

# Partially Fluorinated Polymer Networks: Synthesis and Structural Characterization

L. A. Miccio, R. Liaño, P. E. Montemartini, P. A. Oyanguren

*Nanomaterials Group, Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina*

Received 13 October 2010; accepted 16 January 2011

DOI 10.1002/app.34204

Published online 4 May 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Functionalization of epoxy-based networks by the preferential surface enrichment of perfluorinated tails to achieve hydrophobic surface is described. The selected fluorinated epoxies (FE) were: 2,2,3,3,4,4,5,5,6,6,7,7,8,9,9,9-hexadecafluoro-8-trifluoromethyl nonyloxirane (FED3) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro nonyloxirane (FES3). Two series of crosslinked fluorinated epoxy-based materials containing variable fluorine contents (from 0 to 5 wt % F) were prepared using formulations based on partially fluorinated diamine, epoxy monomer and a curing agent. The epoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA) while the curing agents were either propyleneoxide diamine (JEFFAMINE) or 4,4'-methylenebis(3-chloro 2,6-diethylamine) (MCDEA). It was found that depending on the curing agent employed, homogeneous distribution of fluorine or

phase separation distinguishable at micrometer or nanometer scale was obtained when curing blends initially homogeneous. The morphology and composition of partially fluorinated networks were investigated on a micrometer scale combining scanning electron microscopy and X-ray analysis. When curing with JEFFAMINE, samples were homogeneous for all fluorine proportions. In contrast, MCDEA-cured blends showed fluorine-rich zones dispersed in a continuous epoxy-rich phase. A completely different morphology, characterized by a distribution of irregular fluorine-rich domains dispersed in an epoxy-rich phase, was obtained when curing blends initially immiscible. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 608–616, 2011

**Key words:** networks; fluoropolymers; phase separation

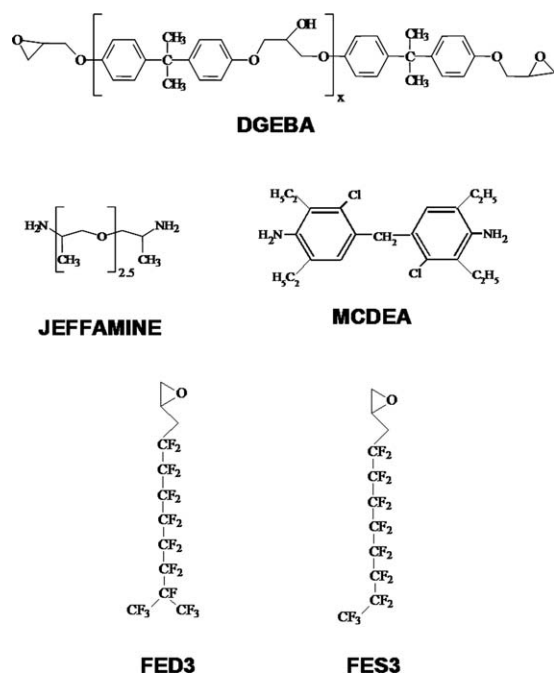
## INTRODUCTION

The polymer surface acts as such an important bridge between the polymer bulk and the outer environment and many specific surface properties, such as wettability, paintability, adhesion susceptibility, biocompatibility, and so on, depend on it.<sup>1,2</sup> These properties often demand special molecular structures which just cannot be satisfied only by single homopolymer material. Then, the surface modification has been developed as an effective way to obtain the acceptable surface of the materials to broaden their application. Conventional polymer surface functionalization always depends on the chemical or physical techniques including corona, plasma or flame treatment chemical reaction, surface grafting, surface coating or etching of finished articles, and so on. However, the complicated processes and the specialized equipments are always

required for using these techniques. Especially, for the intricate articles, the completed and uniform functional surface cannot be easily achieved. In addition, the expensive post-treatment has also greatly limited the application of these methods. Then, much attention has been focused on the exploitation of the new low-cost, reliable methods for the large-scale polymer surface functionalization,<sup>3</sup> and amphiphilic networks.<sup>4,5</sup> Among them, the selective migration of functionalized additives in host polymer to achieve the designed surface is being researched as a method with high potentiality.<sup>6–11</sup> Because of the thermodynamic incompatibility among the components in a polymer blend, the component with the lowest surface energy will spontaneously aggregate at the air interface to reduce the system's interfacial tension if the blend is equilibrated in air. On the basis of the above concept, large numbers of the functional additives have been developed and extensively applied in many fields for their obvious effect on the surface functionalization. The typical structure of functional additives were usually composed of two parts: the functional chain segments to modify the material's surface and other chain segments to assure its compatibility with host polymer.<sup>12,13</sup> When the objective is to increase the hydrophilicity, an additive containing high polarity chain segments

Correspondence to: P. A. Oyanguren (oyanguren@intema.gov.ar).

Contract grant sponsors: University of Mar del Plata, National Research Council (CONICET), National Agency for the Promotion of Science and Technology (ANPCyT).



**Figure 1** Chemical structure of the epoxy monomer (DGEBA), amines (JEFFAMINE and MCDEA), and fluorinated epoxides (FES3 and FED3).

should be introduced. Conversely, fluorine-based component was usually introduced into the primary chain of host polymer when the additive was applied to enhance the surface hydrophobicity of the material, because of its low surface energy and good selective migration to air interface.<sup>14–16</sup>

In addition, as alkyl- and perfluoroalkyl chains are thermodynamically not miscible with each other, the possibility of phase separation has to be considered. In this case, fluorinated species initially dissolved in the monomers of the system to be modified, phase separate due to an increase of the molecular weight of the thermosetting resin during isothermal cure. These systems represent typical examples of a reaction-induced phase separation during a step polymerization.<sup>17–20</sup> As the performance of the modified material depends on the morphologies generated and their relationships with the required properties, it is important to analyze the thermodynamic and kinetic factors involved in the phase separation process.

In a previous study<sup>21</sup> we reported the preparation and the surface characterization (in terms of liquids of different polarities by contact angle measurements) of two series of networks containing perfluoroalkyl end-capped or side-chain based on an epoxy system with different fluorine contents. The synthesized perfluoroalkyl side-chain epoxy-networks characterized by ionic interaction between fluorinated acid and polymer chains, exhibited a decrease in water contact angles with fluorine

content. It was demonstrated that this behavior is related with the increasing concentration of polar ammonium and carboxylate groups at the surface. Epoxy networks synthesized having perfluoroalkyl end-capped bonded by an ester group, showed hydrophobic behavior in very good agreement with the segregation of fluorine to the surface. The hydrophobic behavior of fluorinated acids having comparable chain-length was compared. It was confirmed the strong role of the  $\text{CF}_3$  moieties at the surface of the fluorinated material.

Pursuing this research line, we investigated here the synthesis and characterization of epoxy-based networks containing variable fluorinated tail content, and with distinct differences in the molecular structure of the unit building blocks. We used two different curing agents, one aliphatic and the other aromatic, while keeping the fluorinated side chains constant. The main objectives of the work reported here are: (i) to investigate the effect of a fluorinated tail on the thermoset chemistry using two different curing agents, (ii) to analyze miscibility behavior and/or the phase separation process of fluorinated species, and (iii) to determine the corresponding thermal properties. The effects of important parameters such as bulk composition, crosslink density, main chain flexibility, and curing conditions, on fluorine species migration and/or phase separation were described elsewhere.<sup>22</sup>

## EXPERIMENTAL

### Materials and samples preparation

The chemical structures of reactants are shown in Figure 1. The selected fluorinated epoxies (FE) were: 2,2,3,3,4,4,5,5,6,6,7,7,8,9,9,9-hexadecafluoro-8-trifluoromethyl nonyloxirane (Sigma-Aldrich, FED3) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro nonyloxirane (Sigma-Aldrich, FES3). The diamine employed was propyleneoxide diamine (JEFFAMINE D-230, Huntsman). Partially fluorinated JEFFAMINE monomers (F-JEFFAMINE) were prepared by reaction of FE with a known excess of diamine at 100°C for 120 min in sealed tubes. In this step the fluorinated epoxide was chemically bonded to the diamine. Subsequently, the remaining unreacted amine groups were cured using an epoxy monomer based on Diglycidyl ether of bisphenol A (DER331, Dow, DGEBA), with a mass per mol of epoxy groups equal to 174.3 g mol<sup>-1</sup>. Curing reaction was carried out at 100°C for the time necessary to obtain total conversion of the reactants in the presence of 10 wt % toluene. The diamine was used at a stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. Depending on the fluorinated epoxide employed, the resultant fluorinated networks

containing from 0 to 5 wt % F, were called FES3-DGEBA-JEFFAMINE and FED3-DGEBA-JEFFAMINE.

Selected amounts of F-JEFFAMINE prepared by reaction of FES3 with JEFFAMINE using  $r = \text{eq. amine/eq. epoxy} = 4$ , were blended with DGEBA. These blends were cured with an aromatic amine hardener, 4,4'-methylenebis(3-chloro 2,6-diethylani-line) (MCDEA) (Lonza). The resultant partially fluorinated networks, containing from 0 to 5 wt % F, were called FES3-DGEBA-MCDEA. The hardener was used at a stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. The dissolution temperatures was 90°C while curing reaction was carried out at different temperatures (150 and 180°C), for the time necessary to obtain total conversion of the reactants.<sup>20</sup> After curing, samples were postcured by a stepwise increase of the temperature up to 200°C for 1 h.

## Measurements

Cloud-point temperatures ( $T_{cp}$ ) of F-JEFFAMINE/DGEBA and unreacted mixtures: FE-DGEBA-JEFFAMINE and FES3-DGEBA-MCDEA, containing different total fluorine concentrations, were determined using transmission optical microscopy (TOM). A Leica DMLB microscope provided with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600) was used for this purpose. Temperature was increased until a homogeneous solution was obtained, kept constant for 1 min, and then decreased at a cooling rate of 1°C/min, until the temperature at which a second phase was first observed. This procedure was repeated until a constant value was obtained.

Reaction heats and glass transition temperatures ( $T_g$ ) were determined by differential scanning calorimetry (DSC). A Shimadzu DSC-50 and a Perkin-Elmer DSC-Pyris 1 were used, both operating under nitrogen flow. Dynamic curing reactions and measurements of  $T_g$  were conducted at a heating rate of 10°C/min. The  $T_g$  value was taken at the onset of the transition.

Fourier transform infrared spectroscopy was performed using a FTIR Thermo Scientific Nicolet 6700 and Genesis II Matson spectrometers. The later is provided with a heated transmission cell (HT-32, Spectra Tech) and a programmable temperature controller (Omega, Spectra Tech,  $\Delta T = \pm 1^\circ\text{C}$ ). Near-infrared spectroscopy (NIR), 7000–4000  $\text{cm}^{-1}$ , was used to determine polymerization kinetics. All spectra were collected at 8  $\text{cm}^{-1}$  resolution with a scanning rate of 4  $\text{cm s}^{-1}$  and 24 scans per slice. The sample was placed between two glasses using a 1 mm rubber spacer. Reaction was carried out at 100°C. The peak at 4538  $\text{cm}^{-1}$  (assigned to the conjugated epoxy  $\text{CH}_2$  deformation band with the

aromatic CH fundamental stretch)<sup>23</sup> was used to monitor the disappearance of the epoxy group, and primary amine combination band at 4940  $\text{cm}^{-1}$ .<sup>24</sup> Both peaks were normalized to the reference band at 5056  $\text{cm}^{-1}$  (assigned as a phenyl combination band)<sup>25</sup> for reactions involving DGEBA monomer, and at 4334  $\text{cm}^{-1}$  for reactions involving specifically JEFFAMINE. The epoxy and primary amine group conversions at any time  $t$  are calculated from the initial areas of peaks at 4538  $\text{cm}^{-1}$ ,  $A_{EP,0}$ , and 4940  $\text{cm}^{-1}$ ,  $A_{PA,0}$ , with respect to the area of the reference peak,  $A_{ref,0}$ , and their corresponding values at time  $t$ ,  $A_{EP,t}$ ,  $A_{PA,t}$ , and  $A_{ref,t}$ , according to the following equation:

$$X = 1 - [(A_t)(A_{ref,0})]/[(A_0)(A_{ref,t})] \quad (1)$$

The theoretical molecular weight between crosslinks ( $\overline{M_c}$ ) was calculated by assuming full conversion by eq. (2), previously employed by Lesser and Crawford<sup>26</sup>:

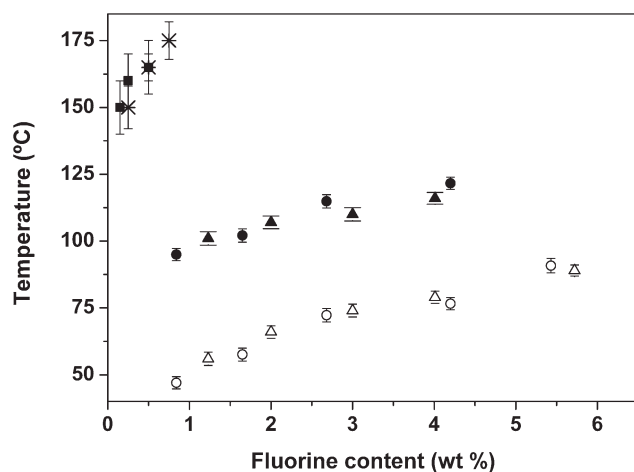
$$\overline{M_c} = \frac{2 \left( Me + \sum_{fa=2}^{\infty} \frac{M_{fa}}{fa} \Phi_{fa} \right)}{\sum_{fa=3}^{\infty} \Phi_{fa}} \quad (2)$$

where  $Me$  is the epoxy equivalent weight of the resin,  $M_{fa}$  is the molecular weight of the  $fa$ -th functional amine,  $\Phi_{fa}$  is the mol fraction of amine hydrogens provided by the  $fa$ -th functional amine and  $fa$  is the amine functionality.

The sample was examined by scanning electron microscopy (SEM), using a JEOL JSM-6460LV microscope. The composition was analyzed by x-ray Energy Dispersive Spectroscopy (EDS) investigations. The system used was an EDAX Genesis XM4 - Sys 60, equipped with Multichannel Analyzer EDAX mod EDAM IV, Sapphire Si(Li) detector and Super Ultra Thin Window of Be, and EDAX Genesis version 5.11 software. The last technique was used to detect fluorine and chloride contents in the different phases present. The analysis was done in the air- and substrate-sides and fractured surfaces.

## RESULTS AND DISCUSSIONS

As it was explained in the experimental section, all networks were synthesized employing variable fluorine concentration in which the perfluorinated tail is tethered at one end of JEFFAMINE. The reaction product, F-JEFFAMINE, is then mixed with network precursors (epoxy and diamine) and cured at constant temperature. The difference between the partially fluorinated networks is the structure of the curing agent employed and the initial miscibility of the system. In the following sections, we discuss to what extent the polymer structure and fluorine



**Figure 2** Cloud point temperatures,  $T_{cp}$  for: (asterisks) F-JEFFAMINE-DGEBA, (closed circles) FED3-DGEBA-JEFFAMINE, (closed triangles) FES3-DGEBA-JEFFAMINE, (closed squares) FES3-DGEBA-MCDEA, (open circles) FED3-DGEBA-JEFFAMINE containing 10 wt % toluene, and (open triangles) FES3-DGEBA-JEFFAMINE containing 10 wt % toluene, before any reaction epoxy-amine has taken place, as a function of fluorine concentration.

concentration can influence the miscibility behavior in the series of partially fluorinated epoxy-based networks synthesized.

### Nonreactive systems

The cloud point curve of the F-JEFFAMINE-DGEBA quasi-binary system is shown in Figure 2 (asterisks). It is typical of a system exhibiting upper critical solution temperature (UCST) behavior, i.e., the miscibility increases with temperature. The one-phase region is located above the cloud point curves. The addition of the diamine is known to turn the system at time  $t = 0$  (no reaction) into a quasi-ternary mixture. It is very important to analyze the homogeneity of reactive mixtures before any reaction has taken place. It depends on the initial temperature and total fluorine concentration. The miscibility behavior for JEFFAMINE- and MCDEA-based reactive mixtures (closed symbols) is compared to the F-JEFFAMINE/DGEBA  $T_{cp}$  on the same Figure 2. The addition of the diamines actually modifies the quasi-binary phase diagram: MCDEA does not provoke any change (squares) whereas JEFFAMINE increases the miscibility of reactive mixtures (triangles and circles). In both series we observed that miscibility increases with temperature, it means an UCST behavior. Increasing the fluorine concentration leads to an increase in the required temperature to generate one-phase mixtures. The possibility of using high dissolution temperatures has to be discarded for samples containing JEFFAMINE. The reasons are the high rate of DGEBA-JEFFAMINE reaction under

these conditions, and the possible loss of the diamine during curing.<sup>21</sup> To overcome the incompatibility of these reactive mixtures, toluene was added. As can be seen in Figure 2, open symbols, by adding 10 wt % toluene to the FE-DGEBA-JEFFAMINE reactive system the required temperature to obtain homogeneous solution decreases dramatically. The miscibility behavior seems to be not much influenced by the architecture of the perfluorinated chain (FES3 or FED3).

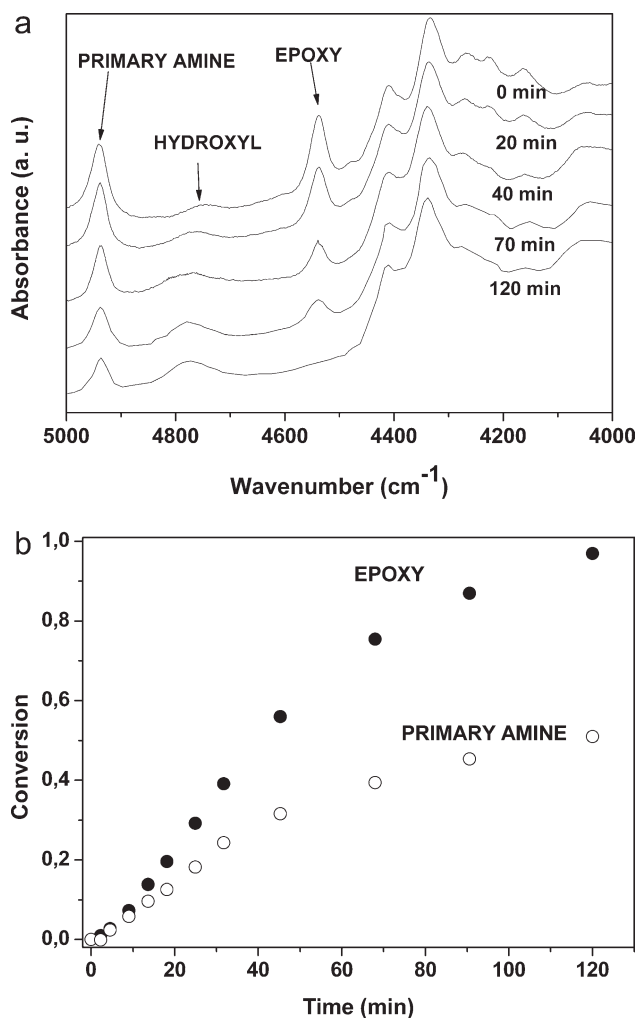
Concerning MCDEA-based mixtures, the addition of different solvents did not improve the miscibility of the system. This limits the maximum amount of F-JEFFAMINE to be incorporated to network precursors to obtain a homogeneous solution at the cure temperature (e.g., 0.5 wt % F).

To have homogeneous initial solutions, reactive mixtures containing both curing agents were polymerized at temperatures located above  $T_{cp}$ .

### Jeffamine-based systems

The chemical reactions that take place during the cure of an epoxy resin are well known and have been extensively studied in the literature.<sup>27,28</sup> It is generally agreed that, under appropriate kinetics conditions, the following reactions are possible in an epoxy-amine mixture: primary amine-epoxy, secondary amine-epoxy, hydroxyl-epoxy, and epoxy-epoxy. Furthermore, it is also known that compounds containing oxygen-hydrogen or nitrogen-hydrogen bonds can act as catalysts for epoxy-amine and epoxy-hydroxyl reactions. Since each of those reactions yields a new hydroxyl group, the autocatalytic path in epoxy-amine mixtures must be taken into account. Fortunately, the general equation for the rate of epoxy-amine reactions can be simplified by a judicious choice of components and reaction conditions. First, epoxy homopolymerization is reported to occur only in the presence of Lewis base (or acid) type catalyst<sup>29</sup> and can be neglected in their absence. Second, the importance of the etherification reaction between epoxy and hydroxyl groups has not been firmly established. It is known that depends on the temperature,<sup>30</sup> the basicity of the diamine,<sup>31</sup> and increases with a large excess of epoxy groups.<sup>32</sup>

NIR spectroscopy was chosen to monitor the reactions *in situ* because its ability to quantitatively follow the concentration changes of different functional groups in epoxy/amine systems is well documented.<sup>33,34</sup> The evolution in NIR spectra during FES3-JEFFAMINE ( $r = 4$ ) reaction at 100°C at various times is plotted in Figure 3(a). The trends displayed by the major peaks of relevance in epoxy/amine systems are evident: a progressive decrease in epoxy absorption ( $4538\text{ cm}^{-1}$ ) during reaction and a decrease in amine absorption ( $4940\text{ cm}^{-1}$ ), indicating



**Figure 3** (a) NIR spectra of a FES3-JEFFAMINE formulation with  $r = 4$ , during reaction at  $T = 100^\circ\text{C}$  at different reaction times. (b) Epoxy and primary amine conversions as a function of reaction time. The average error in the conversion value is  $\pm 0.05$ .

that the primary amine reacted with epoxy to be converted in a secondary amine. Another interesting peak is due to the hydroxyl combination band, which is found at  $4780\text{ cm}^{-1}$ . This band corresponds to the hydroxyl groups generated as product of the epoxy-amine reaction and confirms that condensation took place. Conversion [calculated with eq. (1)] versus time curves obtained for epoxy and primary amine groups are plotted in Figure 3(b). As can be seen, the epoxy group is completely reacted after  $\sim 120$  min. In addition, the primary amine conversion after 120 min is  $\sim 0.45$ , which is higher than the maximum theoretical value considering that there were used four amine equivalents per equivalent of epoxy. This is probably due to some evaporation of the diamine during curing, as the device where the sample is placed is not completely sealed.

Heat of reaction values of the second stage are shown in Table I. Experimental values are in close

agreement with other results reported in the literature survey.<sup>35,36</sup> The fact that reaction heats are constant for all formulations revealed that reaction heats are not influenced by the presence of FE. Though not shown, peak temperatures are constant indicating that the reaction rate of epoxy-amine polymerization is not influenced by the presence of FE, probably due to the low amounts of fluorinated monomer used. However, the introduction of modifiers into an epoxy system inevitably alters the cure mechanism. The understanding of what role the fluorinated tail and/or the hydroxyl groups generated during FE and JEFFAMINE reaction might play in interactions and/or exchange reactions with epoxy during cure is essential. It is necessary to consider two opposing effects with the incorporation of F-JEFFAMINE to network precursors. On one hand, epoxy-amine reaction implies the formation of a hydroxyl group. As long as more FE is incorporated into the system, the concentration of hydroxyl increases. It is well known that compounds containing OH groups can act as catalysts for epoxy-amine reaction.<sup>27,37</sup> On the other hand, it has to be considered the decrease in primary amine groups as more FE is incorporated into the system. It is well known that a diamine exhibits low reactivity of the secondary amine with respect to the primary one.<sup>36</sup>

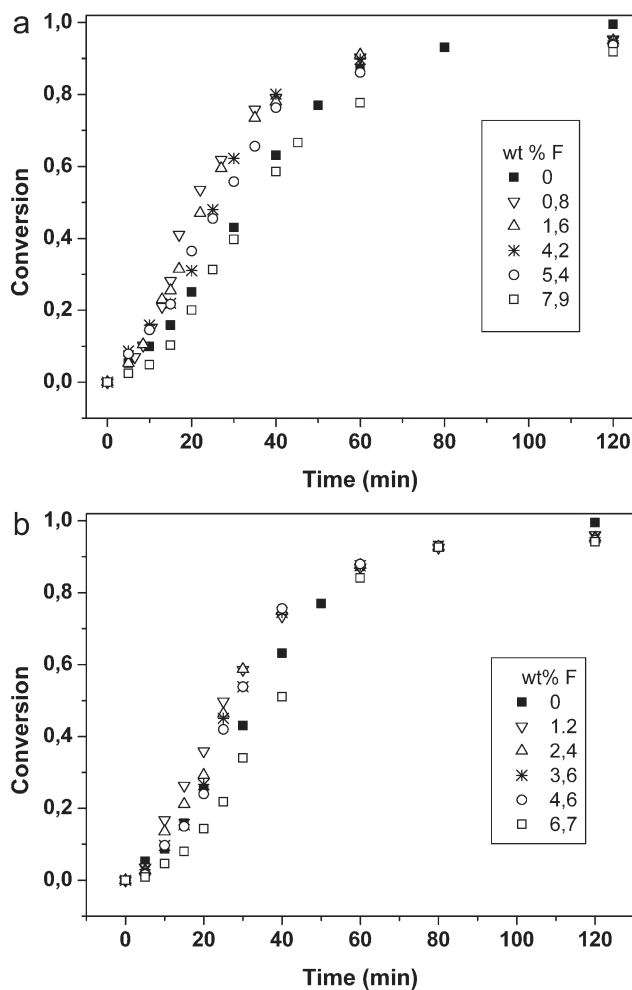
The experimental evolution of epoxy conversion (calculated with eq. (1) with time for JEFFAMINE-based system containing variable fluorine concentration is presented and compared with the neat system in Figure 4 for both FE. The results shown in this figure demonstrate that the reaction rate of the epoxy is clearly enhanced by the presence of F-JEFFAMINE for fluorine concentration up to 5–6 wt % for both FE. It seems that hydroxyl groups provided by the reaction between FE and JEFFAMINE easily catalyzed the epoxy-amine reactions. However, greater fluorine contents provoke a slower cure reaction rate. As expected, the decrease in primary amine concentration begins to be important.

All partially fluorinated networks synthesized were transparent, independent of fluorine content and cure conditions. No noticeable phase separation during the course of polymerization took place.

Another factor to be discussed is the influence of fluorinated tail on the ultimate glass transition temperature of the synthesized networks. The reaction

**TABLE I**  
Heats of Reaction ( $\Delta H$ ) of DGEBA-JEFFAMINE and FE-DGEBA-JEFFAMINE Systems

Epoxy system	wt % F	$\Delta H$ (kJ/eq)
DGEBA-JEFFAMINE (neat)	0	105
FES3-DGEBA-JEFFAMINE	3	107
FES3-DGEBA-JEFFAMINE	5	109



**Figure 4** The extent of reaction versus time at 100°C for neat and fluorinated networks containing variable fluorine content: (a) FED3-DGEBA-JEFFAMINE; (b) FES3-DGEBA-JEFFAMINE. The average error in the conversion value is  $\pm 0.05$ .

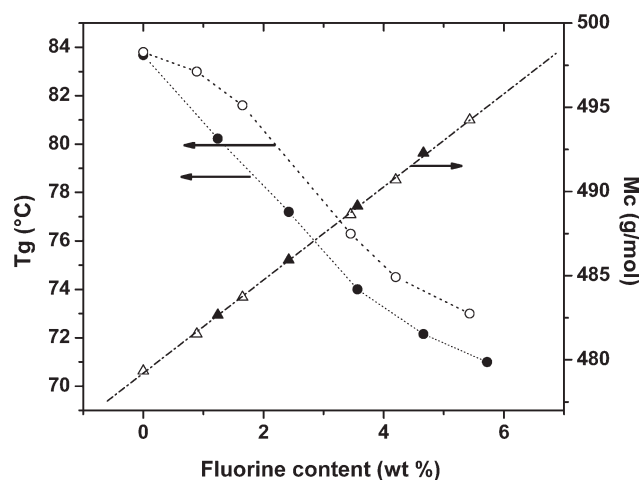
of FE with the diamine reduces the crosslink density, and consequently, it is expected to cause a decrease in the glass transition temperature. Figure 5 shows both the  $T_g$  and the molar mass between crosslinks,  $\overline{M}_c$ , dependence on fluorine concentration for both fluorinated network series. As seen in Figure 5, the reduction in  $T_g$  is linked to the increase in  $\overline{M}_c$ , which defines crosslink density.  $T_g$  values keep on decreasing as the amount of fluorine increases for all the systems analyzed.

#### MCDEA-based systems

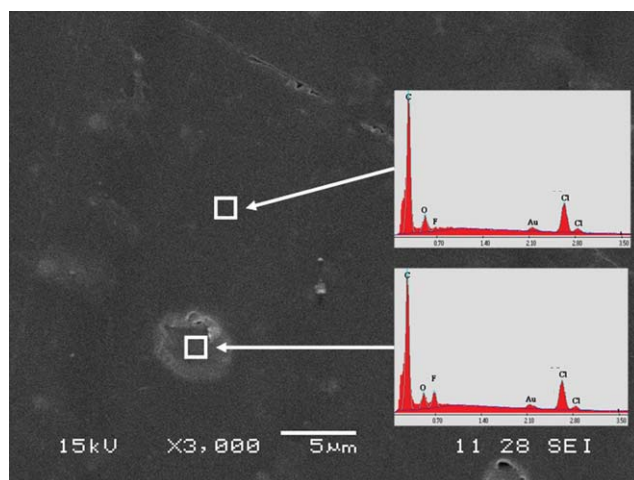
Concerning MCDEA curing agent, the temperature required to ensure the achievement of an initial homogeneous solution is very high (see Fig. 2), but the possibility of using high dissolution temperatures is possible as the diamine reactivity is low. Therefore, 180°C was chosen as the upper cure temperature

that enabled us to study the evolution during curing for samples initially miscible. As we discussed before, the maximum amount of fluorine in the mixtures was limited to 0.5 wt %. In blends containing this fluorine concentration or less, the advance in the epoxy-amine reaction produced the phase separation of a fluorine-rich phase dispersed in the epoxy-rich matrix. All formulations initially miscible were opaque after curing, independent of fluorine content and cure conditions. Morphological analysis was performed on MCDEA-cured samples containing various fluorine contents and cured at different temperatures. The main factors determining the morphologies generated were the initial miscibility of the components and the initial fluorine concentration.

It was found that blends initially homogeneous, phase separate during polymerization leading to two-phase morphology consisting in a random distribution of approximately spherical zones dispersed in the epoxy-rich phase. Figure 6 shows the domain structures observed by SEM of a sample fractured at room temperature containing 0.5 wt % F and cured at 180°C. X-ray microanalysis can be a useful tool for the determination of the actual elemental composition of the different zones present in the final morphologies obtained. Also shown in Figure 6 is x-ray microanalysis results corresponding to the different zones marked with a square on the SEM micrograph. The spectrum corresponding to the bright domains shows significant amount of fluorine, confirming that it is the fluorine-rich phase. However, the composition of the matrix, which appears dark, reveals a weak signal corresponding to fluorine element. Both zones analyzed show important chloride signal arising from MCDEA.



**Figure 5** Glass transition temperature,  $T_g$ , and molecular weight between crosslinks,  $\overline{M}_c$ , of FED3-DGEBA-JEFFAMINE (unfilled symbols) and FES3-DGEBA-JEFFAMINE (filled symbols) fluorinated epoxy networks.

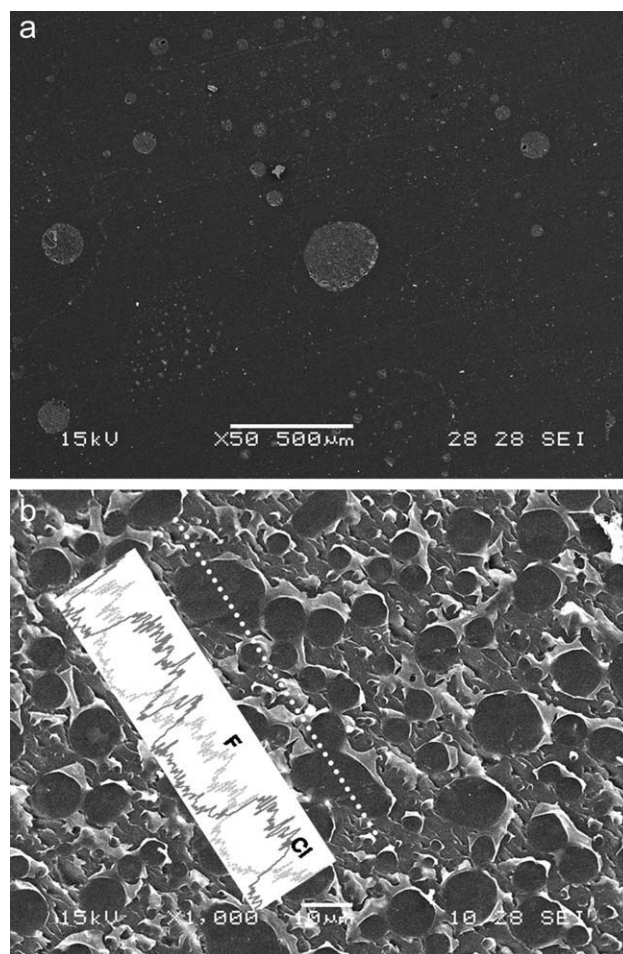


**Figure 6** SEM micrograph performed on MCDEA-cured sample initially miscible containing 0.5 wt % F cured at 180°C. Results of x-ray analysis (fluorine and chloride) obtained in different locations (marked with a square) of the SEM micrograph are also shown. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

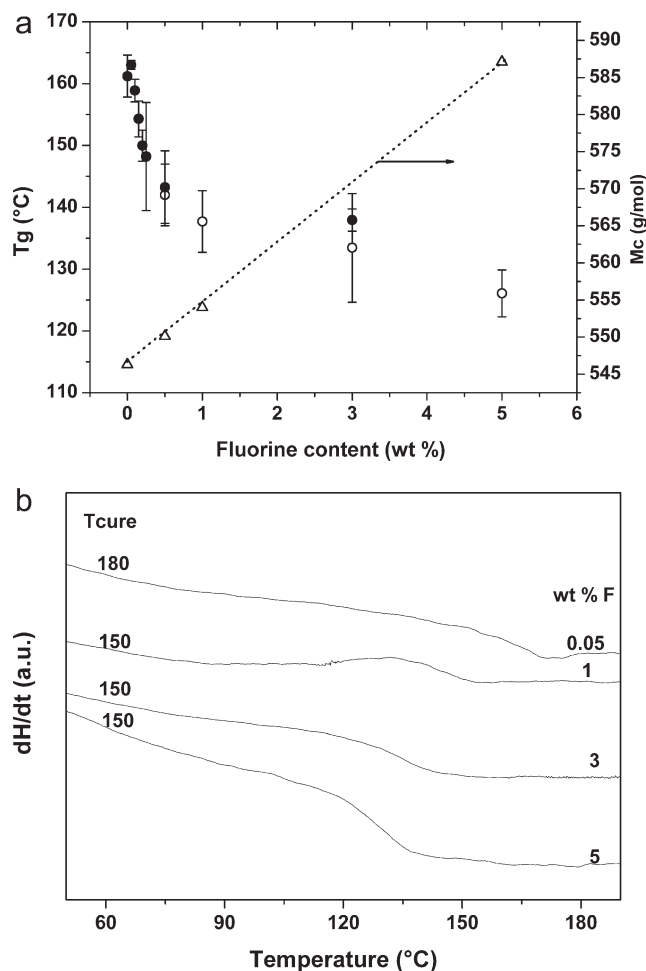
When curing samples located inside the immiscibility window, the system is initially nonhomogeneous. In this case, the reaction is carried out in different phases with unknown epoxy-amine concentration in each phase. Initial heterogeneous blends consisting on two immiscible phases suffer additional phase separation during the cure reaction, generating complex double phase morphology. Final morphologies consist on a dispersion of large and irregular fluorine-rich domains in an epoxy-rich matrix. Figure 7(a) shows fluorine-rich domains present in an initially heterogeneous sample containing 3 wt % F cured at 180°C. Moreover, using a higher amplification, the presence of double phase morphology is evident. From x-ray data, qualitative analysis was done through the white line marked on the micrograph, as shown in Figure 7(b). The spectra obtained at different locations of the SEM micrograph showed two different phases inside the initially fluorine-rich domain. One of them possesses chlorine coming from MCDEA and the other exhibits a fluorine signal proceeding from the incorporated partially fluorinated amine (F-JEFFAMINE). From these results, it can be inferred that the originally dissolved epoxy-MCDEA species in the fluorine-rich phase had been segregated as particles of variable size and were surrounded by a continuous fluorine-rich thread.

Figure 8(a) shows the influence of cure temperature and fluorine content on the ultimate glass transition temperature of the synthesized networks. Typical DSC thermograms are shown in Figure 8(b). As we have mentioned, the incorporation of F-JEFFAMINE reduces the crosslink density, and consequently, it is expected to cause a decrease in the

glass transition temperature. Figure 8(a) also shows the molar mass between crosslinks,  $\overline{M}_c$ , dependence on fluorine concentration for this fluorinated network series. The marked decrease in  $T_g$  values is probably related to other effect than the reduction of the crosslink density. The cure temperature affects the solubility of the mixture, the mass transfer process and the extent of phase separation by fixing the viscosity at the cloud point. For fluorine content higher than 0.5 wt %, the mixtures are initially immiscible, and the reaction is carried out in different phases with unknown epoxy-amine concentration in each phase. The lower the curing temperature and/or the higher the fluorine total concentration is, the more immiscible the system is. Under these circumstances the stoichiometric ratio moves away the initial ratio of epoxy to amino-hydrogen groups equal to 1, and as a result,  $T_g$  values keep on decreasing as cure temperature is decreased and/or the total



**Figure 7** Morphological analysis on MCDEA-cured sample initially immiscible containing 3 wt % F cured at 180°C: (a) SEM micrograph; (b) Higher amplification of (a) showing the double phase morphology of the fluorine-rich domain. Results of x-ray analysis (fluorine and chloride) obtained in different locations of the SEM micrograph marked with the white line.



**Figure 8** FES3-DGEBA-MCDEA fluorinated epoxy networks: (a) Glass transition temperature,  $T_g$ , and molecular weight between crosslinks,  $\bar{M}_c$ , of samples cured at: 150°C (unfilled circles) and 180°C (filled circles), as a function of fluorine concentration. (b) Typical DSC curves.

fluorine content is increased. The resulting  $T_g$  results are characterized by a high dispersion of data. This was expected from the different morphologies that could be obtained. An interesting observation is the fact that fully cured epoxy blends exhibit one  $T_g$  value, independently of fluorine content in the samples [see Fig. 8(b)].

## CONCLUSIONS

In this study we have synthesized and characterized two series of partially fluorinated crosslinked epoxy-based polymers, each with distinct differences in the molecular structure of the unit building blocks. The fluorine migration and/or reaction-induced phase separation taking place in a reactive epoxy solvent containing a perfluorinated tail attached to a diamine was analyzed. The morphology and composition of partially fluorinated networks was investigated on a

micrometer scale combining scanning electron microscopy and x-ray analysis. JEFFAMINE-cured samples were homogeneous for all fluorine proportions. In contrast, MCDEA-cured blends showed fluorine-rich zones dispersed in a continuous epoxy-rich phase. A completely different morphology, characterized by a distribution of irregular fluorine-rich domains dispersed in an epoxy-rich phase, was obtained when curing blends initially immiscible.

## References

- Chan, C. M. *Polymer Surface Modification and Characterization*, 1st ed.; Hanser: New York, 1994; Chapter 1.
- Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surface: From Physics to Technology*, 1st ed.; Wiley: New York, 1994; Chapter 1.
- Bergbreiter, D. E. *Prog Polym Sci* 1994, 19, 529.
- Hu, Z.; Finlay, J. A.; Chen, L.; Betts, D. E.; Hillmyer, M. A.; Callow, M. E.; Callow, J. A.; DeSimone, J. M. *Macromolecules* 2009, 42, 6999.
- Hu, Z.; Chen, L.; Betts, D. E.; Pandya, A.; Hillmyer, M. A.; DeSimone, J. M. *J Am Chem Soc* 2008, 130, 14244.
- Lee, H.; Archer, L. A. *Macromolecules* 2001, 34, 4572.
- Lee, H.; Archer, L. A. *Polymer* 2002, 43, 2721.
- Pan, D. H., Jr.; Prest, J. *Appl Phys* 1985, 58, 2861.
- Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. *Macromolecules* 1988, 21, 2166.
- Thomas, R. H.; O'Malley, J. J. *Macromolecules* 1979, 12, 323.
- Schmidt, J. J.; Gardella, J. A., Jr.; Salvati, L. *Macromolecules* 1989, 22, 4489.
- Mori, H.; Hirao, A.; Nakahama, S.; Senshu, K. *Macromolecules* 1994, 27, 4093.
- Robinson, K. L.; Paz-Bàñez, M. V.; Wang, X. S.; Armes, S. P. *Macromolecules* 2001, 34, 5799.
- Jannasch, P. *Macromolecules* 1998, 31, 1341.
- Bérengrère, R.; Romani, S.; Bernard, B.; Patrick, L. D. *Polymer* 2005, 46, 3579.
- Walters, K. B.; Schwark, D. W.; Hirt, D. E. *Langmuir* 2003, 19, 5851.
- Galante, M. J.; Borrajo, J.; Williams, R. J. J.; Girard-Reydet, E.; Pascault, J. P. *Macromolecules* 2001, 34, 2686.
- Oyanguren, P. A.; Riccardi, C. C.; Williams, R. J. J.; Mondragón, I. J. *Polym Sci B Polym Phys* 1998, 36, 1349.
- Girard-Reydet, E.; Sévignon, A.; Pascault, J. P.; Hoppe, C. E.; Galante, M. J.; Oyanguren, P. A.; Williams, R. J. J. *Macromol Chem Phys* 2002, 203, 947.
- Giannotti, M. I.; Foresti, M. L.; Mondragón, I.; Galante, M. J.; Oyanguren, P. A. *J Polym Sci B Polym Phys* 2004, 42, 3953.
- Miccio, L. A.; Fasce, D.; Schreiner, W.; Montemartini, P. M.; Oyanguren, P. A. *Eur Polym Mater* 2010, 46, 744.
- Miccio, L. A.; Liaño, R.; Schreiner, W. H.; Montemartini, P. E.; Oyanguren, P. A. *Polymer* 2010, 51, 6219.
- Fedtko, M. *Makromol Chem Macromol Symp* 1987, 7, 153.
- Liu, H.; Uhlherr, A.; Varley, R.; Bannister, M. *J Polym Sci Part A: Polym Chem* 2004, 42, 3143.
- Poisson, N.; Lachenal, G.; Sautereau, H. *Vib Spectrosc* 1996, 12, 237.
- Crawford, E. D.; Lesser, A. J. *J Polym Sci Part B: Polym Phys* 1998, 36, 1371.
- Mijovic, J.; Fishbain, A.; Wijaya, J. *Macromolecules* 1992, 25, 979.
- George, G. A.; Cole-Clarke, P.; St. John, N.; Friend, G. *J Appl Polym Sci* 1991, 42, 643.



29. Byrne, C. A.; Hagnauer, G. L.; Schneider, N. S. *Polymer* 1983, 4, 206.
30. Riccardi, C. C.; Williams, R. J. J. *J Appl Polym Sci* 1986, 32, 3445.
31. Dusek, K. *Polym Mater Sci Eng* 1983, 49, 378.
32. Dusek, K.; Bleha, M.; Lunak, S. *J Polym Sci Polym Chem Ed* 1977, 15, 2393.
33. St John, N.; George, G. *Polymer* 1992, 33, 2679.
34. Fernández, R.; Blanco, M.; Galante, M. J.; Oyanguren, P. A.; Mondragon, I. *J Appl Polym Sci* 2009, 112, 2999.
35. Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. J. *J Polym Sci* 1984, 29, 2481.
36. Rozenberg, B. A. *Adv Polym Sci* 1985, 75, 113.
37. Cole-Clarke, P.; St. John, N.; Friend, G. *J Appl Polym Sci* 1991, 42, 643.