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► **To cite this version:**

Thi Khanh Ly Nguyen, Sébastien Livi, Bluma Guenther Soares, Sébastien Pruvost, Jannick Duchet-Rumeau, et al.. Ionic liquids: A New Route for the Design of Epoxy Networks. ACS Sustainable Chemistry & Engineering, 2016, 4 (2), pp.481-490. 10.1021/acssuschemeng.5b00953 . hal-01396548

HAL Id: hal-01396548

<https://hal.science/hal-01396548v1>

Submitted on 12 Oct 2023

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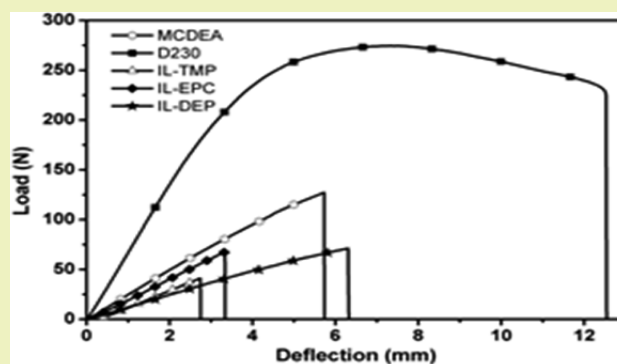
Ionic liquids: A New Route for the Design of Epoxy Networks

Thi Khanh Ly Nguyen,^{†,‡} Sébastien Livi,^{*,†,‡} Bluma G. Soares,[§] Sébastien Pruvost,^{†,‡}
Jannick Duchet-Rumeau,^{†,‡} and Jean-François Gérard^{†,‡}[†]CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université de Lyon, F-69003 Lyon, France[‡]CNRS, UMR 5223, Ingénierie des Matériaux Polymères, INSA Lyon, F-69621 Villeurbanne, France[§]PEMM-COPPE, Centro de Tecnologia, Universidade Federal do Rio de Janeiro, 21941-972 Rio de Janeiro, Brazil

Supporting Information

ABSTRACT: A new way to synthesize epoxy networks was reported in this work using phosphonium based ionic liquids combined with phosphinate, carboxylate, and phosphate counter-anions. The influence of the chemical nature of the anions was investigated on the polymerization kinetics of epoxy systems as well as the thermal and mechanical properties of epoxy–IL networks. In all cases, ILs displayed a high reactivity toward epoxy prepolymer and led to the formation of poly epoxy networks with high epoxy group conversion, i.e., up to 90%. In addition, epoxy–IL networks have high hydrophobicity and an excellent thermal stability (above 350 °C) under N₂ with the glass transition temperatures (*T_g*) ranging from 90 to 140 °C depending on the chemical structure of ILs. For the first time, the mechanical properties of epoxy–IL networks were also evaluated in terms of flexural properties and fracture toughness (*K_{IC}*).

KEYWORDS: Ionic liquids, Epoxy networks, Morphology, Mechanical properties, Reactive additives



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, nonflammability, but also high versatility, ionic liquids are become excellent functional additives to polymer matrixes.^{1,2} In fact, ILs are more and more used as processing aids of renewable resources,^{3,4} as a solvent of polymerization,^{5–8} lubricants,^{9–11} or plasticizers^{12–14} in advanced polymer materials, compatibilizers of thermoplastic and biopolymer blends,^{15–17} building blocks for designing nanostructured polymers,^{18,19} or as surfactant agents in nanocomposites.²⁰ 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.^{21–23}

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.^{24–29} Thus, ILs bearing epoxide groups either on the cation or the counter-anion were synthesized by Matsumoto et al.^{24–26} to design ionic conductive epoxy–amine networks.²⁷ 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

CO₂ permeability and selectivity.^{28,29} (ii) ILs can be also combined as additives or comonomers to conventional epoxy prepolymers or epoxy–amine reactive systems.^{30–40} In fact, the incorporation of a small amount of ionic liquids (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.^{30,31,35} 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.³³ 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.³⁴

In recent years, ILs have been also reported as new alternatives to conventional amines used as hardeners (comonomers) of epoxy prepolymer.^{22,39,40} In 2009, Rhama-thullah et al. highlighted that imidazolium salt associated with a dicyanamide counteranion could be used as a latent curing agent.³⁶ In addition, various authors have demonstrated that ILs based on imidazolium and pyridinium cations acted as

Special Issue: Ionic Liquids at the Interface of Chemistry and Engineering

Received: August 27, 2015

Revised: October 6, 2015

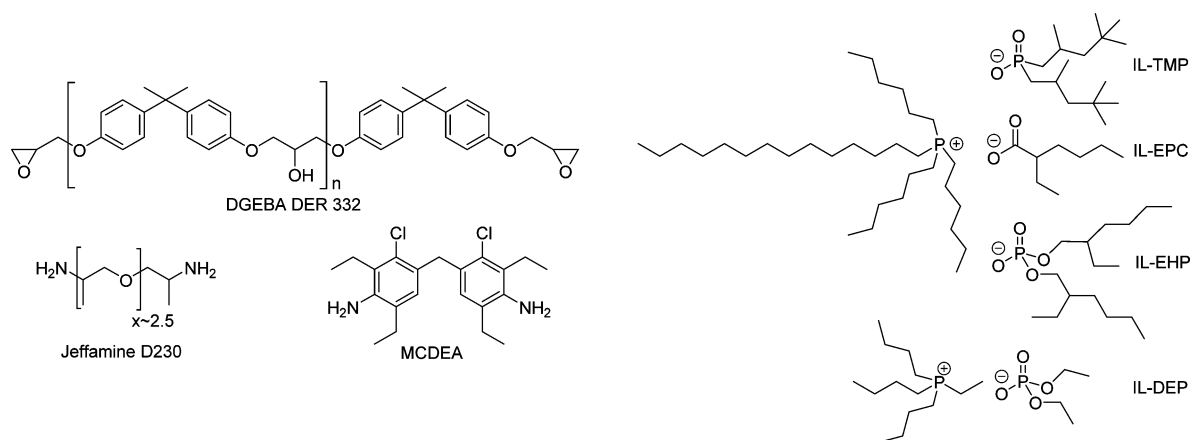


Figure 1. Chemical structures of DGEBA, Jeffamine D230, MCDEA, and phosphonium ionic liquids.

Table 1. Curing Conditions of Epoxy–Amine and Epoxy–IL Systems

epoxy	curing agent	concentration (phr)	curing protocol
DGEBA	MCDEA	54 (a/e = 1) ^a	1 h@150 + 2 h@180 + 1 h@200
	D230	34 (a/e = 1)	2 h@80 + 3 h@125 + 1 h@200
	IL-TMP	10 (a/e = 0.03) ^b	2 h@80 + 3 h@120 + 1 h@200
	IL-EPC	10 (a/e = 0.02)	2 h@80 + 3 h@120 + 1 h@200
	IL-EHP	30 (a/e = 0.06)	2 h@80 + 3 h@180 + 3 h@200
	IL-DEP	30 (a/e = 0.14)	2 h@80 + 3 h@160 + 3 h@200

^aa/e is the amino hydrogen to epoxy ratio. ^bIn the case of IL, a/e is the IL anion to epoxy ratio considering that each IL anion reacts to one epoxy group.

initiators and curing agents of diglycidyl ether of bisphenol A prepolymer (DGEBA) through cationic polymerization to prepare epoxy–IL networks.^{30,31,38} 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 counteranions were also very good candidates to replace amines.^{39–41} In fact, Soares et al., Livi et al., and Nguyen et al. clearly demonstrated that the basic nature of the phosphinate and dicyanamide anions allowed the polymerization of the epoxy prepolymer via anionic polymerization.^{23,39–41} 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.³⁹ Very recently, Maka et al. have also studied epoxy networks cured with imidazolium and phosphonium ILs combined with dicyanamide anion.²³ 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 counteranions 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 counteranion) was investigated on the polymerization kinetics of epoxy prepolymer, thermal (ATG, DSC), and thermomechanical properties (DMS) as well as on the morphology and surface properties of epoxy–IL networks. In addition, 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.

EXPERIMENTAL SECTION

Materials. Diglycidyl ether of bisphenol A (DGEBA) based epoxy prepolymer (DER 332, Dow Chemical) with epoxide equivalent weight of 175 g·mol⁻¹ was considered. Two conventional diamine comonomers, i.e., an aromatic diamine, 4,4'-methylene bis(3-chloro-2,6-diethylaniline)–MCDEA (Lonzacure, AHEW = 95 g·mol⁻¹) and an aliphatic diamine, polyoxy-propylene-diamine–Jeffamine D230 (Hunstmann, AHEW = 60 g·mol⁻¹) 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 1. The ionic liquids denoted IL-EPC (triethyl(tetradecyl)-phosphonium 2-ethylhexanoate), IL-EHP (triethyl(tetradecyl)-phosphonium bis(2-ethylhexyl)phosphate), and IL-TMP (triethyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate) have the same cation combined with carboxylate, phosphate, and phosphinate counteranions, respectively. IL-DEP (tributyl(ethyl)-phosphonium diethylphosphate) possesses the same phosphate anion as IL-EHP, but combined with a phosphonium cation, functionalized with shorter alkyl groups.

Preparation of Samples. DGEBA and curing agents (ionic liquid or diamine) were mixed with a suitable ratio under stirring at room temperature for 30 min. The mixture was then degassed in an ultrasonic bath for 15 min, 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 1.

The amount of ionic liquids depending on the chemical structure of ILs was chosen based on previous studies.^{22,40} In fact, our previous works on the use of ionic liquids combined with phosphinate and phosphate counteranions as an initiator of the epoxy polymerization allowed us to identify the optimal concentrations, i.e., 10 phr (phosphinate) and 30 phr (phosphate), to obtain solid samples with better properties and without exudation phenomenon.^{22,40} In addition,

knowing that IL-EPC and IL-EHP have the same reactivity as ILs denoted IL-TMP and IL-DEP respectively, the same amount of ILs was used. The curing protocol was also tuned for each epoxy–ILs system in order to complete the curing reaction and obtain the fully cured networks.

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⁻¹ under nitrogen flow of 50 mL·min⁻¹. The weight of samples was between 9 and 10 mg in all 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⁻¹) from 4000 to 500 cm⁻¹ to follow the curing reaction. The conversion of epoxide group was calculated from the area of absorption peaks at 1184 cm⁻¹ (corresponding to the C–O bonds) and 914 cm⁻¹ (epoxy function) at a given reaction time, *t*, using the following equation:²²

$$\chi\% = \frac{(A^0 - A^t)}{A^0} \times 100\% \quad (1)$$

where *A*⁰ and *A*^{*t*} are the *A*₉₁₄/*A*₁₁₈₄ 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. Nondispersive (polar and H-bond) and dispersive components of surface energy were determined according to the Owens–Wendt theory.⁴² Surface tensions of phosphonium ionic liquids (denoted IL-TMP, IL-EPC, IL-DEP, and IL-EHP) and Jeffamine D230 were measured from a pendant drop method.⁴³

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⁻¹ under nitrogen atmosphere.

Dynamic mechanical spectroscopy (DMS) 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⁻¹ for a temperature range from 30 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. Five samples for each system were analyzed using a MTS tensile instrument with a 1 kN load cell and a fixed span length of 60 mm at a speed of 2 mm·min⁻¹ at room temperature. Flexural strength at break was calculated using the following equation:

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

where *F* (N) is the load at break, *L* (m) the span length, and *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:

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

where *F* (N) and *d* (m) is the load and the deflection at break, respectively. (*L*³/(4*bh*³)) is the correction factor for the slope of the load–deflection curve.

Fracture toughness (*K*_{1c}) of epoxy–IL samples was determined using compact tension specimen figuration according to ISO 13586 Standard (Figure S1, Supporting Information). 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*) was to be maintained between 0.2 and 0.8. The *K*_{1c} specimens were then tested in tension mode using a MTS tensile instrument with a 1 kN load cell at a speed of 10 mm·min⁻¹. Then fracture toughness was calculated using the following equation:

$$K_{1c} = f(a/w) \frac{F_Q}{h\sqrt{w}} \quad (4)$$

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 (eq 5):

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

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*_{1c} specimens. The samples were cleaned using ethanol⁴⁴ and then coated with gold.

RESULTS AND DISCUSSION

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.

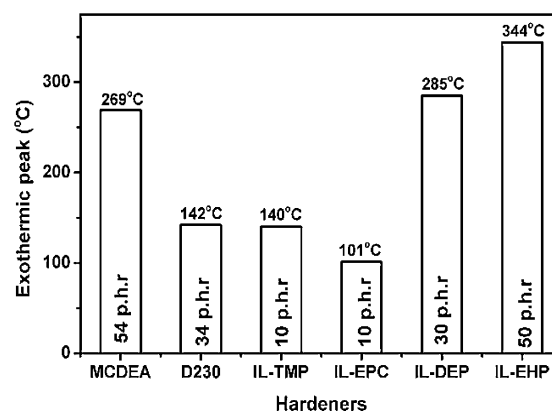


Figure 2. Reaction enthalpy peak temperature (DSC, 10 K·min⁻¹) of different epoxy reactive systems.

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 D230.⁴⁵ In all cases, phosphonium ILs combined with phosphinate, carboxylate, and phosphate counteranions 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.^{22,40} In contrast, ILs combined with phosphate counteranions 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 by Nguyen et al. between IL-DEP and IL-TMP.⁴⁰ Indeed, they have demonstrated that the reactivity of the ionic liquids is controlled by their basicity.⁴⁰ 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. Other authors have shown that the Lewis base such as imidazoles initiates a self-perpetuating anionic polymerization verified by NMR that the imidazole participates in the formation of the network by covalent bonds, confirming the role of imidazole as a curing agent.^{46,47} These results confirm the mechanisms that we have proposed in previous works where the phosphinate, phosphate, and dicyanamide counteranions bind covalently to the network and initiate the polymerization.^{22,39,40} 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 necessary to prepare 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.

FTIR Analysis. As the Jeffamine D230 and MCDEA amines have been widely studied as epoxy hardeners in the literature,^{48–50} 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 epoxy group conversion of different epoxy-IL systems calculated according to eq 1 is presented in Figure 3 as a function of curing time.

As expected, FTIR spectra of epoxy-IL mixtures during the reaction show a decrease of absorption peak at 914 cm^{-1} corresponding to epoxide group justifying the opening of epoxide ring during curing process.^{22,39,40} At the end of each curing protocol, this absorption peak was nearly disappeared

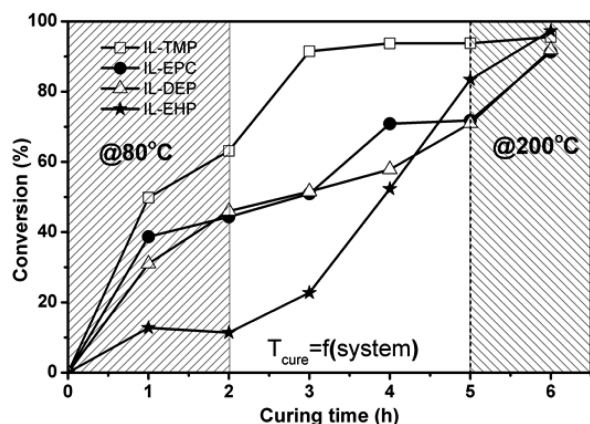


Figure 3. Epoxide group conversion as a function of curing time calculated from FTIR spectra of different epoxy-ILs systems during cure (see Table 1 for curing schedules that differ for each reactive system).

suggesting a total conversion. In fact, a constant increase in the conversion of the epoxy groups is observed in Figure 3 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 $80\text{ }^{\circ}\text{C}$), epoxy systems based on IL-EPC and IL-TMP (10 phr) have exhibited a higher conversion of epoxy 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 $160\text{ }^{\circ}\text{C}$ as well as a postcuring at $200\text{ }^{\circ}\text{C}$ during 3 h are required for IL-EHP and IL-DEP, respectively. In contrast, 3 h at $120\text{ }^{\circ}\text{C}$ and 1 h at $200\text{ }^{\circ}\text{C}$ 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 $80\text{ }^{\circ}\text{C}$ 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%.

Morphology of the Resulting Epoxy Networks. To reveal a possible structuration of ILs in epoxy networks, transmission electronic microscopy (TEM) is the suitable tool. TEM micrographs of epoxy cured with IL-TMP, IL-EPC, IL-DEP, and IL-EHP are presented in Figure 4.

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.^{39,40} 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 4, left). This phenomenon is commonly encountered in the modified reactive systems (thermosets) using elastomers, thermoplastics, or block copolymers.^{51–55}

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.^{56,57} The morphology of such ionomers consists of small dispersed ionomer particles imbedded 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.⁵⁸ With a similar behavior to ionomers, ILs open a new route in the preparation of nanostructured thermosets.

Surface Properties of Epoxy Networks. Surface energy of epoxy networks were determined by a sessile drop method. Then, the polar and dispersive components of the epoxy networks were calculated by using the Owens-Wendt method from the contact angles with water (Figure 5), and diiodomethane and are summarized in Table 2.

The incorporation of ILs, whatever their chemical nature (IL-TMP, 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 $33\text{ mJ}\cdot\text{m}^{-2}$ ^{59,60} (Table S1, Supporting Information). Slight differences were observed depending on the chemical nature of

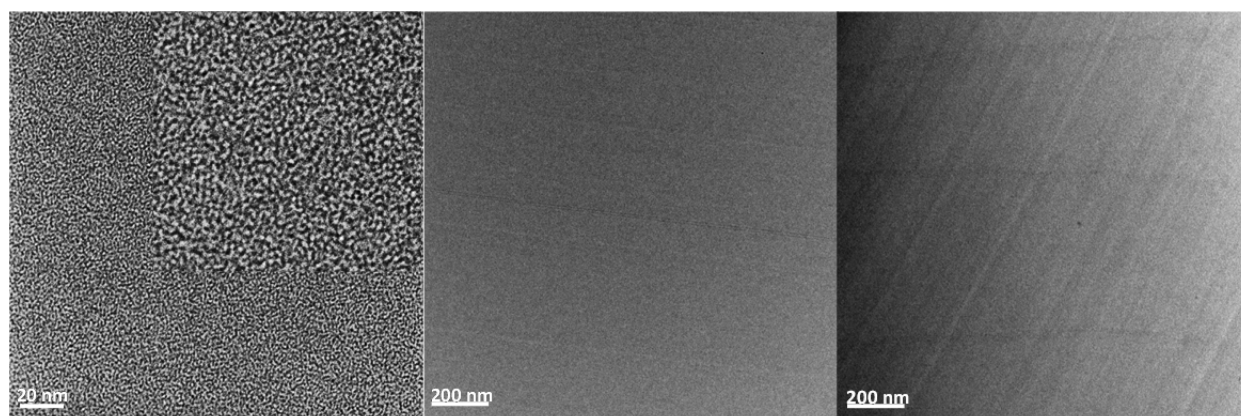


Figure 4. TEM micrographs of IL-EPC (left), IL-TMP (middle), and IL-DEP (right) networks.

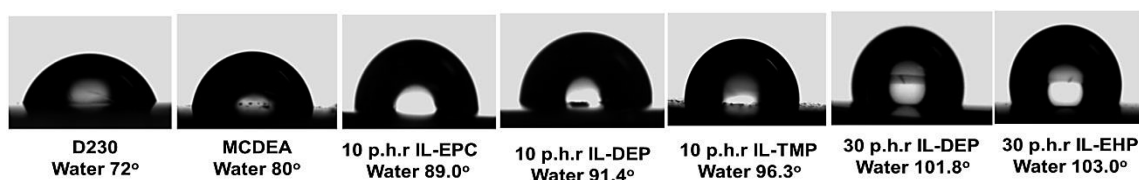


Figure 5. Contact angle with water on surfaces of epoxy networks cured with different types of ILs and different IL amounts.

Table 2. Contact Angles and Surface Energy of Epoxy Networks Measured by Sessile Drop Method

curing agent	Θ water (deg)	Θ CH ₂ I ₂ (deg)	γ nondispersive (mJ·m ⁻²)	γ dispersive (mJ·m ⁻²)	γ total (mJ·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

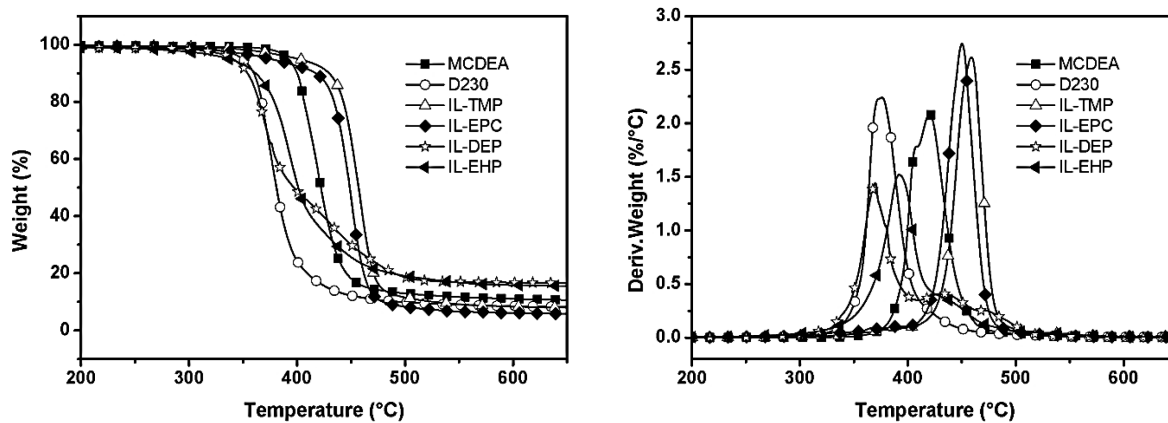


Figure 6. Weight loss as a function of temperature (TGA, DTGA) of epoxy networks: MCDEA (■), Jeffamine D230 (○), IL-TMP (Δ), IL-EPC (◆), IL-DEP (☆), and IL-EHP (◀) (heating ramp 20 K·min⁻¹, N₂ atmosphere).

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 COO⁻ group) leads to the formation of a slightly less hydrophobic epoxy network. On the opposite, IL-EHP and IL-TMP generate a reduction in the polar component of epoxy systems due to the presence of long alkyl chains on the phosphinate (1 mJ·m⁻²) and phosphate (0.12 mJ·m⁻²) counteranions. 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.

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 6.

In all cases, the TGA curves highlight an excellent thermal behavior of the epoxy–amine and epoxy–IL networks, i.e., degradation temperature at maximum of DTGA curve of over 350 °C. In the case of epoxy cured with Jeffamine D230 and 4,4'-methylene-bis 3-chloro-2,6-diethylaniline (MCDEA), thermal degradation temperatures of 375 and 418 °C were obtained. According to the literature, this higher degradation temperature (418 °C) for the epoxy–MCDEA system is explained by the presence of aromatic groups.⁶¹ 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 DTGA peaks are included between 450 and 460 °C. Although, the use of ionic liquids combined with phosphate counteranions, 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 counteranion (Figure 6). 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 an 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.³⁹ 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.

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 DMS. The temperature of α -relaxation related to the glass transition T_α from the maximum of $\tan \delta$ as well as the storage modulus, E' , in the rubbery state (E'_R) are listed in Table 3 and the DMS spectra are given in Figure S2 of the Supporting Information. In

Table 3. Thermomechanical Behavior of Epoxy Networks Cured by Different Curing Agents

curing agent	T_α^a (°C)	E'_R^b (MPa)	ν_e^c (mol·m ⁻³)
MCDEA	160	16	1385
D230	100	16	1591
IL-TMP	140	104	9412
IL-EPC	144	124	11 121
IL-DEP	117	16	1527
IL-EHP	98	14	1399

^a α : Relaxation Temperature from DMS at 1 Hz. ^bRubbery state storage modulus from DMS, determined at $T_\alpha + 30$ (K) ^cCross-link density calculated from DMS

addition, cross-link density, ν_e (mol·m⁻³) of epoxy networks (assuming homogeneous networks) was also estimated using the elasticity theory:^{41,62,63}

$$\nu_e = \frac{E'_R}{3RT_R} \quad (5)$$

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 ($R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

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

The glass transition temperatures (considering T_α value) and cross-link densities of the epoxy–amine systems (MCDEA and D230) are in agreement with the literature.^{30,64–66} The same ranges of cross-link density (1400–1600 mol·m⁻³) are obtained for the two amines. As expected, MCDEA cured epoxy networks have higher T_α values (160 °C) compared to Jeffamine D230 cured epoxy networks (100 °C). This difference of T_α 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.⁶⁷

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, whereas epoxy networks cured by IL-TMP and IL-EPC are close to epoxy–MCDEA networks with T_α values above 140 °C. Moreover, the cross-link density of epoxy networks filled with IL-EPC (11 121 mol·m⁻³) and IL-TMP (9412 mol·m⁻³) are significantly higher compared to epoxy–MCDEA networks and epoxy networks based on phosphate–ILs. In the case of phosphate counteranions 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_α values 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. Thus, IL-EPC and IL-TMP having the high value of T_α is attributed to the very high cross-linking densities.⁴⁷

Mechanical Behavior of Epoxy Networks. 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-DEP 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.

Fracture Toughness (K_{Ic}). The values of the critical stress intensity factor K_{Ic} were measured for epoxy–amine and epoxy–IL networks (Table 4).

In the case of epoxy networks cured with Jeffamine D230 and MCDEA, the values of the fracture toughness are similar to the ones reported in the literature. In fact, many authors reported K_{Ic} values of about of 0.6 and 1.24 MPa·m^{1/2} for epoxy–MCDEA and epoxy–Jeffamine networks, respectively.^{68–71} This difference in mechanical behavior between the two diamine hardeners provides from their different chemical structure. Indeed, the aromatic amine, i.e., MCDEA, that has a rigid structure and a high steric hindrance leads to the

Table 4. Mechanical Behavior (Determined at Room Temperature) of Epoxy Networks Cured by Different Curing Agents

curing agent	E_r^a (GPa)	σ_R^b (MPa)	K_{Ic} (MPa·m ^{1/2})
MCDEA	2.30	77.1	0.56
D230	2.71	81.5	1.05
IL-TMP	1.61	24.6	0.39
IL-EPC	2.39	49.5	0.37
IL-DEP	2.22	68.8	0.64
IL-EHP			

^{a,b}Flexural modulus and flexural strength from flexural tests.

formation of a more brittle epoxy network whereas 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} value of 0.64 MPa·m^{1/2}. This difference in fracture toughness between epoxy–IL networks is related to their cross-linking densities. In fact, the epoxy–IL networks having the highest cross-linking 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 cross-link density has led to a decrease in fracture toughness.⁷² Other authors have also reported the same phenomenon on epoxy–amine networks in the literature.^{73–78} However, the relationship between the cross-link 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 7.

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 7a,b,c). In contrast, epoxy cured with Jeffamine D230 and also IL-DEP show a very rough fracture surface with ridges, river marks, and tortuous cracks (Figure 7e,f). According to the literature, such features are the signature of a higher energy for the crack propagation, i.e., a higher fracture toughness.^{44,79}

Flexural Properties. The flexural modulus and the flexural strength of epoxy–amine and epoxy–IL networks are summarized in Table 3. The load-deflection traces are also given in Figure S3 of the Supporting Information.

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.^{44,79–83} Thus, the addition of the flexible amine (Jeffamine D230) leads to a ductile behavior with a high flexural modulus of 2.7 GPa whereas 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 with ionic liquids. According to the numerous cation/anion combinations, this new route for the preparation of epoxy networks looks very promising.

CONCLUSION

In conclusion, different phosphonium ionic liquids were studied as new curing agents for epoxy prepolymer and compared to epoxy cured with aliphatic or aromatic diamines (Jeffamine D230, MCDEA). Thus, we demonstrated that a small amount

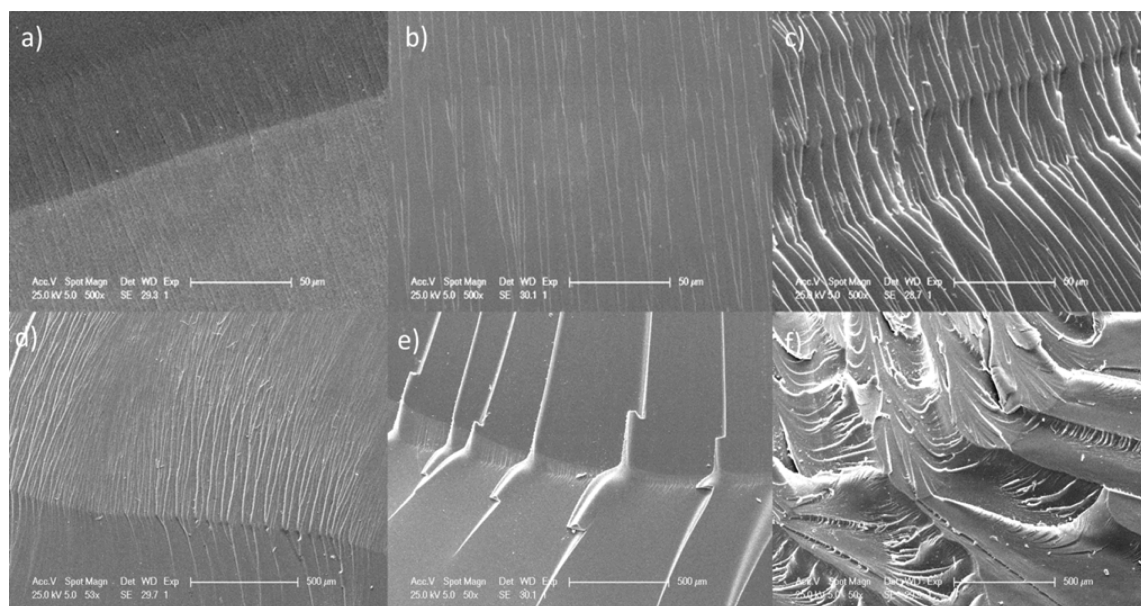


Figure 7. Fractured surfaces of epoxy networks cured with IL-EPC (a), IL-TMP (b), and MCDEA (c) at magnification of $\times 500$ (up) and MCDEA (d), IL-DEP (e) and D230 (f) at magnification of $\times 50$ (down).

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 between 90 and 140 °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.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.5b00953](https://doi.org/10.1021/acssuschemeng.5b00953).

Configuration for fracture toughness specimens, DMS spectra (storage modulus and $\tan \delta$) and force-deflection curves of epoxy networks, and table of materials surface tension (DGEBA, amines, and ionic liquids) (PDF).

■ AUTHOR INFORMATION

Corresponding Author

*S. Livi. E-mail: sebastien.livi@insa-lyon.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from Ministère de l'Enseignement Supérieur et de la Recherche (MESR).

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