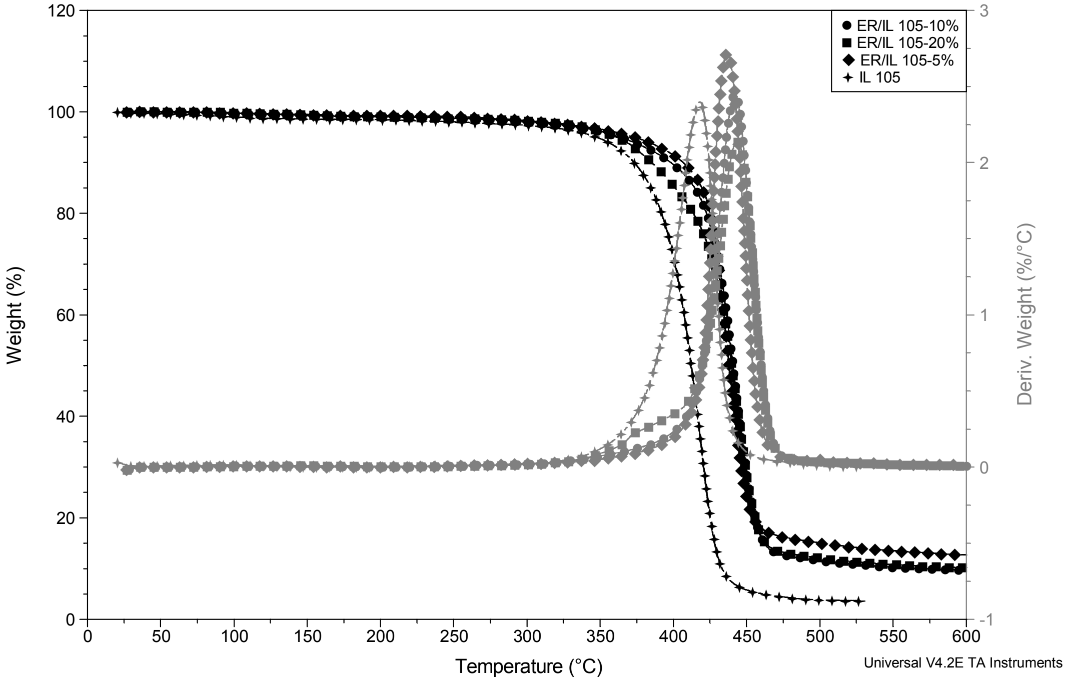


Figure 6. Evolution of the weight loss as a function of temperature (TGA, DTG) of IL 105 (+), and epoxy-IL networks (ER/IL 105): (♦) ER-IL 105 5 phr, (●) ER-IL 105 10 phr, (■) ER-IL 105 20 phr.

The TGA analysis highlights an excellent thermal stability of the epoxy networks. In fact, the degradation temperature of the maximum of DTG peak is around 440 °C. Compared to conventional epoxy systems based on DGEBA cured with aliphatic monomer such as jeffamine (D230, D400), the use of phosphonium ionic liquid leads to a significant improvement of the thermal behavior of the epoxy networks (+ 40-50 °C)[21,24]. However, an increase in the concentration of ionic liquid (20 phr) leads to the appearance of a shoulder peak at 385 °C in the DTG curve. To determine the nature of the degradation peak, the thermal stability of the phosphonium ionic liquid was also investigated by TGA. Thus, this shoulder peak corresponds to the degradation of the pure ionic liquid (IL 105)[24]. Furthermore, these results clearly demonstrate the presence of free ionic liquid in the epoxy network from a high concentration of IL 105 introduced (between 10 and 20 phr of IL).

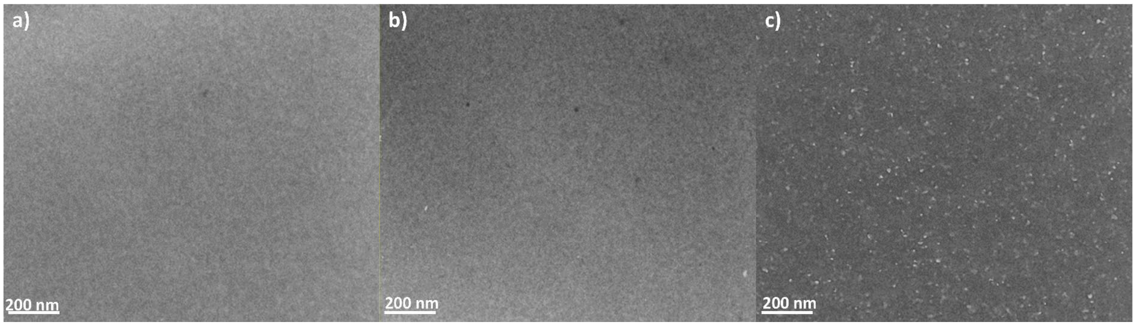
3.4. Morphology of epoxy-IL networks

To reveal the existence of phosphonium ionic liquid as ionic domains into the epoxy matrix, the transmission electronic microscopy and the atomic force microscopy are the suitable tool.

3.4.1. Transmission electronic microscopy (TEM)

Due to a slight difference in electron density and assuming that a portion of the phosphonium ionic liquid is involved in the formation of the epoxy network, the DGEBA/IL 105 containing 5, 10 and 30 phr were investigated (Figure 7).

Figure 7. TEM micrographs of the epoxy-IL cured systems with (a) 5 phr, (b) 10 phr and (c) 30 phr of phosphonium ionic liquid.



The influence of the phosphonium ionic liquid concentration on the morphologies of curing epoxy networks was studied by transmission electronic microscopy. Thus, the TEM micrographs show that for concentrations included between 5 and 10 phr of IL used, no presence of the phosphonium ionic liquid is observed. In fact, these TEM images confirm a good miscibility between IL 105 and the epoxy prepolymer. Therefore, the epoxy network loaded with the highest concentration (30 phr) was also studied. In the opposite, TEM micrographs show the formation of ionic clusters of the size of 20-30 nm characterized by the white spots. In addition, an excellent distribution of ionic liquid in epoxy network is achieved. The formation of these ionic aggregates clearly highlights a miscibility limit between the epoxy prepolymer and the ionic liquid. This phenomenon is well known in the epoxy formulations involving block co-polymers as modifiers[29-34]. Indeed, many authors have demonstrated that the use of amphiphilic block copolymers could lead to self-assembly or microphase separation mechanisms and these phenomena are due to the miscibility of the subchains of block copolymers[31-34]. However, unlike the block copolymers which can be formed of miscible or immiscible constituent subchains, the key parameter that controls the structuration of ILs in the epoxy matrix is its concentration. Finally, the use of ionic liquids as additive agent opens a new alternative to the block copolymers in the formation of nanostructures in the thermosets.

3.4.2. Atomic force microscopy (AFM)

The morphology of the phase-separated blends was also investigated by atomic force microscopy. Thus, AFM was used to examine a larger area of the epoxy networks containing phosphonium ionic liquids. In fact, from the TEM micrographs, a high concentration (30 phr) of the IL 105 leads to a structuration in the epoxy matrix. However, to confirm a possible nanostructuration to a lower concentration of IL, epoxy-IL networks containing 10 and 20 phr of IL 105 were investigated by AFM. Figure 8 highlights various surface types as a function of the concentration of ionic liquid included in the polymer matrix (10 phr and 20 phr).

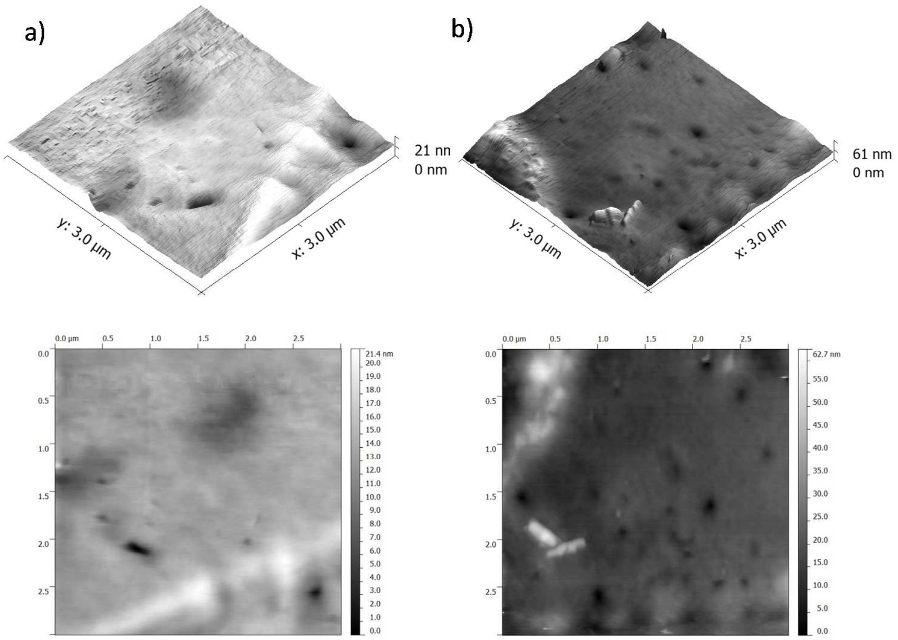


Figure 8. AFM micrographs of epoxy-IL systems with different IL concentration: (a) 10 phr, (b) 20 phr.

In the epoxy-IL networks containing 10 phr of phosphonium ionic liquid, a continuous epoxy-rich matrix with a poor distribution of some ionic domains of IL is obtained. As for the epoxy network containing 20 phr of ionic liquid, an increase of the ionic clusters was observed. Futhermore, an excellent distribution of the ionic liquid is obtained. Thus, the higher charged polymer sample, *i.e.* containing 20 phr of phosphonium IL show more open porosity which corresponds to the influence of the added ionic domains size on the surface of the polymer. In addition, in both cases, the size of the ionic domains is about 15-20 nm. Finally, a true structuration is observed when 20 phr of the ionic liquid is introduced into epoxy matrix which confirms the presence of free ionic liquids resulting in a decrease of the modulus at rubbery plateau, previously observed.

Moreover, the RMS which is considered as the standard deviation of the height distribution of points within the AFM image increases with the amount of IL. In fact, 20 phr of phosphonium salt leads to RMS roughness of 19.9 nm compared to 2.19 nm for the epoxy networks filled with 10 phr of IL. These results are confirmed in the literature for thermosets filled with different nanoparticles such as layered silicates, silica or block copolymers[35-38]. Afzal et al have demonstrated that the addition of 25 wt% of silica in epoxy matrix induces an increase of the RMS (23.79 nm compared to 2.31 nm for 5 wt% of silica)[35].

4. Conclusions

In this work, we have demonstrated that the ionic liquid based on phosphonium cation combined with dicyanamide counteranion can be used as reactive building blocks in an epoxy system. In fact, the use of the ionic liquid in the preparation of epoxy networks leads to good thermomechanical properties and with an excellent thermal stability (> 400°C). In addition, phosphonium ionic liquid generates a phase separation which has been demonstrated for the first time by transmission electronic microscopy and atomic force microscopy. These results are promising and open new perspectives in the field of energy where the ionic liquid can be used as ionic channels for lithium salts to ensure the conduction properties.

Acknowledgements

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