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Toughening of tetrafunctional (TGDDM) epoxy resins with telechelic extended perfluoroligomers

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Telechelic extended perfluoroether oligomers containing carboxylic acid terminal groups were found to be miscible in mixtures of a tetrafunctional epoxy resin (TGDDM) and methyl nadic anhydride. After curing the resin system remained transparent. SAXS examination revealed the presence of a two-phase morphology with domains of the order of 16–17 nm. The glass transition of the cured resin system showed a maximum at perfluoroether concentrations in the region of 5% and remained at about the same level as the unmodified system at concentrations as high as 20 wt %. The critical strain energy release rate (Gc) for these systems was found to increase very rapidly in the region of 5 to 15 wt % fluoroligomer to reach values about 8 times higher than those obtained for the control resin system. This was accompanied by a small reduction in modulus and yield strength. The main reason for the enhanced toughness, however, is attributed to the increased size of the yield zone at the crack tip. The fluoroligomer modified cured resin systems exhibited an unusual change in water diffusion characteristics. At about 15 wt % concentration of fluoroligomer modifier the diffusion coefficient increased by a factor of 70, while the equilibrium water absorption was reduced by more than 10 wt %.

1. Introduction

For more than thirty years it has been demonstrated that difunctional epoxy resins, particularly those based on bisphenol A (DGEBA) can be toughened by the addition of low molecular weight butadiene acrylonitrile copolymers containing functional terminal groups, such as carboxylic acid (CTBN) or primary amine (ATBN) [1–4]. The toughening component reacts with the resin prior to gelation, giving rise to the formation of high molecular weight species of reduced solubilty, which precipitate out into a multitude of particles assuming final dimensions in the region of 1 to 10 μm [5].

It is widely accepted that the mechanism by which such rubbery inclusions increase the fracture toughness of glassy polymers, such as crosslinked epoxy resins, is the promotion of shear yielding in the surrounding matrix, and through the formation of microcavities within the particles and in the interfacial regions [6].

The use of CTBN type of oligomers, however, has not been found to be particularly effective with tetrafunctional epoxy resins, such as tetraglycidyl diamino diphenyl methane (TGDDM), even though phase separation of the oligomer takes place as in the case of difunctional DEGBA resins [7]. This has been attributed to the excessive brittleness of the resin, which makes it difficult for the matrix surrounding the rubber particles to reach the yielding conditions. Since tetrafunctional epoxy resins are primarily used for high temperature applications, modifications with CTBN oligomers are not particularly appropriate owing to their low thermal oxidative stability [8].

Several attempts have been made to find alternative modifiers to CTBN to overcome the stated difficulties [9]. To this end several authors have used engineering thermoplastics, such as polysulphones and polyetherimides. Although phase separation through particle precipitation takes place and interfacial adhesion can be increased with the use of functionalised polymers capable of reacting with the epoxy resin, a large concentration (more than 30 wt%) is normally required to achieve a substantial increase in toughness, as opposite to 10–20% normally required for CTBN systems [10].

The drive to find suitable toughening agents for multifunctional epoxy resins, also capable of reducing water absorption, has induced some authors to examine polydimethylsiloxane and fuorinated polymers, particularly in the form of reactive oligomers [11]. Takahashi *et al.* have investigated the use of several

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amine terminated silicone oligomers in epoxidised novolac resins for possible applications as encaplsulants for semiconductor integrated devices [12]. Total miscibility of silicone oligomers in the unreacted resin was achieved, however, only with phenyl methyl silicones which produced completely transparent (monophase) products on curing. The use of copolymers of phenyl methyl silicones and dimethyl silicones, on the other hand, has produced a morphology consisting of small dispersed particles.

Cecere *et al.*, however, found that these siloxane systems were not very effective in increasing the fracture toughness of epoxy resins [13]. The use of siloxane based systems was extended, in later years, to block copolymers of polydimethylsiloxane and polyethylene oxide [14]. As for the case of CTBN oligomers these systems were found to be effective in toughening only difunctional epoxy resins. Mascia *et al.* have used telechelic extended carboxyl terminated perfluoroligomers to improve the fracture resistance of difunctional epoxy resins [15, 16]. Curing the epoxy resin/fluoroligomer/anhydride hardener mixtures with a tertiary amine catalyst produced transparent products, the structure of which consisted of essentially interpenetrating heterophase domains. Prereacting the fluoroligomer with an excess epoxy resin, under controlled conditions, prior to the addition of the hardener and catalyst, on the other hand, produced the typical phase separation of CTBN systems of multicomponent particles dispersed in the epoxy matrix. Although the fracture toughness expressed in terms of critical strain energy release rate (G_c) was found to increase for all systems, the ductility measured as the maximum strain at break was found to increase only for the case of particle dispersed systems.

The purpose of the present study is to determine the capabilities of carboxyl terminated telechelic extended perfluoroether oligomers (PFO) to enhance the fracture toughness and reducing the water absorption of tetrafunctional (TGDDM) based resin mixtures in the form of IPNs.

2. Experimental

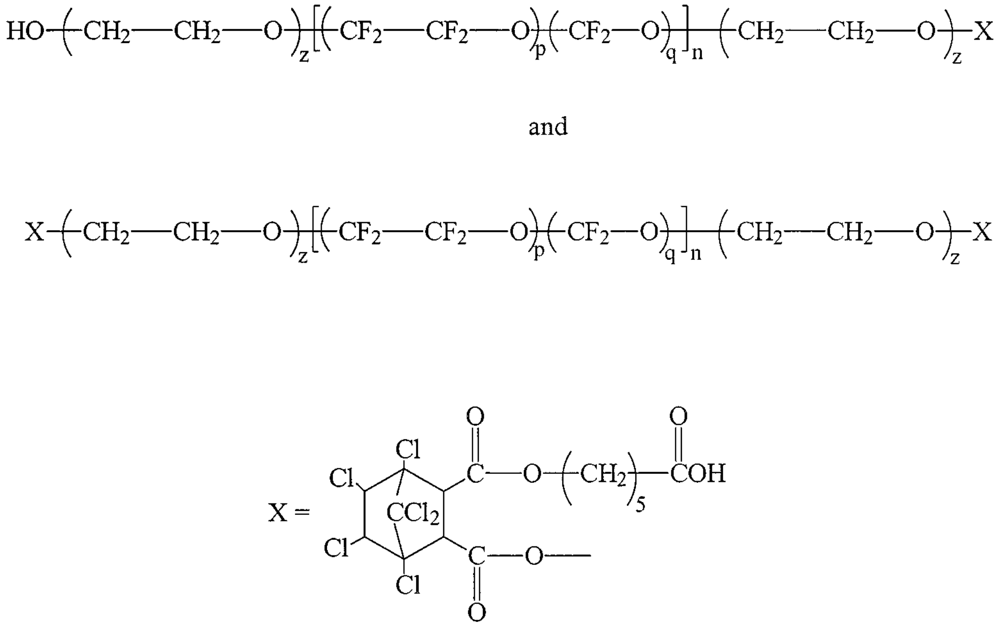
2.1. Materials

a) Epoxy resin: Tetraglycidyl 4,4′ diaminodiphenylmethane (TGDDM), supplied by Ciba Geigy.

b) Hardener: Methylbicyclo 2,2,1 heptene 2,3 dicarboxylic acid anydride (methyl nadic anhydride, MNA) from Fluka.

c) Accelerator: Benzyl dimethyl anyline (BDMA) from Aldrich.

d) Perfluoroligomer (PFO): Carboxylic acid terminated and chain extended perflouoroether oligomer, having the following chemical structure



($z = 1.5$; p/q molar ratio $= 0.67$; $n = 10$)

This was prepared according to a previously published procedure [15].

2.2. Preparation and curing of resin mixtures

The resin mixtures were prepared by mixing the epoxy resin, hardener and perluoroligomer at 80°C followed by a short heat treatment in a vacuum oven, also at 80°C, in order to remove air bubbles. The mixture was then cooled to room temperature and the accelerator added while slowly stirring the mixture.

Samples for evaluation were produced by casting the resin mixture in flat rectangular moulds and cured in steps, starting with a gelation stage at 120°C for 6 hours

TABLE I Composition of the investigated mixtures

TGDDM (parts)	MNA (parts)	PFO (parts)	TGDDM (wt %)	MNA (wt %)	PFO (wt %)
100	80	—	55.6	44.0	—
100	80	5	54.1	43.2	2.7
100	80	10	52.6	42.1	5.3
100	80	15	51.3	41.0	7.7
100	80	20	50.0	40.0	10.0
100	80	30	47.6	38.1	14.3

and followed by a 3 hour curing period at 150°C and a 1 hour post curing step at 180°C. The details of the formulations examined are given in Table I.

2.3. Morphology characterization of cured resin mixtures

a) *Scanning electron microscopy (SEM).* The morphology of the cured samples was examined by SEM on specimens fractured in liquid nitrogen as well as on surfaces of specimens from 3-point bending tests. The apparatus used was a Philips SEM mod. XL20 and the fracture surfaces were coated with a gold-palladium layer by vacuum sputtering.

b) *Small angle x-rays scattering.* SAXS intensity profiles were collected for 20 hours (Ni filtered Cu K_α radiation) using a Kratky Kompakt camera equipped with a Braun one-dimensional positional sensitive detector (PSD). The SAXS profiles were smoothed and corrected for the absorption and for the parasitic scattering (background). The smearing effect was corrected by Schmidt program [17].

c) *Mechanical spectroscopy.* Dynamic mechanical tests were carried out over a wide range of temperatures using a Polymer Laboratory DMTA apparatus in 3-point bending. The frequency was 1.0 Hz and the temperature was ramped at 5°C/minute. The temperature of the maximum in the curve obtained from the plot of loss modulus (E'') against temperature was taken to represent the glass transition temperature (T_g) of the material.

2.4. Mechanical properties of the cured resins

Mechanical tests were performed at room temperature using an Instron instrument, model 4505, operated at a clamp separation speed of 1 mm/minute in all cases.

a) *Modulus.* The modulus of the cured resins was measured from tests carried out in a flexural mode at ambient temperature, according to the ASTM D790 method, using rectangular specimens, 60.0 × 6.0 × 4.0 mm, and a span/width ratio of 8 : 1.

b) *Yield strength.* The yield strength was measured in compression using specimens, 12.0 × 6.0 × 4.0 mm, loaded along the length.

c) *Fracture parameters.* Rectangular specimens 60.0 × 6.0 × 4.0 mm were loaded edgewise with a span/width ratio of 8 : 1. The specimen were notched on one side (SEN types) using a mechanical device with a V-shaped tool. A sharp cut (0.2 mm deep) was subsequently introduced at the root of the V- notch by means of a razor blade fixed to a micrometer apparatus. The final value of the notch depth was measured after fracture using an optical microscope.

The fracture data were analysed according to Linear Elastic Fracture Mechanics (LEFM) theory. The critical stress intensity factor, K_c, was determined from the load-displacement curve using the equation

$$K_c = \sigma Y \sqrt{a}$$

where σ is the nominal stress at the onset of crack propagation, a is the initial crack length and Y is a calibration factor obtained from tables quoted in the literature [18].

The critical strain energy release rate, G_c, was estimated from the energy to fracture (U), taken from the area under the load/deflection curve, using the equation

$$G_c = \frac{U}{\Phi B W}$$

where B and W are the thickness and width of the specimen, respectively, and Φ is a factor related to the rate of change of compliance (C) with crack length (a), i.e.

$$\Phi = C \left[\frac{dC}{d\left(\frac{a}{W}\right)} \right]^{-1}$$

The values of Φ were obtained from the tables quoted in the literature [19].

d) *Water absorption characteristics.* Gravimetric sorption measurements were carried out on 0.10–0.25 mm thick samples previously dried over night at 100°C under vacuum to ensure complete removal of absorbed water. The predried specimen were immersed in a deionised water bath thermostatically controlled at 22 (±0.1)°C. Periodically, the samples were removed, blotted and weighed with an analytical laboratory balance.

3. Results and discussion

a) The morphology of the specimens revealed by SEM examinations is illustrated by the micrographs in Fig. 1. These reveal the existence of a very fine morphology with domains in the submicron range, similar to those previously identified with difunctional resin systems [15, 16].

b) The SAXS intensity profiles for various epoxy resin containing different amounts of fluoroligomer are shown in Fig. 2. These profiles have been smoothed and corrected for the absorption and the parasitic scattering (background).

The profile of the neat matrix in the low angle region is very close to the background profile [20, 21]. In practice the system is liquid-like and does not produce

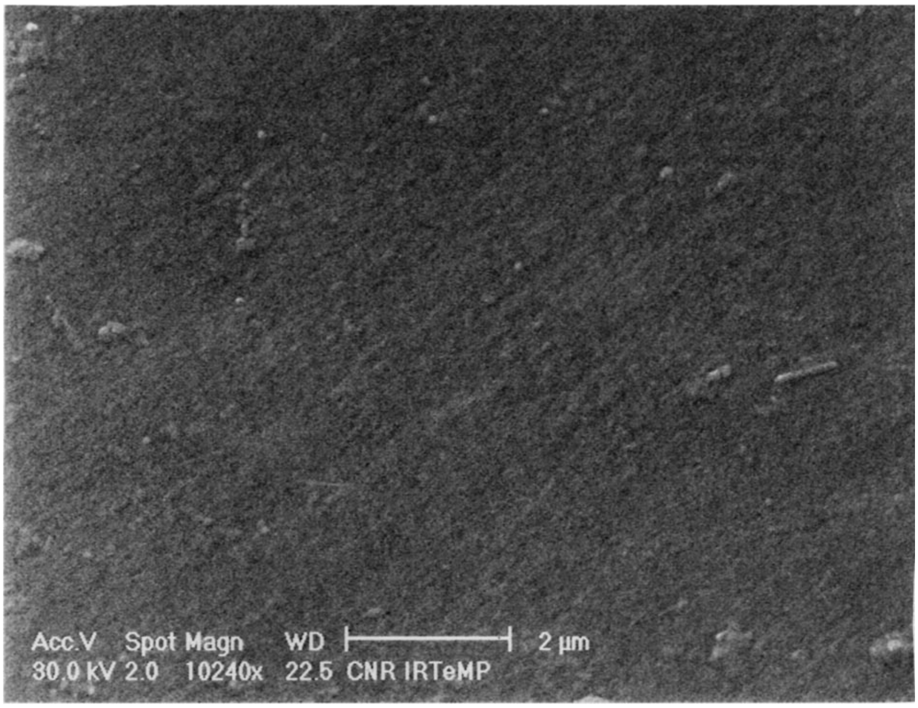


Figure 1 SEM micrograph of fractured surface of specimen of sample of epoxy resin mixture containing 14.3 wt% fluoroligomer. (Specimen fractured in liquid nitrogen).

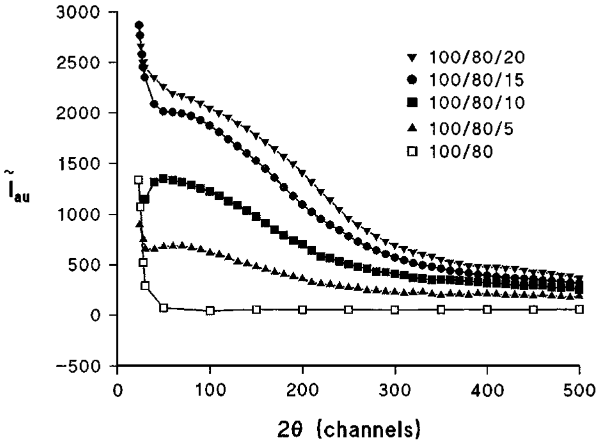


Figure 2 SAXS spectra of epoxy resin mixtures containing different amounts of fluoroligomer. (Intensity profiles are smoothed and corrected for absorption and for background scatter).

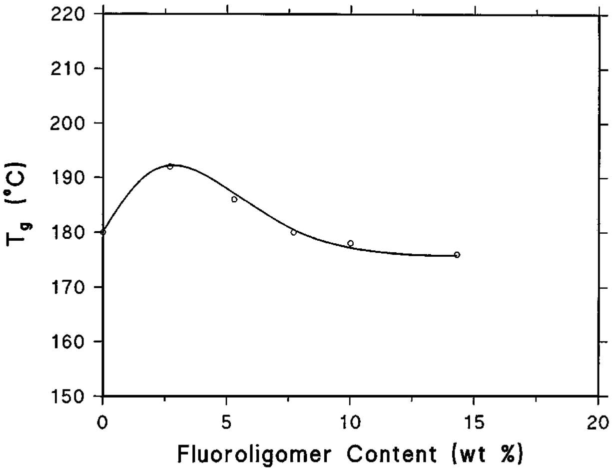


Figure 3 Plot of glass transition temperature (T_g) against fluoroligomer content for various epoxy resin mixtures. (T_g values were estimated from the maximum of the loss modulus as a function of temperature).

any discrete scattering. A noticeable interference effect arises by adding PFO to the system, the effect of which increases gradually with increasing the PFO content. In comparison the morphology of the base resin is completely featureless.

The interdomain distance, as determined by the Desmear SAXS profile (17) for a typical morphology of fluoroligomer modified systems, say formulation TGDDM/MNA/PFO = 100/80/15, is around 16–17 nm.

c) A plot of T_g values against the concentration of perfluoroligomer is shown in Fig. 3. This reveals the occurrence of a maximum at around 5 wt% PFO, reaching limiting values that are of the same magnitude as the base (unmodified) epoxy resin. This behaviour clearly confirms the presence of a two phase structure without any plasticization effects of the surrounding epoxy matrix. The maximum in T_g occurs at about the same PFO concentration seen for difunctional epoxy resins, using the same amounts of curatives, and is related to the change in curing kinetics brought about by the interaction of the acid groups of the oligomer with the BDMA catalyst. These studies are to be reported elsewhere [22].

d) A linear decrease in modulus with increasing concentration of fluoroligomer, over the range examined, is observed from the plot in Fig. 4. The reduction in modulus relative to the unmodified resin amounts to less than 20% for fluoroligomer content of 14.7 wt%. An approximate calculation based on the law of mixtures indicates that the modulus of the floroligomer containing

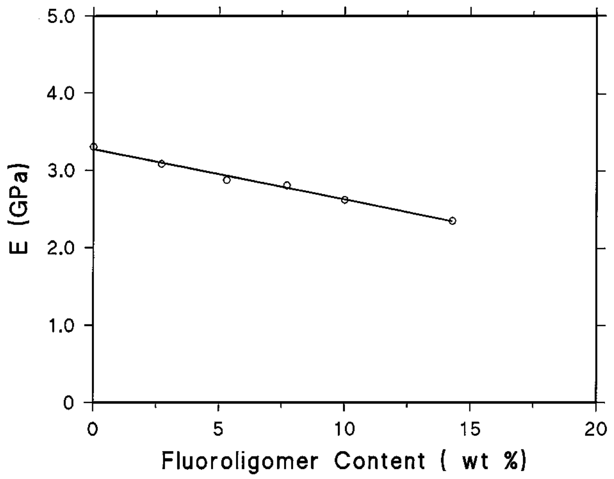


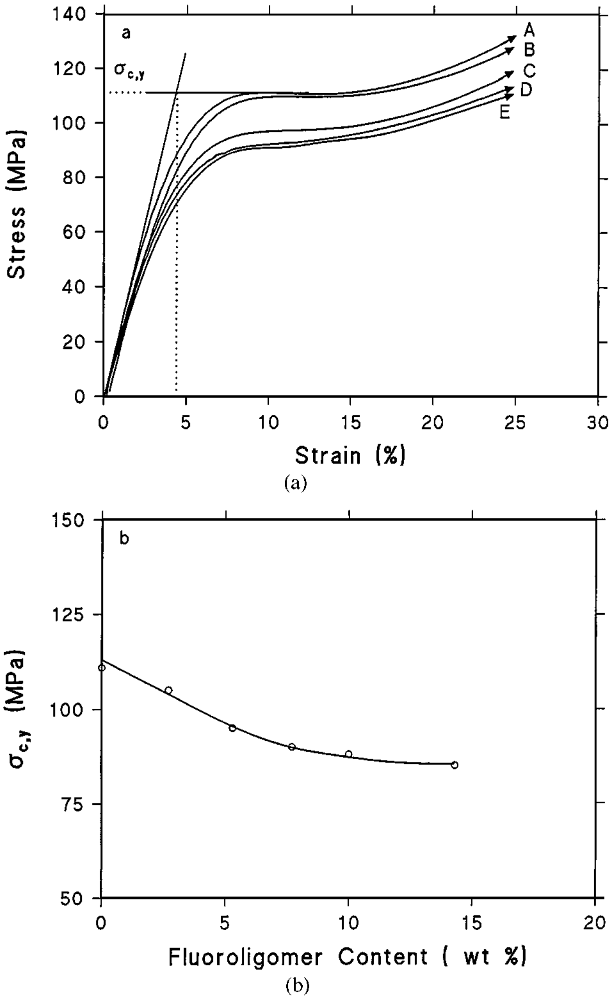
Figure 4 Plot of flexural modulus against fluoroligomer content.

phase is greater that 1 MPa. Even if it can be presumed that the PFO phase contains large amounts of epoxy resin/hardner [15, 16], thereby increasing its effective volume fraction, the modulus value that can be estimated for this component is still in excess of 1 MPa. For a three-dimensional network of co-continuous phases the calculation would give an even higher modulus value, suggesting that the physical state of the fluoroligomer dispersed phase is more likely to be equivalent to that of a soft/ leathery material rather than a rubbery polymer.

e) Typical stress/strain curves derived from the measurements in compression are shown in Fig. 5a for nominal strains up to 25%. These illustrate that all samples, including the base resin, fail through plastic deformations.

A plot of yield strength as a function of fluoroligomer content is shown in Fig. 5b. The yield strength was taken at the intersect of the tangents of the curves taken before and after the occurrence of plastic deformations (see Fig. 5a). These show a monotonic decrease in yield strength, relative to the base resin, similar to that observed for the modulus.

It is estimated that the stress acting on the dispersed fluoroligomer phase at the yield point is greater than 10 MPa, confirming the suggestion made earlier that this is unlikely to be rubbery in nature, despite the very low T_g value of the original unextended fluoroligomer i.e. in the region of -120°C. Hence the dispersed phase is expected to contain a substantial amount of epoxy/hardner



(a)

(b)

Figure 5 (a) Nominal stress/strain curves in compression for epoxy resin mixtures containing different amounts of fluoroligomer. (b) Plot of yield strength against fluoroligomer content.

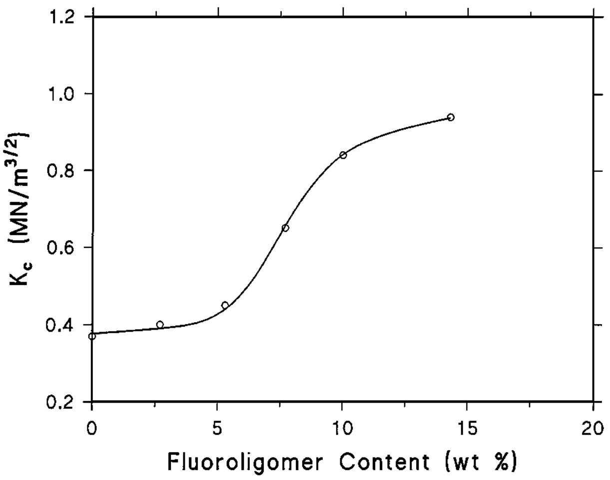


Figure 6 Variation of critical stress intensity factor (K_c) with increasing fluoroligomer content of epoxy resin mixtures.

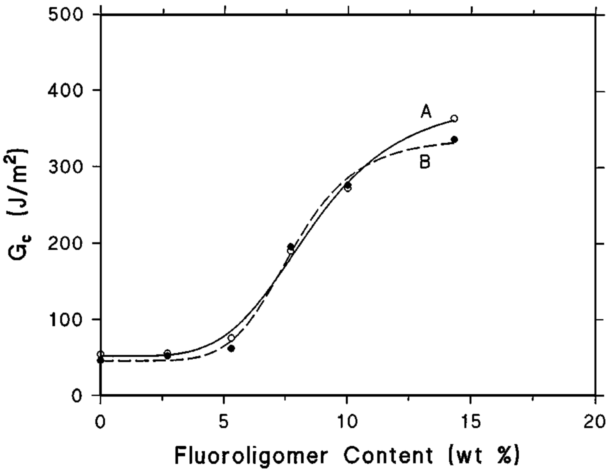
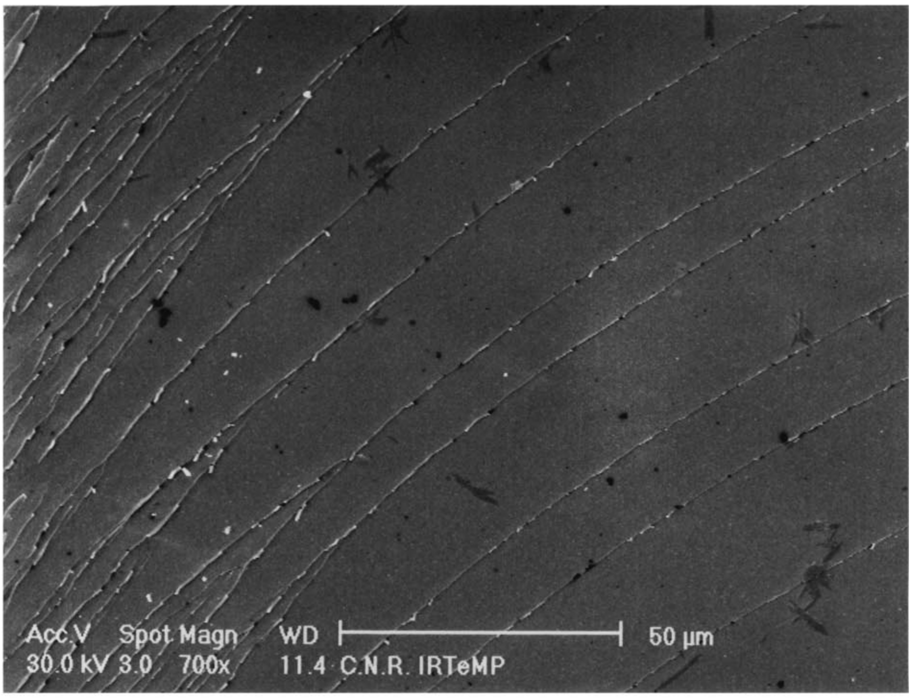


Figure 7 Variation of critical strain energy release rate (G_c) with increasing fluoroligomer content of epoxy resin mixtures. Curve A: experimental values; Curve B: values calculated from equation $G_c = K_c^2/E$.

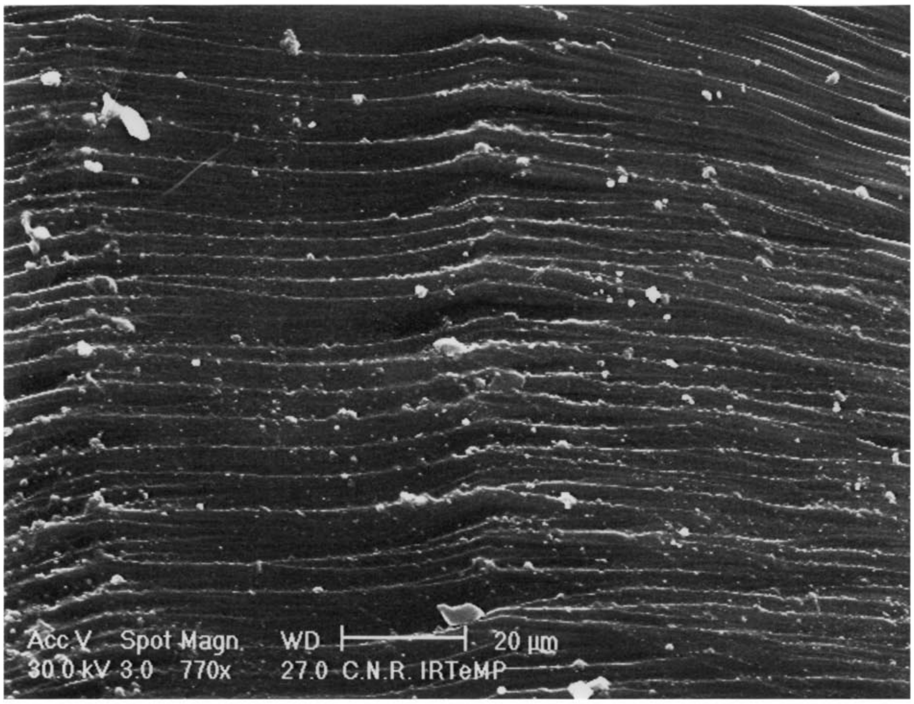
to provide a crosslinked system with a less tight network of the surrounding pure epoxy/hardener system.

f) The fracture parameter K_c is reported in Fig. 6 as a function of the perfluoroether content of the epoxy resin mixture. A sigmoidal curve is obtained exibiting a rapid increase at concentrations around 5–7 wt% PFO, levelling off at fluoroligomer concentations around 10 wt%. The toughening effect of the fuoroligomer is even more pronounced when the fracture data are expressed in terms of variation of G_c values, as shown in Fig. 7. The G_c values calculated from the expression $G_c = K_c^2/E$ were also plotted on the same diagram. The fact that the two sets of values are very similar is indicative of the applicability LEFM principles to the systems investigated and also points out to the reliability of 3-point bending tests in such systems to estimate "equivalent" elastic parameters in glassy polymeric systems.

One notes that the fracture toughness data are at least as high as those reported for systems whereby CTBN containing particles have been forced to precipitate via the use of selective catalyst systems, using an aromatic



(a)



(b)

Figure 8 SEM micrographs of surface of specimens from fracture toughness tests: (a) Base epoxy resin. (b) Epoxy resin mixture containing 14.3 wt% fluoroligomer.

amine instead of an anhydride as hardener. In the case of CTBN modified systems, however, much higher concentrations of toughening oligomer were used that for the present systems.

It is remarked also that, in previous work on difuctional DEGBA resin mixtures where the PFO based phase was present as interpenetrating domains, it was found that the co-continuous phases were less effective than the equivalent particulated two phase systems, and that much higher loadings were necessary to obtain appreciable increases in toughness. The phase separated systems through particle formation are presently being investigated to obtain a better understanding of the toughening mechanism of such perfluoroligomers, as these differ substantially from CTBN systems in so far they are not expected to produce true solution in the uncured state bur are likely to be present as micellae which will readily bring about phase separation during curing.

Typical SEM micrographs of the fracture surface of specimens from the LEFM tests in regions near the crack tip are exemplified in Fig. 8. These reveal a very smooth surface for the base resin while the modified specimens have a rippled appearance and a series of closely spaced ridges. Both features are indicative of the occurence of plastic deformations at the crack tip during fracture propagation. In the light of this observation the Dugdale model was used to estimate the size of the yield zone at the crack tip [23] as a function of the fluoroligomer content, using the equation:

$$R = \frac{\pi}{8}\left(\frac{K_c}{\sigma_{t,y}}\right)^2$$

where R is the length of the yield zone and $\sigma_{t,y}$ is the yield strength in tension, assuming that the value of the yield strength in tension is 3/4 the value obtained in compression tests. The calculated values of R were plotted against the the fluoroligomer content, as shown in Fig. 9. This graph reveal a rapid increase in size of the yield zone at around 5 wt % fuoroligomer content, similar to that observed for K_c and G_c plots.

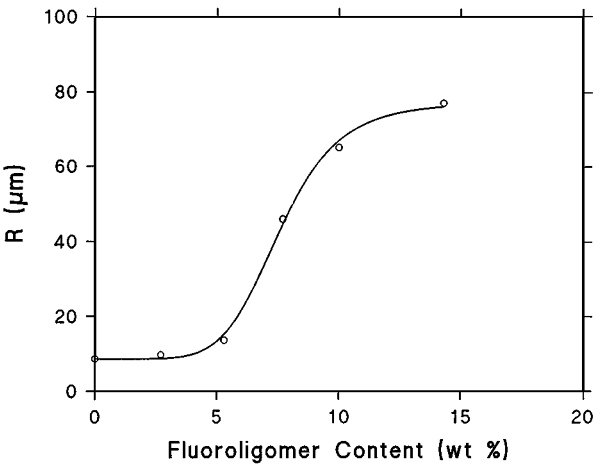


Figure 9 Estimated length of the yield zone at the crack tip (Dugdale model) as a function of the fluoroligomer content of the epoxy resin mixtures.

It must be stressed that such increase in K_c and G_c values was not observed previously for difunctional epoxy resins with a comparable morphology. Whether this is due to the more brittle nature of the tetrafunctional resins or to subtle differences in morphology is to be examined in future work, as it is the effect of inducing particle precipitation in tetrafunctional resins.

g) Plots of water absorption as a function of the immersion time in water at 22°C are shown in Fig. 10a for the base resin (curve A) and the resin mixture containing 14.7 wt % fluoroligomer (curve B). In Fig. 10b the sorption isotherms are presented as Fickian plots from which the diffusion coefficient, D, is calculated from the expression

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{1/2}$$

These plots show that the presence of continuous phase of an oligomer rich component decrease appreciably the amount of water absorbed up to equilibrium, while increasing the diffusion coefficient. The values of D are respectively 8.15×10^{-5} m^2 s^{-1} for the resin containing the perfluoroligomer modifier and 1.20×10^{-4} m^2 s^{-1} for the base resin. This corresponds to a 70 fold increase in the water diffusion coefficient.

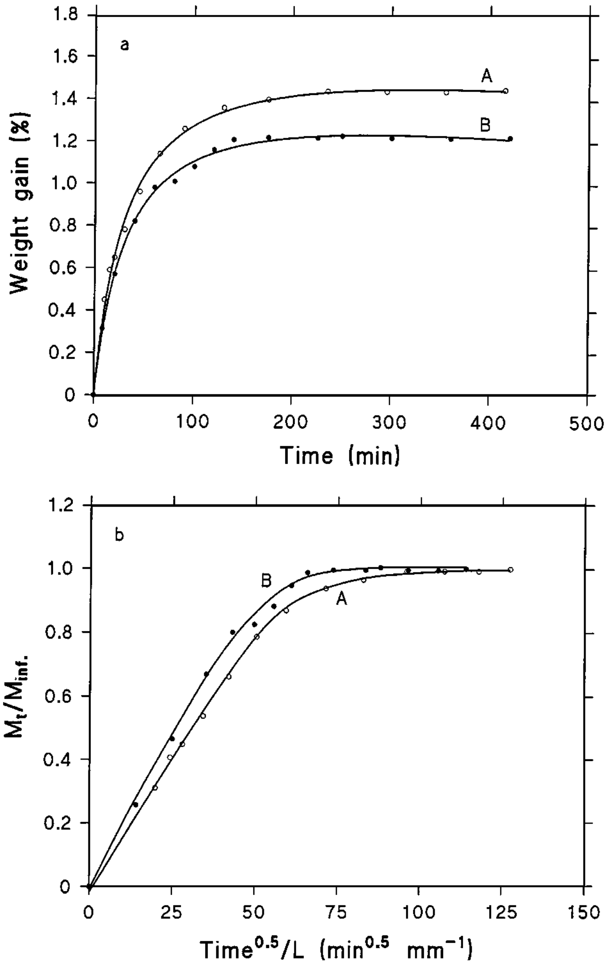


Figure 10 (a) Water sorption at 22°C for base resin (curve A) and resin mixture containing 14.3 wt% fluoroligomer (curve B). (b) Fick's plot of isothermal water sorption at 22°C for base resin (curve A) and resin mixture containing 14.3 wt% fluoroligomer (curve B).

4. Conclusions

From the present studies on the use of functionalised perfluoroether in tetrafunctional (TGDDM) epoxy resins it is possible to derive the following main conclusions:

1. Curing the epoxy resin mixtures by direct addition of the anhydride hardener and tertiary amine catalyst produces a two phase system with interdomains distances in the region of 16–17 nm.
2. The fluoroligomer phase contains a certain amount of epoxy resin, and possibly hardener, but it segragates totally from the main epoxy/hardener, thereby leaving the T_g of the main epoxy phase essentially unaltered.
3. The fracture toughness of cured systems increases rapidally from around 5 wt% PFO and appears to level off at about 15 wt%.
4. The presence of hydrophobic perfluoroether based interconnected domains brings about a notable reduction in the maximum amount of water absorbed and an increase of the water diffusion coefficient.

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