



Journal of Polymer Science Part B

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Journal:	<i>Journal of Polymer Science Part B: Polymer Physics</i>
Manuscript ID:	draft
Wiley - Manuscript type:	Original Article
Date Submitted by the Author:	n/a
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Keywords:	fluoropolymers, modification, thermosets



**Synthesis and Characterization of an Epoxy Based Thermoset Containing a
Fluorinated Thermoplastic**

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Abstract

A novel fluorinated thermoplastic (FT) was synthesized from diglycidyl ether of bisphenol A (DGEBA) and 3-(trifluoromethyl)aniline. FT was found to be miscible with DGEBA as shown by the existence of a single glass transition temperature (T_g) within the whole composition range. On the basis of several experimental techniques, it was found that etherification reaction takes place between FT and DGEBA upon heating. A DGEBA-aromatic diamine (4,4'-methylenebis(3-chloro 2,6-diethylaniline) formulation was modified with the FT. The influence of FT on the epoxy-amine kinetics was investigated. Both structural parameters, gelation and vitrification, were found to be affected by etherification reaction between epoxy and hydroxyls groups belonging to FT. The presence of ether linkages induced modification of the stoichiometry of the system. In addition, the curing conditions influence on FT migration towards the surface was studied on samples prepared with 20 wt % of modifier. SEM–EDX analysis confirmed that the surface of the modified systems exhibits notable fluorine enrichment within the uppermost 200 μm .

Keywords: Fluoropolymer; Modification; Thermoset

INTRODUCTION

Curing of epoxy resins is one of the most common procedures in synthesis of thermosetting materials. Due to their excellent mechanical and thermal properties, epoxy networks are used in a wide range of applications covering composite materials, adhesives, coatings, materials for encapsulation, etc.

The incorporation of fluorine into polymers has been extensively explored because of the unique characteristics of fluorine substitution. The carbon-fluorine bond is one of the strongest organic bonds. The introduction of trifluoromethyl (CF_3) groups into polymers improves chemical resistance, surface, electrical, mechanical, and optical properties of the polymers compared to the non fluorinated materials.^{1,2} From a molecular level perspective, a uniformly organized array of CF_3 groups would be a surface with the lowest surface tension.³ Completely fluorinating a polymer produces a low surface energy, of course, but gives little latitude in tailoring other desired properties such a glass transition temperature, processability, the absence of porosity, and low cost. Low surface energy is preferably attained by deploying a small number of fluorinated groups on the surface where they will be most effective. It has been shown that small amounts (0.2-1.0 %) of fluorocarbon additives significantly reduce the surface energy of the hydrocarbon polymer.⁴ However, the utility of these additives is limited by the incompatibility of fluorocarbons with hydrocarbons. To circumvent some of these problems, we became interested in the synthesis of a conventional epoxy-amine polymer containing fluorinated groups. Our initial efforts are focused on the use of this fluorinated polymer as modifier of an epoxy based thermoset.

In the present article a convenient way of synthesizing a thermally stable thermoplastic polymer containing CF_3 groups is reported. The fluorinated thermoplastic (FT) was synthesized with a slight excess of epoxy groups with the idea of promoting

chemical bonds with the growing epoxy-amine copolymer. We investigated the transformations that take place in FT-modified materials such as vitrification, gelation, phase separation, and reaction kinetics. Then, FT was evaluated as a potential surface modifier. FT-modified materials having low fluorine content (less than 2 wt %) were investigated by SEM–EDX analysis. In addition, the effect of cure conditions on FT migration has been discussed.

EXPERIMENTAL

Materials

A diglycidyl ether of bisphenol A (DGEBA) epoxy resin (DER 331, Dow, $M_n = 356.84$ g/mol) and 3-(trifluoromethyl) aniline (TFA, Aldrich) were used to synthesize a fluorinated thermoplastic polymer (FT). FT was employed as modifier of epoxy-amine formulations based on the same DGEBA resin and an aromatic amine curing agent 4,4'-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA, Lonza).

Sample Preparation

Binary blends DGEBA-FT with different compositions were prepared by dissolving the components at 150 °C during 30 min to allow a good mixing.

Modified epoxy resins containing 0-50 wt % FT were prepared as follows. DGEBA and the required FT amount were dissolved at 150 °C for 30 min. A stoichiometric amount of MCDEA was then added during the cooling stage, at about 90 °C.

Equipment and Characterizations

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 cure reactions were conducted at different curing rates: 0.5, 2, and 10 °C/min. Measurements of T_g were conducted at a heating rate of 10 °C/min. The transition was taken as the temperature corresponding to the onset of heat capacity base-line change. The increase in T_g as a function of reaction time, was determined at the following curing temperatures: 150, 170 and 200 °C for neat formulations; and 150 and 200 °C for 20 wt % FT-modified blends. Samples were cured inside the DSC cell isothermally for prespecified times, which were expressed as the corresponding conversion values using the polymerisation kinetics determined by near-infrared spectroscopy.

Fourier transform infrared spectroscopy was performed using a Genesis II Matson spectrometer, provided with a heated transmission cell (HT-32, Spectra Tech) and a programmable temperature controller (Omega, Spectra Tech, $\Delta T = \pm 1$ °C). Near-infrared spectroscopy (NIR), 7000-4000 cm^{-1} , was used to determine the polymerisation kinetics. All spectra were collected at 8 cm^{-1} resolution with a scanning rate of 4 cm/s and 24 scans per slice. The sample was placed between two glasses using a 1 mm rubber spacer. The reaction was carried out at a series of selected temperatures in the range between 150 and 200°C. The extent of reaction (x) at any time t is calculated from the initial heights of epoxy and reference peaks, $H_{e,0}$ and $H_{r,0}$, respectively, and their corresponding values at time t , $H_{e,t}$ and $H_{r,t}$, according to the following equation:

$$x = 1 - (H_{e,t} / H_{r,t}) / (H_{e,0} / H_{r,0}) \quad (1)$$

The peak at 4530 cm^{-1} (assigned to the conjugated epoxy CH_2 deformation band with the aromatic CH fundamental stretch)⁵ was used to monitor the disappearance of the epoxy group, and primary amine combination band at 4940 cm^{-1} ,⁶ both normalized

to the reference band at 5056 cm^{-1} (assigned as a phenyl combination band).⁷ The mid-infrared (MIR) spectroscopic details were recorded in the $400\text{-}4000\text{ cm}^{-1}$ range. The windows for the transmission cell were NaCl disks.

Molar mass distributions were determined by size exclusion chromatography (SEC, Knauer K-501, RI detector Knauer K-2301), and the following set of Phenogel 5 μ -columns: 50 Å, 100 Å, and M2. Tetrahydrofuran (THF) was used as a carrier at 1 ml/min. Molecular weights refer to a polystyrene calibration using polystyrene standards.

Gelation times were measured by curing samples at 150 and 200 °C, for prespecified times, and determining the solubility in THF. Gelation was ascribed to the incipient formation of an insoluble fraction. Gel times were expressed as the corresponding conversion values, x_{gel} , using the polymerization kinetics determined by NIR measurements.

FT modified DGEBA-MCDEA samples were cured at 150 and 200 °C at different times, and subsequently extracted with THF for 24 h. The sol fraction was then analysed by SEC.

The indices of refraction of neat epoxy network after complete cure and FT were measured with an Abbe's refractometer (Atago 1T), following the standard method for index of refraction of transparent organic plastics (ASTM D542-90).

Plaques of 2 mm thickness for neat and FT-modified systems were prepared using a glass mould coated with released paper. Alternatively, a 20 wt % FT modified sample was cured inside a mould consisting of two glass plates spaced by a rubber cord of 1.5 mm diameter. Cure was carried out in an oven at 200 °C for 2 h, and at 150 °C for 4 h. The later was post-cured by a stepwise increase of the temperature up to 200 °C for 1 h. Plaques were fractured at room temperature. The cross sections obtained were

mounted on graphite stubs and coated with a thin layer of Au in a sputter coater (Pelco 91000). Samples were observed and analyzed using a JEOL 35 CF scanning electron microscope (SEM) coupled with EDAX DX-4 energy dispersive X-ray system (EDX) with ultra thin window. The last technique was used to detect fluorine content in fractured surfaces. The microscope was operated at 15 kV accelerating voltage. EDX system was calibrated at this kV value. Quantitative EDX analysis was performed by the standardless procedure. SEM-EDX analyses were carried out in several microareas selected along the air-polymer interface and the cross section of the samples to obtain representative results. The same operational conditions were used in order to compare the elemental concentration measurements.

RESULTS AND DISCUSSION

Synthesis of the Fluorinated Polymer

A fluorinated linear polymer was synthesized from DGEBA and 3-(trifluoromethyl)aniline (TFA, Aldrich) at a stoichiometric ratio, $r = 1.23$, where r is defined as epoxy groups / amine groups. Monomers were mixed at room temperature and reaction was performed inside closed tubes, in order to avoid TFA loss through volatilisation from the reaction mixture, in an oven at 150 °C for 4h.

The final product was characterized by FTIR, DSC and SEC. The number-average molecular weight of the FT, determined by SEC, was 2,600 g/mol. The glass transition temperature, obtained from DSC measurements was 74.7 °C. The chain structure of the polymers was confirmed by FTIR. The MIR spectrum showed characteristic absorptions for the CF_3 group at around $1321 \pm 9 \text{ cm}^{-1}$ and $1179 \pm 7 \text{ cm}^{-1}$, together with some strong absorption bands in the region 1100-1300 cm^{-1} for the C-O and C-F stretching vibration.

Binary Blends

The epoxy resin and FT repeat unit possess structural similarities. In addition, some epoxy chains of DGEBA contain pendent hydroxyl groups capable of interacting with the FT through hydrogen bonding. Moreover, in certain conditions hydroxyl groups can react with epoxy groups by an etherification mechanism. Both structural similarities, physical and chemical interactions play an important role in DGEBA-FT miscibility and fluorinated species freedom of movement. In order to analyze DGEBA-FT binary blends behaviour, samples containing up to 50 wt % FT were studied before and after being treated at 150 and 200 °C for various lengths of time.

IR spectroscopy is a powerful technique to detect any interaction between DGEBA and FT. The full MIR spectra of binary blends before and after thermal treatment do not show any shift or modification of the epoxy (915 cm^{-1}) and CF_3 (1321 cm^{-1} and 1179 cm^{-1}) peaks. Unfortunately, the characteristic band of ether bond (1120 cm^{-1}) is overlapped with those ones belonging FT. The most noticeable changes are associated with the broad hydroxyl stretching frequency region of $3000\text{--}4000\text{ cm}^{-1}$. It was shown that this region is the most sensitive to hydrogen bonding interaction.⁸ Figure 1 shows MIR spectra of pure epoxy resin, FT, and few compositions of DGEBA-FT blends in the region $3000\text{--}4000\text{ cm}^{-1}$. The OH band appeared at 3360 cm^{-1} and at 3506 cm^{-1} for FT and pure epoxy, respectively. These results can be explained in terms of specific interactions between the hydroxyl groups present in FT. Apparently, the presence of inter- and intramolecular hydrogen bonding markedly affects the OH absorption in the fluorinated thermoplastic. The frequency difference between both pure components is a measure of the average strength of inter- and intramolecular interaction. This would imply that the self association of hydroxyl groups is

considerably stronger in FT than pure epoxy resin. Upon blending, the following changes occur: the OH band is shifted to the low frequency side to 3445 cm^{-1} for 80 wt % epoxy resin, and to 3377 cm^{-1} for 50 wt % epoxy resin in the blends. Consequently, as the concentration of epoxy resin is reduced in the blends the OH band further shifts to the lower frequency side, indicating stronger hydrogen bonding. After heat treatment at $200\text{ }^{\circ}\text{C}$, the DGEBA-FT blends spectra showed that the OH band remains constant in frequency, broadness and relative area. It seems that the strength of the intermolecular interaction between the hydroxyl groups presented in FT and epoxy resin is not affected by thermal treatments.

Changes in NIR spectra of a binary blend with 50 wt % FT when heating to $200\text{ }^{\circ}\text{C}$ were analysed. It was observed that the epoxy peak (4530 cm^{-1}) exhibited a slightly diminishing as the time was increased, indicating that an epoxy-consuming reaction took place. The extent of such reaction, however, was not great. Approximately, the 10 % epoxy groups disappeared during reaction at $200\text{ }^{\circ}\text{C}$ for 2h.

The glass transition temperatures of unreactive DGEBA-FT blends with various FT concentrations have been measured by DSC. The visual transparency and the single T_g on the whole composition range of the samples suggest complete miscibility of the fluorinated polymer with the epoxy resin. Figure 2 shows the measured glass transition temperature versus weight fraction of FT (white circles). The dashed curve representing the variation of the glass transition temperature with composition was plotted using the Gordon-Taylor equation:⁹

$$T_g = (\omega_{\text{DGEBA}} T_{g\text{DGEBA}} + k \omega_{\text{FT}} T_{g\text{FT}}) / (\omega_{\text{DGEBA}} + k \omega_{\text{FT}}) \quad (2)$$

where ω represents the mass fraction of the particular component and the adjustable parameter k is 0.5.

After adding the diamine, the system at $t=0$ (no reaction) turns into a quasi-ternary mixture. The T_g of initial systems, DGEBA-MCDEA-FT are compared to the binary system DGEBA-FT on the same Figure 2 (black circles). As can be seen, the addition of the diamine actually does not modify the miscibility of the reactive system. A single T_g that increases with FT concentration was observed for all the samples.

Binary blends were subjected to heating at 200 °C for 2h and DSC characterization was then performed on these blends to determine their glass transition behaviour. Figure 2 shows a comparison of the T_g values of the as-prepared (white circles) and heated (asterisks) blends as a function of composition. After heat treatment at 200 °C, the blends still exhibited a single T_g , suggesting a single-phase behaviour of the blends. However, the T_g values of the thermally treated blends increased when compared to the as-prepared (unheated) blends of the same composition. The magnitude of the increment depends on the TF concentration (see Fig. 2). It should be pointed out that when heating was conducted at 150 °C the time required to obtain the same T_g values was approximately double the required at 200 °C, i.e. 4h. On the other hand, for the same blend heated for longer times at a given temperature, higher T_g values were obtained.

Tests of solvent resistance were performed on the reacted blends to assess possible effects of heating on network formation. All blend compositions were readily dissolved in THF, indicating that no network structure was formed between the two components.

On the basis of DSC and FTIR results, we can conclude that: i) DGEBA-FT blends exhibit complete miscibility, and ii) etherification reaction between FT and DGEBA occurs upon heating. However, the solubility behaviour of the system indicates that the extent of the formed chemical links is not significant.

Influence of FT on Reaction Kinetics and Structural Parameters

The chemical reactions that take place during the reaction of an epoxy resin are well known and have been extensively studied.^{10,11} 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. The last possibility, namely homopolymerization requires the presence of a Lewis base (or acid) type catalyst¹² and can be neglected in its absence. The relevance of the etherification reaction with respect to the two amine reactions depends on the nature of the diamines. For aromatic diamines the low reactivity of the secondary amine with respect to the primary one, and the higher temperatures needed to produce curing, are the principal reasons to consider the occurrence of this reaction.¹³

On the other hand, the introduction of modifiers into an epoxy system inevitably alters the cure mechanism. The understanding of what role the hydroxyl groups in the FT chains might play in interactions and/or exchange reactions with epoxy during cure is essential. As we analysed in the previous section, etherification reaction between FT and DGEBA occurs upon the experimental cure conditions employed.

Neat system and FT-modified materials heat of reaction values are shown in Table 1. In order to analyze the presence of kinetic limitations, DSC scans at different heating rates were carried out for the neat formulation. Topological restrictions are evident, possibly derived from the slower reaction rate of the secondary amine compared to the primary one. Neat formulations heats of reaction for the slowest scanning rate are in accordance with theoretical values of (i.e., 105 ± 5 kJ/eq). Therefore, a heating rate of 0.5 °C/min was selected to cure modified samples. The characteristic revealed in these blends is that the reaction heats are influenced by the

presence of FT, with the value increasing with the FT content in the epoxy blends. The contribution of the etherification reaction heat increases significantly with increase in the FT content. In addition, the higher the FT content the greater the decrease of peak temperatures, indicating that the reaction rate of epoxy-amine polymerization is enhanced by the presence of FT.

NIR 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.¹⁴ The assignment of different bands used for quantitative analysis is listed in Table 2. We proceed to monitor the changes in NIR spectra during the reaction of neat DGEBA-MCDEA systems and its blends with 20 wt % FT cured at different isothermal temperatures. The trends displayed by major peaks of relevance in epoxy-amine reactions were evident in both systems spectra: a decrease in epoxy absorption (4530 and 6080 cm^{-1}); a decrease in amine absorption (5056 and 6670 cm^{-1}); an increase in hydroxyl absorption (7000 cm^{-1}). No differences were found between the neat system and its blend NIR spectra. This was expected due to chain structure of the FT as well as the monomers and reaction products are similar.

The experimental evolution of epoxy conversion (calculated with equation 1) with time for modified systems is presented and compared to the neat system in Figure 3 at 150 (circles), 170 (triangles) and $200\text{ }^{\circ}\text{C}$ (squares). The figure also shows: i) the kinetics modelling of the neat system reported by Girard-Reydet et al.,¹⁵ considering the catalytic and noncatalytic mechanisms as well as etherification reactions between epoxy functions and hydroxyl groups¹⁶ taking into account the initial OH concentration in the epoxy resin (solid lines); and ii) the kinetics prediction for the modified system taking into account the initially present hydroxyl groups in the reaction medium as the sum of the ones present in the epoxy resin and the those provided by the FT (dashed lines). It

was also considered the dilution effect induced by the presence of the modifier. The results shown in this figure demonstrate that the reaction rate of the epoxy is clearly enhanced by the presence of FT. This behavior is consistent with the calorimetric results analyzed before (see Table 1). In other words, hydroxyl groups provided by the modifier easily catalysed the DGEBA-MCDEA reactions. However, the extent of this catalytic effect depends on the cure temperature. Model prediction is excellent for 170 and 200°C, but underestimates FT-modified experimental conversions at 150 °C (see Fig. 3).

In light of the mass balance of the system, the ether linkage concentration (EL) can be calculated as a function of epoxy conversion.⁶ Figure 4 shows the dimensionless ether linkage concentration, DEL, defined as $DEL = EL / EP_0$ where EP_0 is the initial concentration of epoxides, at different cure temperatures and FT contents. As can be seen, the calculated etherification reaction resulted higher for the 20 wt % FT blend cured at 150 °C when comparing with other cure temperatures and blend compositions. The fact that the degree of the etherification reaction is greater for FT-modified blends is understandable on account of the high hydroxyl concentration during cure. In return, it is surprising that the ether linkages formation is more significant when curing at 150 °C compared to 170 and/or 200 °C. This behaviour is probably related with a different temperature dependence of the rate constants for secondary amine-epoxy and hydroxyl-epoxy, reported to be approximately equal.¹⁷ As long as etherification takes place, the epoxy-amine stoichiometry changes, resulting in MCDEA-rich formulations ($r < 1$). If this is the case, it is expected a faster curing rate. There is a plenty of experimental evidence indicating that the epoxy-amine reaction rate increases with increasing in amine component.^{18,19} A possible explanation for the rate enhancement for blends modified with 20 wt % FT and cured at 150 °C is that the ether linkages formation

produces an excess of diamine, which exhibits a well known catalytic action over the epoxy-amine reaction rate.

Table 3 lists experimental values of gel conversion, x_{gel} , for the neat and modified systems. As the network structure is a unique function of conversion, x_{gel} for the neat system may be considered constant and independent of temperature. The modified samples exhibit higher x_{gel} which tend to increase when cure temperature decreases. This evolution of x_{gel} is consistent with the modification of the epoxy-amine stoichiometry induced by the etherification reaction. Blends containing DGEBA, MCDEA and 20 wt % FT were cured at 150 °C and 200 °C. SEC analysis of the soluble products was carried out on these blends at different reaction times before and after gelation. Figure 5 displays partial SEC chromatograms showing FT species distribution (Fig. 5a) and reaction products peaks at different reaction extents (Fig. 5b-d). Before gelation, some elution times of reaction products are superimposed with those corresponding to FT. It is not possible to assure the existence of grafting of epoxy-amine species on FT units (see Fig. 5b). However, the resulting chromatogram after gelation of the species belonging to the sol fraction gives interesting information. Part of the high weight molecular fraction of the FT does not appear in the chromatogram, Fig. 5d, confirming that these species are forming part of the gel when curing at 150 °C. However, the situation is different for the sample cured at 200 °C. As it is evident in Fig. 5c, practically all FT species belong to the sol fraction. These findings are consistent with the kinetics results analysed before.

Returning to the kinetics curves previously analysed (Fig. 3), no sudden change of reaction rates is observed at any time. It is then difficult to assure if phase separation of FT species is taking place or not during curing reaction. Results reported concerning the behaviour of the system after phase separation are completely variable. For example,

Girard-Reydet et al. had reported a decrease in the reaction rate when PEI is used as modifier of DGEBA-MCDEA formulation or no sudden change of reaction rate when DDS is used as curing agent.²⁰ However, other authors have reported an acceleration of the kinetics curve for thermoplastic modified epoxies containing a relatively high fraction of modifier in the initial mixture.^{21,22}

The relationship between the extent of reaction and the glass transition temperature for the neat system, T_g , has been analyzed elsewhere.¹⁵ The DSC results showed clearly that the fully cured epoxy blends exhibit one T_g value, independently of the FT content in the samples. The experimental evolution with conversion for 20 wt % FT cured at 150 and 200 °C is presented in Figure 6. The figure also shows the Fox prediction regarding the blend as a solution of the FT in the growing thermosetting copolymer. The T_g of the thermosetting copolymer at any conversion was calculated with DiBenedetto equation,²³ with the following parameters: T_g of the unreacted monomers ($x = 0$), $T_{g0} = -14$ °C; T_g of the fully cured network ($x \rightarrow 1$), $T_{g\infty} = 155.5$ °C; and the adjustable parameter, $\lambda = 0.7$. The excellent correlation observed for the experimental points with the Fox prediction supports the miscibility of blends and that the network structure is determined exclusively by the conversion level. Therefore, the T_g of the reactive system can be predicted considering it as a solution during the course of polymerization.

Figure 7 shows the ultimate T_g of FT-blends cured under different experimental conditions, as a function of FT content. This figure also shows the Fox prediction for the T_g of the system for comparison purpose. The T_g dependence on composition exhibits a constant decrease with FT content, independently of cure conditions. This trend could be the sum of, at least, two effects. On the one hand, the FT acts as a plasticizer independently if it is linked or not by chemical bonds to the epoxy-amine

network. The occurrence of etherification reaction reduces the crosslink density while the presence of dissolved FT acts as a miscible diluent. Both effects are expected to cause a decrease in the glass transition temperature. On the other hand, the etherification phenomenon between epoxy groups and FT resulted in MCDEA being present in excess of the original formulation ($r = 1$), thus causing a lower ultimate T_g ($r < 1$).

FT Migration

The phenomenon of migration of fluorinated species was studied by SEM-EDX. It is well known that the low surface free energy of the component provides a thermodynamic driving force for migration to the air-polymer interface.²⁴ In the fluorinated modifier studied herein, the CF_3 groups present in the FT would be the responsible of bringing the driving force for migration. Moreover, FT has a rather low molecular weight, epoxy terminal functionalities, and OH groups capable of react with thermoset components via etherification. Low molecular weight facilitates its diffusion within the matrix. Indeed, covalent bonds between the FT and the matrix leads to compatibility and, consequently, FT would not migrate.

In order to analyse FT components migration, samples containing 20 wt % FT (1.9 wt % F) were cured: i) in different moulds, using the same curing schedule, and ii) at different cure temperature in open moulds. Figure 8 compares the cross section morphologies when curing in the presence or absence of a free surface. The sample cured in an open mould, Figure 8a-b, has an anisotropic structure: an approximately 200 μm layer located near the polymer-air interface is observed all along the plaque (see Fig. 8b). In contrast, the sample prepared without any free surface, i.e. cured in a closed mould between two glass plates, shows a homogeneous structure (see Fig. 8c).

The fluorine atomic concentration along the cross section of the sample is expressed in terms of the atomic concentration ratio of F in the 20 wt % FT-modified sample, F_{20FT} , to F in neat FT, F_{neatFT} . The EDX results for the F_{20FT} / F_{neatFT} ratio, which provides a measure of the FT variation, can be appreciated in Figure 9. There are two sets of data that illustrate the F_{20FT} / F_{neatFT} ratio evolution with the distance from the air-polymer interface to the polymer-mould interface when curing in an open mould, or from both mould walls for the sample cured in a closed mould. The first set (asterisks and white circles) reports results for samples cured at different isothermal temperatures under experimental conditions that favour fluorinated component migration, i.e. in the presence of air. It is evident from Figure 9 that FT concentration on the layer is much higher than in the bulk (more than 50 %), which shows an approximately constant value. Inside the layer, a high FT enrichment on the air-polymer interface is observed. The obtained results are practically independent of cure temperature. Nevertheless, neither the 100 % coverage of the sample surface with FT nor the 0 % (absence of fluorine) in the bulk is achieved. The second set (black circles) reports results for the sample cured in a closed mould. EDX analysis provide further evidence, indicating an isotropic fracture surface with a F_{20FT} / F_{neatFT} ratio approximately constant all over the cross section, i.e. from wall to wall of the mould. This sample behaves as expected with uniform fluorine composition.

All FT-modified materials were transparent, independent of FT content and cure conditions. The excellent optical properties of modified materials, even for those which present an anisotropic fracture surface, could be attributed to the negligible difference in the refractive indices of the epoxy thermoset and the modifier. The refractive index of the epoxy network at complete conversion, measured at room temperature, was $n_{\infty} =$

1.5880. The corresponding value for the fluorinated thermoplastic, measured at room temperature, was $n_{FT} = 1.5905$.

CONCLUSIONS

A new fluorinated thermoplastic (FT) has been successfully synthesized. The resulting FT was used to modify an epoxy system.

DGEBA-FT blends present a total miscibility over the whole composition range. In addition, DSC and FTIR results revealed that etherification reaction takes place between FT and the thermoset components during curing.

Considering catalytic and noncatalytic mechanisms, DGEBA-MCDEA reactions were modelled for formulations modified with 20 wt % FT at different cure temperatures. Deviation of the predictions from experimental results occurs at 150 °C. It was found that at this cure temperature the extent of the etherification reaction increases, leading to an amine excess in the formulation that causes an enhancement in the kinetic reaction.

The gel conversions were found to be higher in the modified systems. This is the result of a modification of the stoichiometry provoked by the etherification reaction.

The relationship between T_g and epoxy conversion were predicted for modified formulations considering the blend as a solution during the course of polymerization.

The cross section composition and morphology of 20 wt % FT-modified samples were investigated in terms of cure conditions. SEM-EDX analysis has shown that FT migrates towards the surface when curing in the presence of air, generating anisotropic structures with the presence of fluorine-rich surface layers. It was found that the resulting FT distribution is practically independent of cure temperature.

Analysis of the resulting surface, optical, electrical, and mechanical properties of such FT-modified materials is on the way.

Acknowledgements

The authors thank the financial support of the following Argentine institutions: University of Mar del Plata, National Research Council (CONICET), and National Agency for the Promotion of Science and Technology (ANPCyT).

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FIGURE CAPTIONS

Figure 1. MIR spectra of DGEBA, FT, 80-20 and 50-50 DGEBA-FT blends.

Figure 2. Relationship between T_g (from DSC) and composition in mixtures: (\circ) DGEBA-FT as-prepared; (*) DGEBA-FT after heating at 200 °C for 2h; (\bullet) DGEBA-MCDEA-FT before reaction; (---) Equation (2) with $k = 0.5$.

Figure 3. The extent of reaction versus time at different temperatures for neat (white points) and 20 wt % FT modified epoxy-MCDEA (black points) systems at: 150 °C (circles), 170 (triangles) and 200 °C (squares). The figure also shows: (—) kinetics modelling of neat systems; (---) kinetics modelling of modified systems considering the dilution effect induced by the presence of FT.

Figure 4. Dimensionless ether linkages (DEL) changes as a function of epoxy conversion at different temperatures for neat (white points) and 20 wt % FT modified epoxy-MCDEA (black points) systems at: 150 °C (circles), 170 (triangles) and 200 °C (squares).

Figure 5. Chromatograms of a) FT; and a DGEBA-MCDEA sample modified with 20 wt % FT at various reaction extents and cure temperatures: b) $x < x_{gel}$; and c) $x > x_{gel}$ at 200 °C; d) $x > x_{gel}$ at 150 °C.

Figure 6. Tg as a function of epoxy conversion at (●) 150, and (■) 200 °C for samples modified with 20 wt % FT. The figure also shows: (---) Fox prediction.

Figure 7. Experimental and predicted by Fox equation (---) Tg versus mass fraction of FT for FT-modified samples, obtaining when curing at different conditions: (□) 200 °C, 2 h; (○) 150 °C, 4 h; (*) 0.5 °C/min.

Figure 8. Cross section morphologies obtained by SEM of samples containing 20 wt % FT cured at 150 °C 4 h, 200 °C 1h: a) reacted in an open mould; b) higher amplification of a) showing the epoxy-rich phase; c) reacted in a closed mould.

Figure 9. Fluorine composition depth profiles (EDX) in terms of the atomic ratio of F in 20 wt % FT-modified samples, F_{20FT} , to F in neat FT, F_{neatFT} , along the cross section of samples cured: (○) in an open mould at 150 °C 4 h, 200 °C 1h; (*) in an open mould at 200 °C 2h; (●) in a closed mould at 150 °C 4 h, 200 °C 1h.

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Table 1. Heats of reaction and temperature peaks of neat epoxy (at different curing rates) and blends (at 0.5 °C/min) with various FT contents with a stoichiometric ratio.

wt % FT	Heating rate (°C/min)	ΔH (kJ/eq)	Temperature peak (°C)
0	0.5	99.98	167.0
0	2	77.70	
0	10	59.80	
10	0.5	106.30	155.6
20	0.5	123.82	145.0
50	0.5	273.26	125.7

Table 2. NIR assignments of the relevant bands of epoxy and amine.

Wave number (cm ⁻¹)	Band assignment
4065	Aromatic combination band
4530	Epoxy combination band
4623	Combination band of the aromatic conjugated C=C stretch with the aromatic –CH fundamental stretch
4681	Combination band of the aromatic conjugated C=C stretch with the aromatic –CH fundamental stretch
5056	Primary amine combination (bending and stretching vibrations)
5240	Hydroxyl-water interactions
6080	Terminal epoxy first overtone (C-H stretch)
6670	Combined absorption of primary and secondary amine (first overtone N-H stretch)
7000	Hydroxyl group first overtone

Table 3. Gel conversions, x_{gel} , as a function of FT concentrations and reaction temperatures.

T (°C)	wt % FT	x_{gel}
150	0	0.56
150	20	0.60
200	0	0.55
200	20	0.57

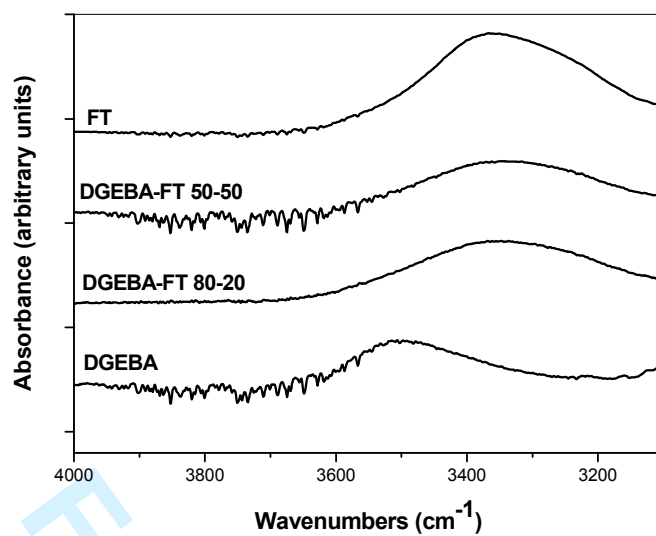


Figure 1, Penoff et al.

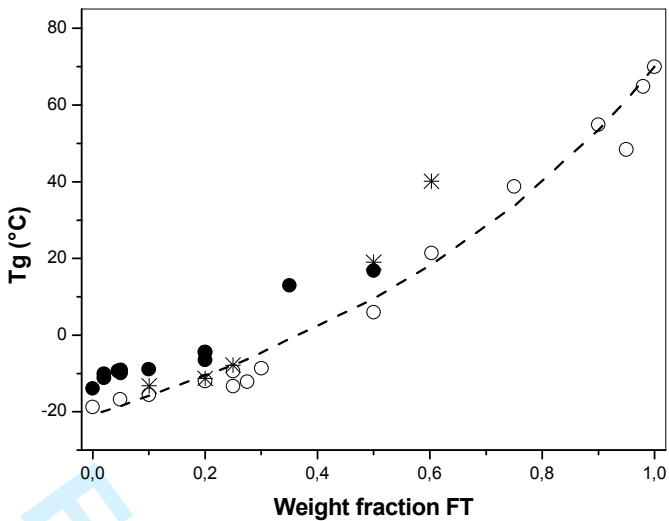


Figure 2, Penoff et al.

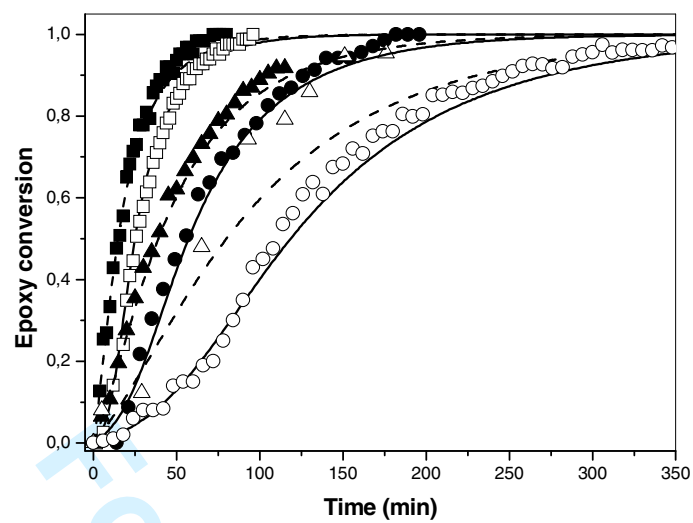


Figure 3, Penoff et al.

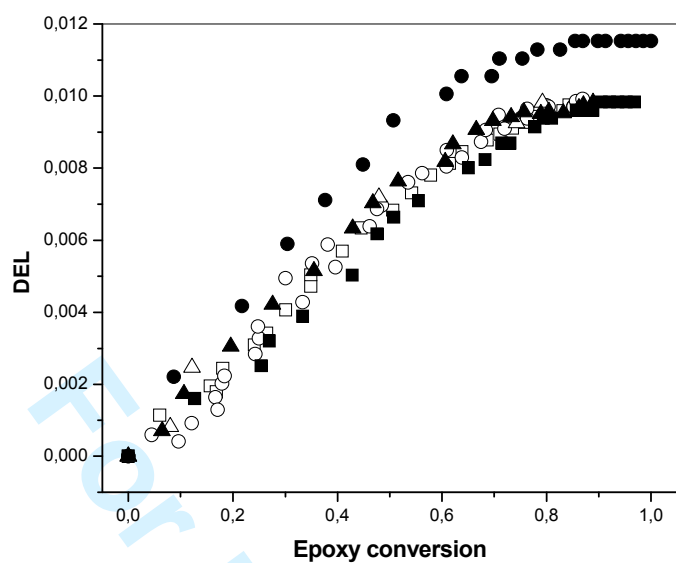


Figure 4, Penoff et al.

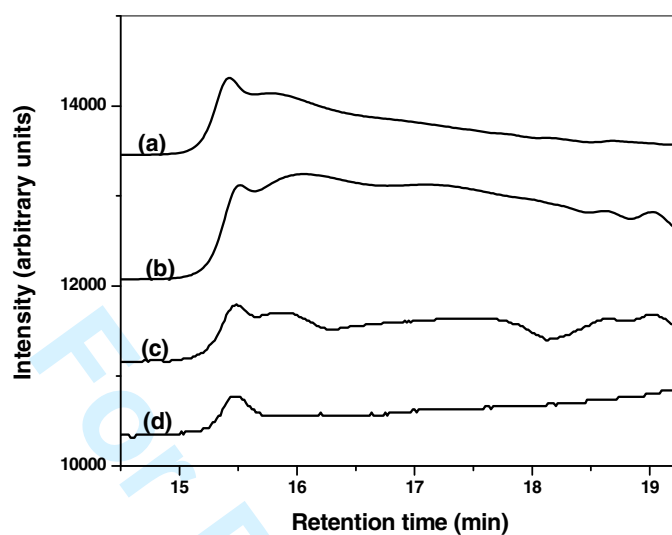


Figure 5, Penoff et al.

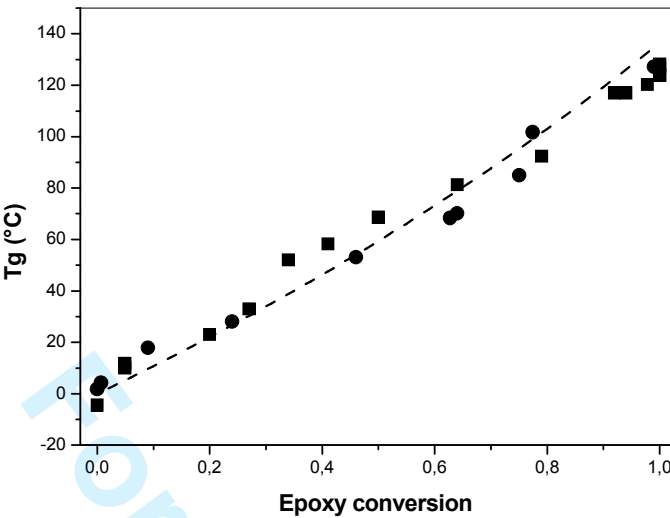


Figure 6, Penoff et al.

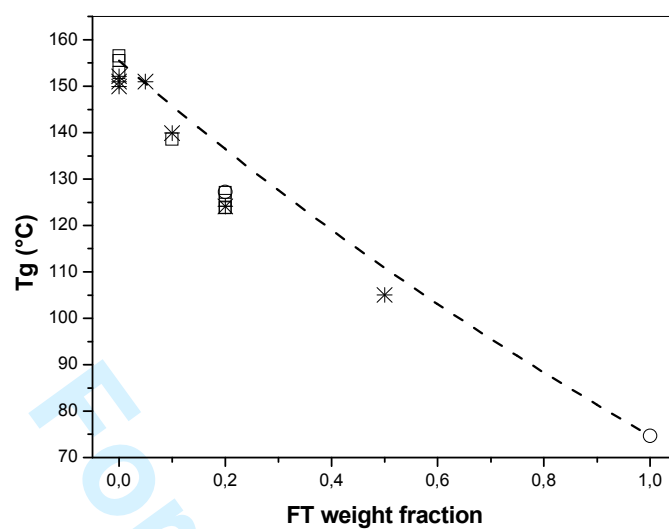


Figure 7, Penoff et al.

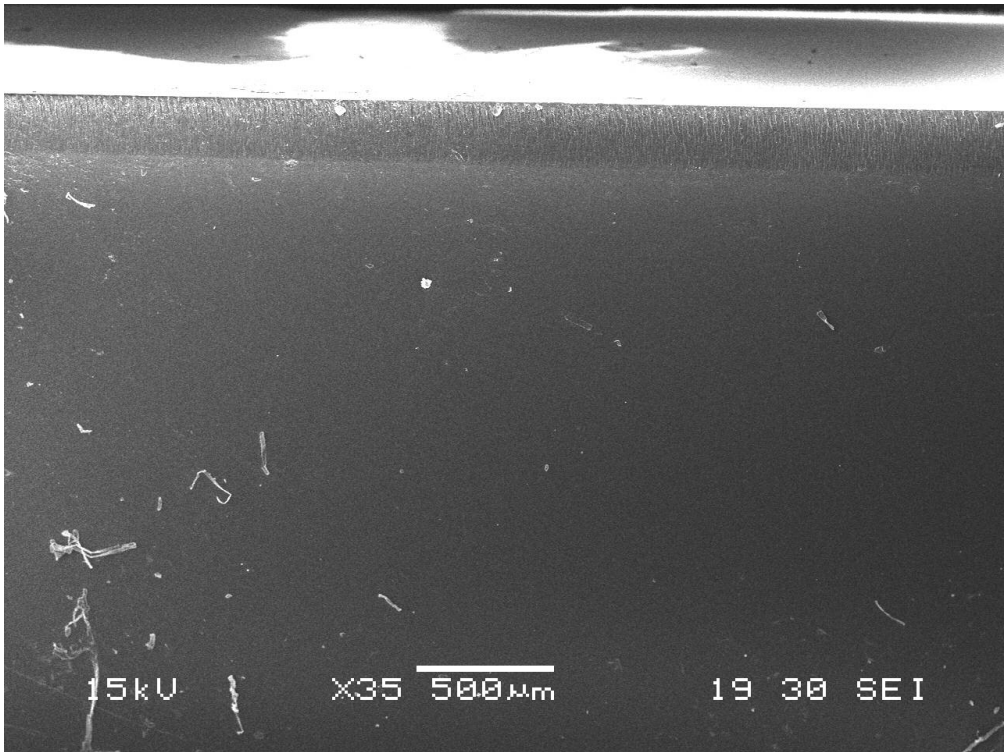


Figure 8a, Penoff et al.

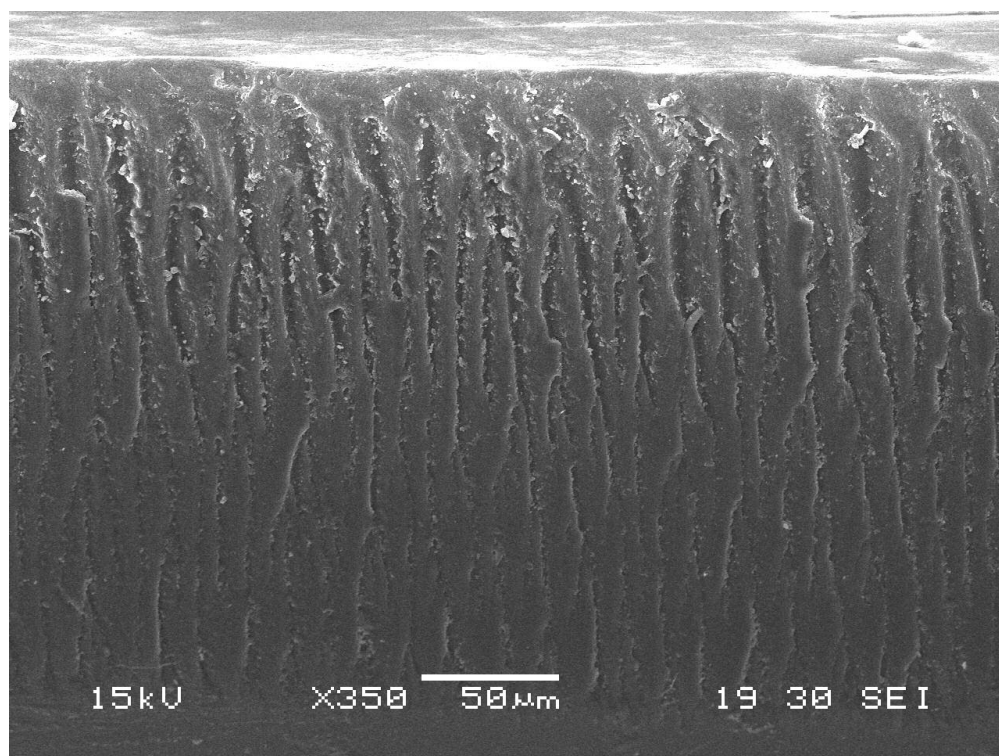


Figure 8b, Penoff et al.

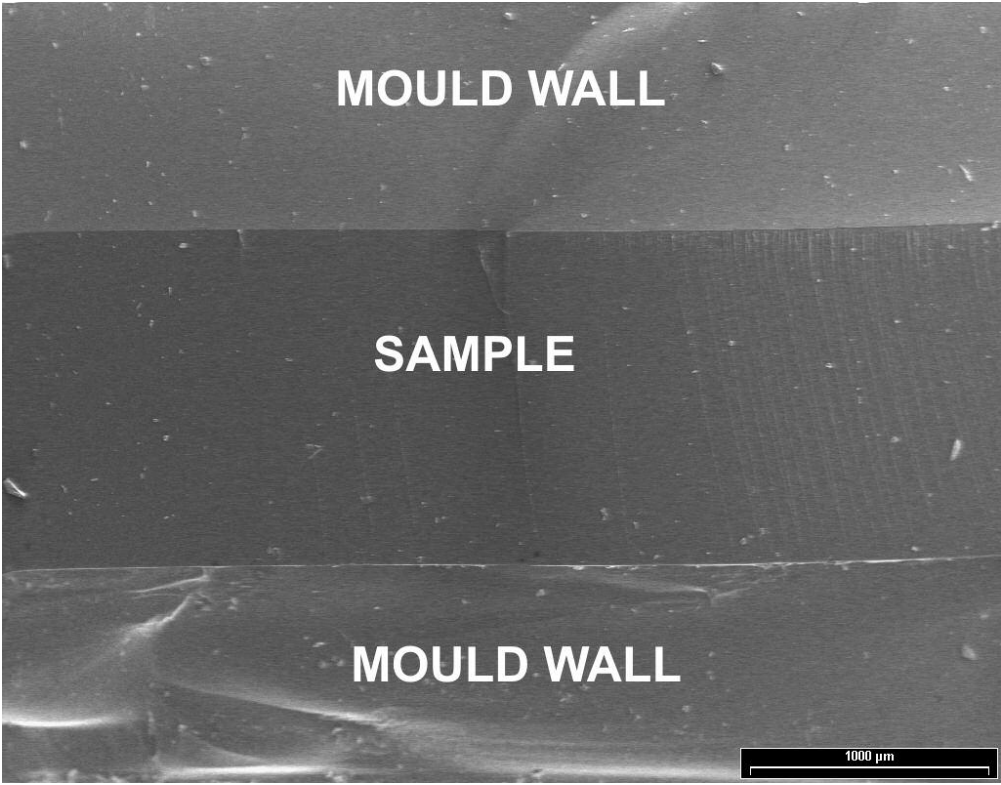


Figure 8c, Penoff et al.

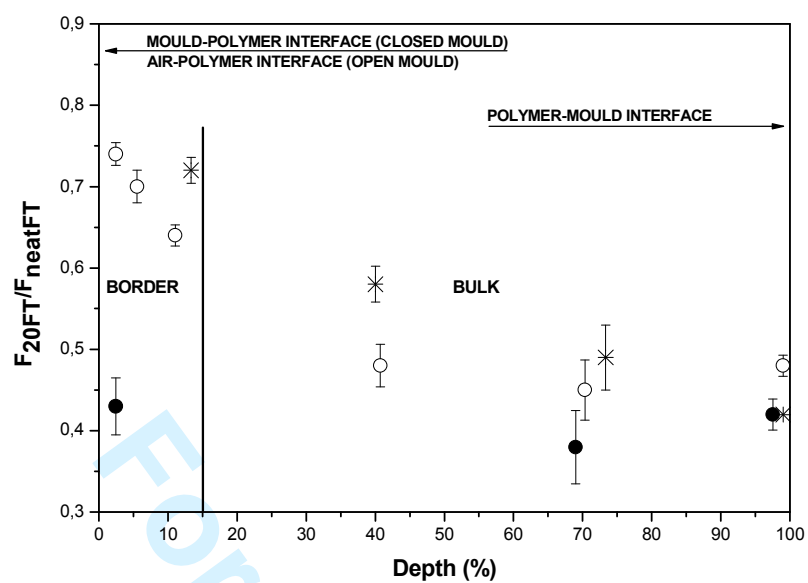


Figure 9, Penoff et al.