

## New Epoxy/Jeffamine Networks Modified with Ionic Liquids

Bluma G. Soares,<sup>1</sup> Adriana A. Silva,<sup>1</sup> Sebastien Livi,<sup>2,3,4</sup> Jannick Duchet-Rumeau,<sup>2,3,4</sup> Jean-François Gerard<sup>2</sup>

<sup>1</sup>Universidade Federal do Rio de Janeiro, Instituto de Macromoléculas, Centro de Tecnologia, Bloco J, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brazil

<sup>2</sup>Université de Lyon, F-69003, Lyon, France

<sup>3</sup>INSA Lyon, F-69621, Villeurbanne, France

<sup>4</sup>CNRS, UMR 5223, Ingénierie des Matériaux Polymères, France

Correspondence to: B. G. Soares (E-mail: Bluma@ima.ufrj.br)

**ABSTRACT:** Diglycidyl ether of Bisphenol A/Jeffamine D400 system was modified with 2.5 and 5.0 phr of ionic liquids based on imidazolium and phosphonium cations denoted *N,N'*-dioctadecyl-imidazolium iodide, or octadecyl-triphenylphosphonium iodide, [OdTPP][I], aiming to develop new networked materials with enhanced performance particularly in terms of mechanical properties and conductivity. The curing behavior was investigated by differential scanning calorimetry, suggesting that the presence of ionic liquids (ILs) accelerates the curing process of the epoxy system. Then, the networked materials were analyzed by dynamic mechanical analysis, and mechanical testing. The presence of the ILs did not affect the glass transition temperature but resulted in a decrease on the storage modulus. By transmission electron microscopy, we have highlighted that the ILs are not miscible inside the epoxy matrix. In fact, a phase separation in nanometric scale has been observed. Measurements of conductivity revealed that the system modified with [OdTPP][I] presented higher dielectric constant and higher electrical conductivity. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39834.

**KEYWORDS:** ionic liquids; morphology; resins; thermal properties; thermosets

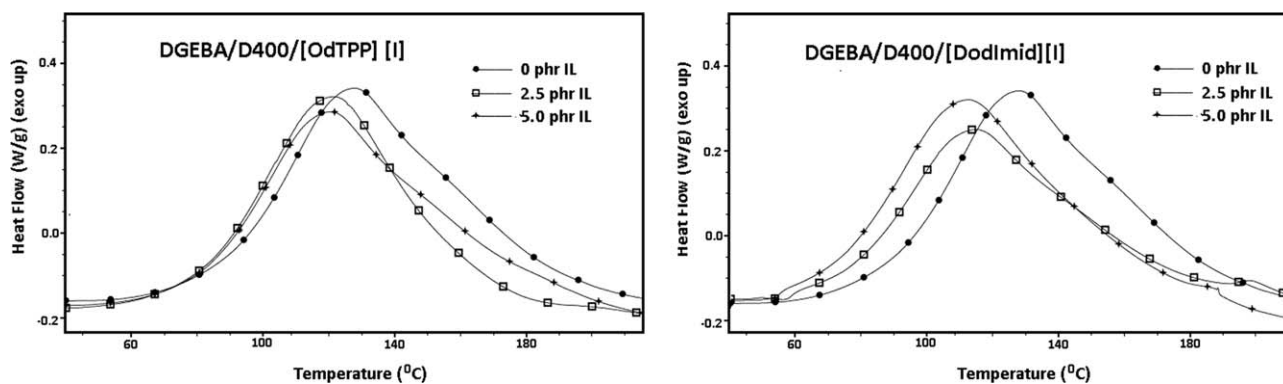
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### INTRODUCTION

Networked epoxy systems are considered versatile materials, which have been used in several important fields such as adhesive, coating, encapsulating materials in micro-electronic industries, matrices for composites, and so on. Some other applications such as solid electrolytes for electrochemical devices can also be considered because of their excellent thermal and chemical resistance. For these applications, the epoxy network must present good ionic conductivity. For this reason, ionic liquids (ILs) appear as very promising additives for the development of new epoxy networks-based materials. Indeed, ILs are organic salts with melting temperature of 100°C and are composed by an organic cation and an organic or inorganic anion.<sup>1,2</sup> In the literature, they have been widely studied as “green solvent” for cellulose,<sup>3,4</sup> and for several organic and polymerization reactions.<sup>2,5</sup> Recently, they have been employed as plasticizer of polymeric compounds,<sup>6–8</sup> and as ionic component for solid polymer electrolytes.<sup>9–11</sup> In the field of networked epoxy systems, ILs have appeared as ionic additives to impart different properties to the material. Sanes et al.<sup>12,13</sup> have investigated the efficiency of imidazolium-based IL in improving the

wear resistance of epoxy networks. Matsumoto and Endo<sup>14,15</sup> combined similar ILs with epoxy resin aiming to develop epoxy networks with high conductivity, by confining the IL inside the network. Glycidyl trimethyl ammonium bis(trifluoromethanesulfonamide) was also compounded with epoxy prepolymer to obtain networked materials with IL linked to the main backbone.<sup>16,17</sup> Some other papers investigated the role of imidazolium-based ILs as thermal curing agent for the polymerization of epoxy systems.<sup>18–21</sup> Recently we have studied the effect of different ILs based on triphenyl-phosphonium-, pyridinium-, and imidazolium-containing octadecyl groups, on the curing behavior and viscoelastic properties of epoxy networks cured at high temperature using 4,4'-methylene-bis-3-chloro-2,6-diethylaniline (MCDEA) as the hardener.<sup>22</sup> These ILs are more hydrophobic than those employed in other studies reported in the literature, because of the presence of long alkyl chains (C<sub>18</sub>) and should present better compatibility with the epoxy prepolymer. The high curing temperature required by the epoxy/MCDEA system used in our previous work promoted the decomposition of the ILs, mainly those derived from ammonium salts, such as imidazolium and pyridinium salts. These



**Figure 1.** DSC thermograms of dynamic scanning at 10°C/min, for DGEBA/D400 as a function of the IL nature.

features resulted in a decrease of the curing time but also resulted in very brittle materials, especially those containing imidazolium-based ILs.<sup>22</sup> Therefore, investigations regarding the mechanical properties could not be performed.

With the aim of developing new solid and flexible electrolyte based on epoxy network we decided to study the role of octadecyl-triphenylphosphonium and dioctadecyl-imidazolium salts in epoxy systems cured with Jeffamine D400. The main advantage of using this hardener is the lower temperature required for achieving the curing of the materials, which is important to avoid or minimize the degradation of the ILs. Additionally, Jeffamine D400 consists of repeating oxypropylene units that can assist the dissociation of the IL salts because of their ether coordination sites. Also the linear structure with molar mass around 400 imparts flexibility to the epoxy network. Such characteristics are very interesting for providing better mechanical properties and ionic conductivity.

In this article, the effect of imidazolium- and triphenylphosphonium-based ILs on the cure behavior, viscoelastic properties, thermal stability, and conductivity was studied. In addition, the nanoscopic structure of the ILs dispersed within the epoxy matrix was also investigated by transmission electron microscopy (TEM).

## EXPERIMENTAL

### Materials

Diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin (EPON 827) was provided by Shell Chemicals. Jeffamine D-400 was supplied by Hunstman. All chemicals used for the synthesis of the ILs, i.e., triphenylphosphine (95%), imidazole (99.5%), octadecyl iodide (95%), and the solvents were supplied from Aldrich and used as received. Octadecyl-triphenyl phosphonium iodide, [OdTPP][I], and N,N'-dioctadecyl-imidazolium iodide, [DODImid][I], were previously synthesized.<sup>23</sup>

### Preparation of DGEBA/IL Blends and Curing Process

Different amounts (2.5 and 5 phr) (phr = part per hundred part of resin) of IL were dissolved with DGEBA under mechanical stirring at 80°C for 5 min. Then, a stoichiometric amount of Jeffamine D400 (32 phr) was added. The mixture was stirred under reduced pressure for 15 min at 70°C to

remove any issuing gases and poured into a silicon rubber molds. The curing protocol used in this work was that suggested by the hardener supplier and corresponds to 2 h at 80°C and 3 h at 125°C.

### Characterization

The curing behavior of the epoxy systems was followed by differential scanning calorimetry (DSC) analysis on a Q10 DSC calorimeter from TA Instrument, in dynamic mode at 10°C/min, from -30 to +200°C. About 5–7 mg of samples were sealed in hermetic aluminum pans and heated under nitrogen atmosphere.

Dynamic mechanical analysis was performed on a Q800 from TA Instrument operating with single cantilever at 1 Hz, 0.1% strain and at a heating rate of 3°C/min from 25°C to 150°C/min.

Thermogravimetry (TGA) was performed with a Q500 TGA from TA Instrument, with platinum pan under 50 mL/min nitrogen flow at a heating rate of 20°C/min.

The tensile tests were performed in an Instron 5569 testing machine at a crosshead speed of 1 mm/min, according to ASTM D-638-5. The values were taken from an average of five specimens.

The TEM is collected on a JEOL JEM-900 apparatus with an accelerating voltage of 80 kV. The samples were ultramicrotomed in sections of 70–80 nm thickness, using a RMC-power Tome X microtome equipped with a diamond knife. Then, the sections are set on copper grids for observation.

AC impedance data used to determine the AC conductivity of the epoxy/IL blends were obtained by impedance spectroscopy using a Solartron SI 1260 gain phase analyzer, interfaced to a Solartron 1296 dielectric interface. The measurements were carried out in a frequency range of 0.1 Hz to 10 MHz with 6 V oscillating voltage.

## RESULTS AND DISCUSSION

### Curing Behavior

The effect of the ILs [OdTPP][I] and [DODImid][I] on the curing behavior of DGEBA/D400 systems was evaluated by DSC analysis in dynamic mode, whose results are illustrated in Figure 1. Both ILs promoted an acceleration of the curing

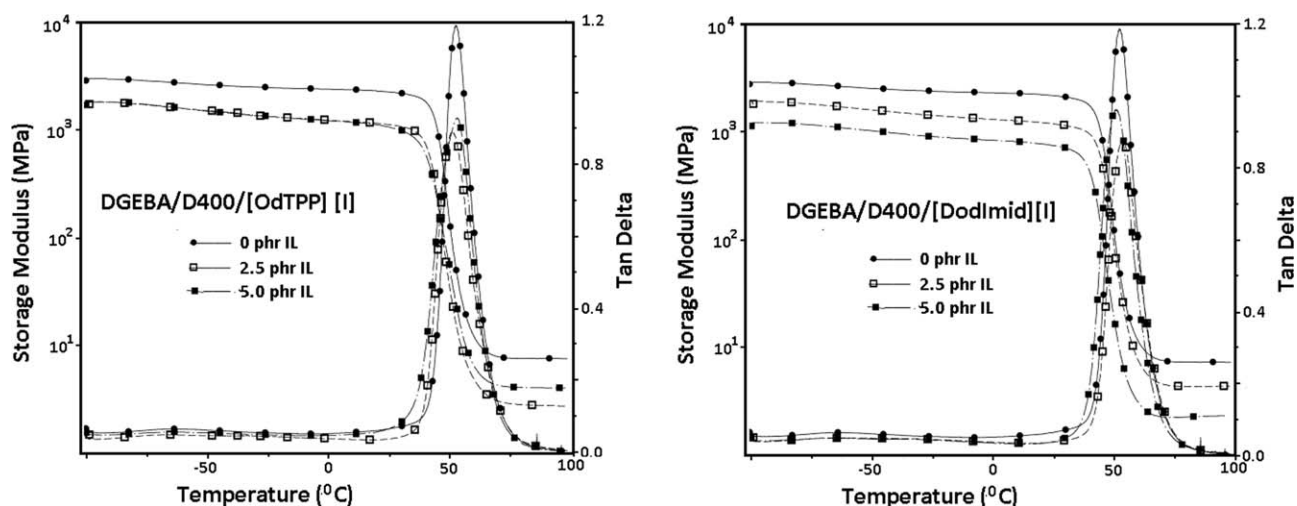


Figure 2. Dynamical mechanical properties of DGEBA/D400 networks modified with ionic liquids.

process of the epoxy system, as indicated by the decrease of the onset curing temperature, even for samples containing 2.5 phr of ILs. The effect is more pronounced for systems containing imidazolium-based IL. In fact, our previous studies reported the ability of [DOdImid][I] IL in curing the epoxy prepolymer without the presence of external curing agent, whose onset temperature stayed around 150°C.<sup>18,22</sup> In the opposite, the [OdTPP][I] IL did not show any ability for curing the epoxy prepolymer. The participation of imidazolium-based ILs as catalysts for the oxirane ring opening by aromatic amines at room temperature has been also reported in the literature.<sup>24,25</sup> Therefore, considering the results observed in the present work, one can assume that the ILs interact with the epoxy group, facilitating the reaction with the amine groups of Jeffamine.

### Viscoelastic Properties

Dynamic mechanical analysis was employed to investigate the effect of different ILs on the viscoelastic properties of DGEBA/D400 networks. The results in terms of tan delta and storage modulus with temperature are illustrated in Figure 2, for systems containing 2.5 and 5.0 phr of ILs. The glass transition temperature ( $\alpha$  transition) of the epoxy matrix, taken at the maximum of the tan delta peak, was not significantly affected by the presence of the ILs, staying in the range of 50–53°C. However, it was observed a decrease of the storage modulus before and after the  $\alpha$  transition, probably because

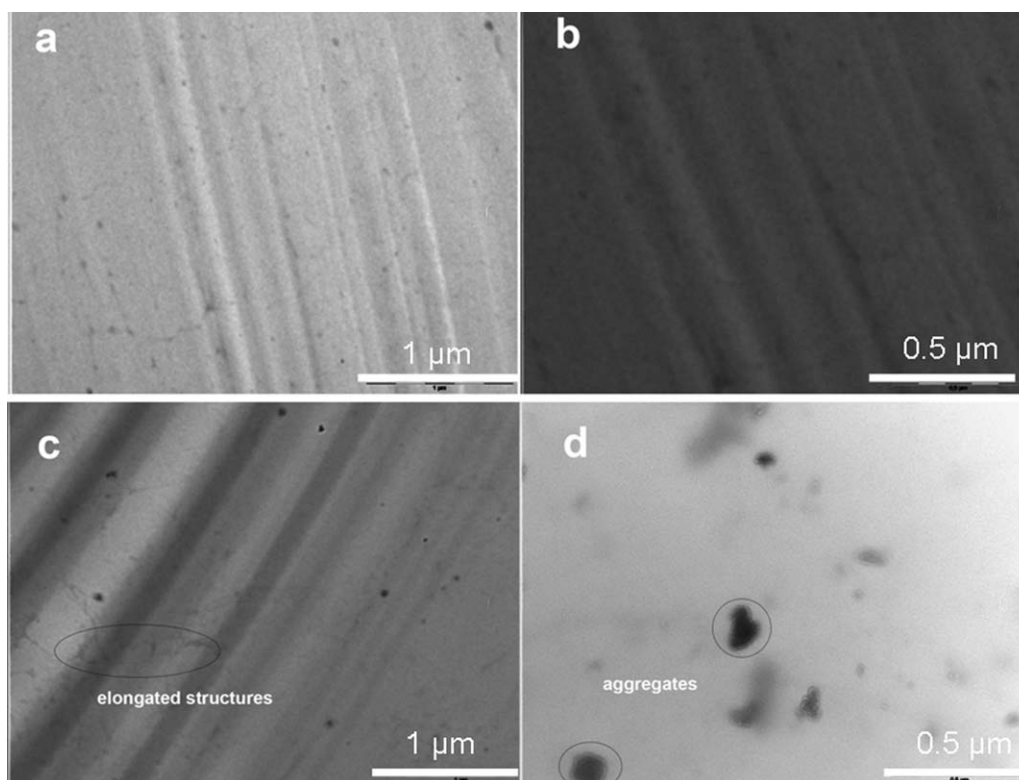
of the functionalization of imidazolium and phosphonium ILs with long alkyl chains that contribute for decreasing stiffness.

### Tensile Properties

The effect of the ILs on the tensile properties of DGEBA/D400 networks is summarized in Table I. The systems modified with imidazolium-based IL display similar ultimate tensile strength as that found for the pure DGEBA/D400 network and an improvement of elongation at break. On the other hand, the addition of triphenyl-phosphonium-based IL resulted in a slight decrease of tensile strength (–10% to –15%) but a significant increase of elongation at break (+196%). These results suggest an improvement of toughness in systems containing ILs and this effect is more pronounced for those modified with [OdTPP][I] IL. The Young modulus also presents a slight decrease with the presence of IL but this property increases with increasing the IL content in the blend. These results suggest also that increasing the amount of ILs, a good compromise between stiffness and elongation at break can be achieved. In addition, the mechanical behavior observed in the present work differs from that for the DGEBA/MCDEA networks modified with the same ILs and studied in our previous work,<sup>22</sup> probably because the curing protocol used in the preparation of DGEBA/D400 networks does not involve high temperatures for long time. In fact, in the previous study, the curing procedure was as follows: 1 h at

Table I. Tensile Properties of DGEBA/D400 Networks as a Function of the Ionic Liquid

Ionic liquid		Ultimate tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
[OdTPP][I] (phr)	[DOdImid][I] (phr)			
0	0	20 ± 2	2.7 ± 0.5	2200 ± 100
2.5	0	17 ± 1	8.3 ± 1.0	1600 ± 150
5.0	0	19 ± 2	7.8 ± 1.5	2050 ± 200
0	2.5	21 ± 1	4.4 ± 0.5	1800 ± 100
0	5.0	21 ± 2	3.5 ± 0.7	2100 ± 140



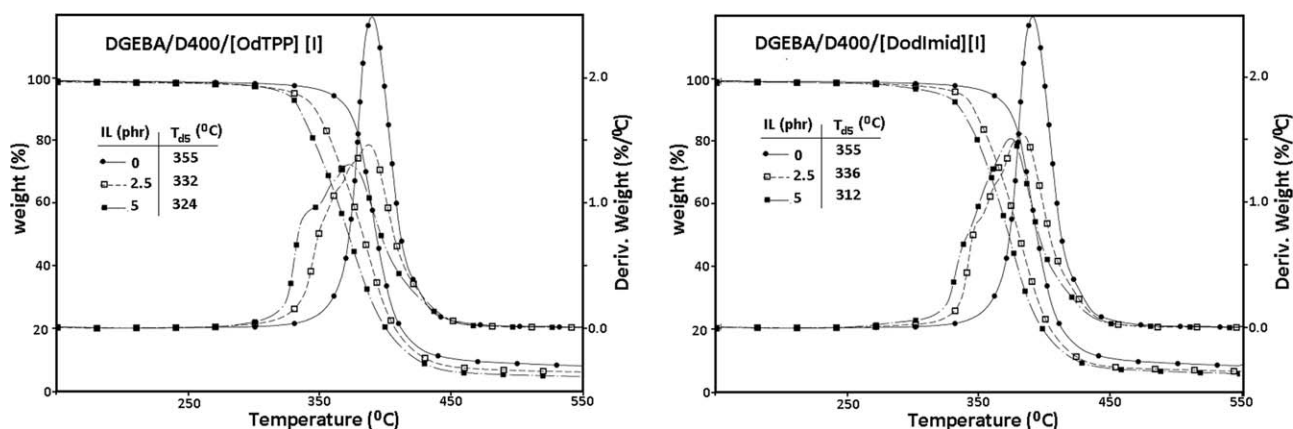
**Figure 3.** TEM micrographs of DGEBA/D400 networks containing 5 phr of (a,b) [DODimid][I] and (c,d) [OdTPP][I] ionic liquid.

150°C, 1 h at 180°C, and 2 h at 200°C, which should impart some IL degradation.

### Morphological Studies

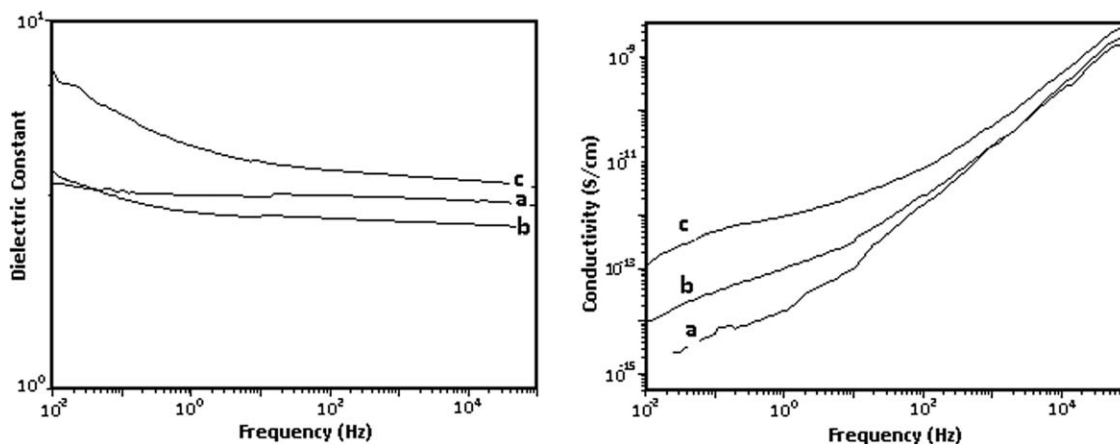
The DGEBA/D400 networks modified with the ILs are completely transparent, which may be an indication of miscibility between the components or a distribution of the IL within the epoxy matrix in nanoscale fashion. The first hypothesis does not agree with the results observed by the  $T_g$  values, as there is no significant change of the glass transition temperature with the addition of the ILs. Therefore, TEM was employed to investigate the nanoscopic structure of these systems. Figure 3 illustrates the TEM micrographs of the epoxy networks containing

5.0 phr of different ILs. All systems present IL phase separated morphologies, indicating that the ILs are not miscible inside the DGEBA/D400 system. The imidazolium-based IL (characterized by the black domains in Figure 3(a,b)) is well dispersed inside the epoxy matrix with particle sizes in the range of 100–200 nm. On the other hand, the distribution of the [OdTPP][I] IL inside the epoxy matrix is not so homogeneous. The micrograph of Figure 3(c) presents several nanodomains with different sizes, together with some thin and elongated structures. In the micrograph taken at higher magnification [Figure 3(d)], some particles appear as aggregates constituted by several small domains surrounded by a black region, which seems to be the IL phase. The white small domains inside these aggregates may



**Figure 4.** Thermogravimetric analysis of DGEBA/IL/D400 networks modified with ionic liquids.





**Figure 5.** Permittivity and conductivity versus applied frequency for the cured DGEBA/IL104 systems, as a function of the IL content.

be related to subinclusions of the epoxy phase, in the IL domains. The morphological situation observed in the present work agrees with the rheological properties reported in our previous work using parallel-plate rheometric analysis.<sup>22</sup> It was observed a significant increase of the viscosity with the addition of 5.0 phr of [DODImid][I] IL in the epoxy prepolymer, in all frequency ranges studied, which is an indication of a better dispersion of this IL inside the epoxy matrix. On the contrary, the triphenyl-phosphonium-based IL did not affect the viscosity of the system, which may be because of the presence of large aggregates and lower interfacial area that contributes for lower interactions. These ILs contain three bulky phenyl groups in the cation moiety and this structure may be responsible for the lowest interactions. The peculiar morphology observed for the DGEBA/D400/[OdTPP][I] system may be responsible for the great improvement of toughness of this material.

#### Thermogravimetric Analysis

The thermal degradation of the different DGEBA/D400 systems is illustrated in Figure 4, as a function of the nature of ILs and their content in the system. Pure DGEBA/D400 network display high thermal stability, with 5% weight loss temperature ( $T_{d5}$ ) higher than 355°C. Both ILs contribute for a decrease of the onset decomposition temperature, but the  $T_{d5}$  for all IL-modified systems kept above 310°C, which is an indication of high thermal stability.

From the derivative weight loss curves, it is possible to observe a shoulder at lower temperature range, suggesting the presence of great amount of material with lower thermal stability (300°C), which could be attributed to the thermal degradation of the IL and some part of the epoxy matrix in the IL neighborhood. According to the literature, the alkyl chains functionalized on the phosphonium and imidazolium cations break at 300°C.<sup>26</sup>

#### Dielectric Properties

The evolution of the dielectric constant and conductivity of the DGEBA/D400/ILs networks as a function of the applied frequency are presented in Figure 5. The presence of [DODImid][I] IL resulted in a slight decrease of the dielectric constant at higher frequencies and present a little increase of this prop-

erty at very low frequency. However, for the DGEBA/D400/[OdTPP][I] system, the dielectric constant is higher than pure epoxy network and it is higher in the low frequency range. This effect is usually observed in polar and heterogeneous systems and is attributed to the increase of the interfacial polarization, also known as Maxwell–Wagner–Sillars polarization, with decrease in frequency.<sup>27</sup> The increased polarization is because of the restricted mobility of the bound charges, which remain accumulated at the interfaces between different phases of the material. Therefore, a increase of the dielectric constant at lower frequency is an indication of polar and heterogeneous system.

In all systems, the conductivity increases with the frequency because of the higher ion mobility at higher frequencies. The conductivity of DGEBA/D400/[OdTPP][I] system is higher than the other systems and this phenomenon is significant in the low-frequency region. This behavior should be explained by the presence of thin and elongated structures attributed to the IL observed in TEM micrograph. Moreover, the lower interaction between the [OdTPP][I] IL and the epoxy matrix should favor a better ionic mobility, which also contributes for an increase of conductivity. The conductivity values are not so high for solid electrolyte applications, probably because of the low amount of IL used in this work. In fact, Matsumoto and Endo<sup>14</sup> have also observed low conductivity for the epoxy/tetraethylenepentamine system modified with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide when used an IL content lower than 40 wt %.

#### CONCLUSIONS

DGEBA/D400 networks were modified with imidazolium- and triphenyl-phosphonium-based ILs with long alkyl chains. The addition of ILs results in a decrease of the storage modulus of the epoxy network without affecting the glass transition temperature.

The presence of IL resulted in an improvement of tensile properties, mainly elongation at break, suggesting an improvement of toughness. This effect was more significant in systems containing octadecyl-triphenylphosphonium iodide as the IL and may be because of the peculiar morphology characterized by the presence of domains of IL with subinclusions of epoxy resin. This system also presented the highest dielectric constant and

conductivity although the values are not good enough for a solid electrolyte, probably because of the low amount of IL used in this work.

From the results obtained in this study, one may conclude that octadecyl-triphenylphosphonium iodide is an interesting alternative for assessing epoxy-based systems, which combine good toughness and conductivity. Although the reached conductivity values are not good enough, these materials present several possibilities of applications of thermoset materials as new polymer electrolytes with a combination of high toughness without changing the glass–rubber transition temperature. Future studies on the use of other hardeners are currently in progress in order to develop more flexible electrolytes.

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