

A new route to design epoxy-thermoplastic thermosets for composite applications

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In this work, we have investigated the impact of the chemical nature of ionic liquids (ILs) used as initiators of epoxy prepolymer on the final properties as well as on the morphologies of the epoxy-thermoplastic thermosets.

Epoxy networks are considered as one of among the most important thermosetting polymers thanks to their excellent thermal stability as well as mechanical performances. In addition, the versatility of epoxy networks with highly commercial availability makes them excellent candidates for different applications such as coatings, adhesives and composites. Nevertheless, the fragility of the epoxy networks requires the addition of thermoplastics or elastomers in order to improve their final properties, especially their fracture toughness. Recently, ionic liquids have emerged as new high-performance additives in the field of polymers, in particular due to their various properties such as their excellent thermal stability, their low saturating vapor pressure or their numerous unlimited cation / anion combinations. Thus, they are increasingly used as lubricants, plasticizers, surfactants, structuring or compatibilizing agents of polymer matrices¹⁻². Very recently, their high potential in epoxy thermosets has also been demonstrated leading to the development of new materials with improved thermal and mechanical properties³⁻⁵. For these reasons, our research group has focused on the development of new epoxy-thermoplastic or epoxy-elastomer networks based on phosphonium ionic liquids.

Materials

Diglycidyl ether of bisphenol A (DGEBA) based epoxy prepolymer (DER 332) with epoxide equivalent weight (EEW) of 175 g·mol⁻¹ was purchased from DOW Chemical Company. OneA 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 g·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 used.

Morphologies of modified epoxy networks

It is well-known that the incorporation of thermoplastics into epoxy networks induces 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. In the case of PPE-modified DGEBA/IL systems (**Figure 1**), 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 systems.

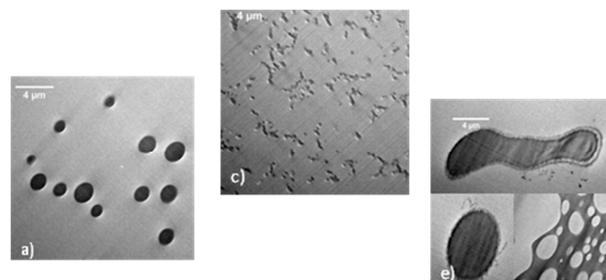


Figure 1. Influence of ionic liquids on the morphologies of epoxy-thermoplastic networks.

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 additional phenomena, 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.

Fracture toughness of modified epoxy networks

According to the literature, the use of thermoplastics as toughening agents of epoxy networks has a significant influence on the fracture toughness. In fact, K_{1c} values are very dependent of several parameters such as the morphologies of the thermoset/thermoplastic blends resulting from the chemical nature of the components of the reactive thermosetting systems and the molar mass of the thermoplastics. When IL-DEP was used as curing agent of epoxy-PPE systems, significant increases of the fracture toughness were observed. In fact, the fracture toughness is about 3 times higher than for the neat network which displays almost the same fracture properties than the brittle epoxy-amine network. These results could be associated with the morphologies of the PPE-modified epoxy/IL-DEP materials leading to an efficient toughening mechanism

References:

- 1-S. Livi, T.N. Pham, J-F. Gérard, J. Duchet-Rumeau, *Macromolecular Chemistry and Physics*, 216 (4), 259-368 (2015).
- 2- S. Livi, L.L. Lins, J. Peter, H. Benes, J. Kredatusova, R.K. Donato, S. Pruvost, *Nanomaterials*, 7, 10.3390/nano7100297 (2017).
- 3- T.K.L. Nguyen, S. Livi, B.G. Soares, H. Benes, J-F. Gérard, J. Duchet-Rumeau, *ACS Sustainable Chem Eng*, 5, 1153-1164, (2017).
- 4- T.K.L. Nguyen, S. Livi, B.G. Soares, G. Barra, J-F. Gerard, J. Duchet-Rumeau, *ACS Sustainable Chemistry and Engineering*, 5 (9), 8429-8438 (2017).
- 4- T.K.L. Nguyen, B.G. Soares, J. Duchet-Rumeau, S. Livi, *Composites Science and Technology*, 140, 30-38, (2017).