Miscibilization of Telechelic Fluoroalkeneoxide Oligomers in Epoxy Resins and Effects on Morphology and Physical Properties

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SYNOPSIS

Hydroxyterminated fluoroalkene oxide oligomers were reacted with chlorendic anhydride and subsequently with ε-caprolactone to produce carboxyterminated perfluoroethers prepolymers that were totally miscible with diglycidylether of bisphenol A. Curing the epoxy resin mixtures with hexahydrophthalic anhydride hardener and benzyl dimethylamine catalyst produced transparent products exhibiting a two-phase co-continuous morphology. Prereacting the fluoroalkeneoxide prepolymers with an excess of epoxy resin prior to the addition of hardener and catalyst, resulted in opaque products displaying a two-phase dispersed particles morphology. The dynamic mechanical spectra of the cured products confirmed the absence of any significant short-range network miscibility and revealed substantial enhancements in β-relaxations in all cases, which are normally associated with microdispersed morphologies. Both systems exhibited much higher flexural strength and ductility than the equivalent unmodified epoxy resins, even at very low levels of addition, 3.5–5.0%. The surface energy was found to be much lower than that exhibited by the unmodified resin system, and the reduction in water absorption was relatively small. The above effects were much more pronounced for products exhibiting a particulate morphology than for systems that exhibited a co-continuous morphology. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Among the many endeavours over the last 20 years or so to enhance the performance of epoxy resins for use in advanced technologies, such as composites and structural adhesives, the two aspects that have predominated are the reduction in water absorption and the enhancement of toughness. The sorbed water plasticises the epoxide network, lowering the glass-transition temperature (T_g), and induces hydrolysis of ester groups. Both phenomena result in the deterioration of mechanical properties.[1-4]

The high cross-linking density of cured epoxy resins, on the other hand, suppresses the formation of crazes and reduces the extent of shear yielding, which are the two operative mechanisms for the development of ductility in glassy polymers.[5]

Role of Fluorine Substituents in Epoxy Resin Networks in Reducing Water Absorption

The hydrophobic nature of fluorine-containing polymers is well known and experience has shown that fluorocarbon polymers set the lower limit for water absorption and water vapour permeability. The chemistry of epoxy resins does not lend itself to the production of networks completely free of hydrophilic groups and consequently higher water sorption levels are to be expected irrespective of the degree of fluorine substitution.

In addition to the intrinsic chemical nature of epoxy resin networks there are morphological heterogeneities and microcracks that make an appreciable contribution to their hygroscopic behaviour.[6] Nevertheless the work pioneered on the synthesis

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of epoxy resins containing fluoro substituents in the oligomeric chains has demonstrated that reductions in water absorption by a factor of up to 10 can be achieved even with the use of conventional curatives, such as amines and anhydrides.[7-13]

Other investigators[14] have achieved similar results by using perfluorobutenyloxyphthalic anhydride as curing agents for a diglycidylether bisphenol A resin.

Hu et al.,[15] on the other hand, have used fluorinated aromatic isocyanates to cap the hydrophilic groups in the epoxide network, derived from the reaction of tetraglycidyl diamino diphenyl methane with diamino diphenyl sulphone, by diffusing the reagents into cast films after being swollen in dimethyl acetamide.

By reacting in solution an acid fluoride functionalised perfluoroligomer with a diglycidyl ether of bisphenol A, Rosser et al.[16] produced a prepolymer subsequently used to modify an epoxy/diaminodiphenyl sulphone resin matrix of a glass cloth composite. Although such a resin system contained dispersed particles of perfluoroether elastomer, an appreciable reduction in water uptake was obtained, which was attributed to the formation of solubilised fluorinated oligomeric species in the matrix layers surrounding the dispersed particles.

Toughness Enhancement of Epoxy Resins

The two approaches that have traditionally been adopted to increase the ductility of epoxy resins are by the addition of monofunctional modifiers to reduce the cross-linking density of the network and by the incorporation of flexible chains in the network. Both methods, however, result in a considerable decrease in the T_g of the cured products, which limits their use in high temperature environments.

More recently, great efforts have been placed in enhancing the toughness, without an appreciable deterioration in the T_g, through the development of a two-phase morphology consisting of small particles of rubbery or ductile particles dispersed in the epoxide matrix.

The systems that have received the greatest attention in the scientific literature are those exploiting the phenomenon of spinodal decomposition to precipitate rubbery particles during the gelation stage of the curing reactions. The best known examples are the systems that utilise carboxy- or amine-terminated butadiene acrylonitrile oligomers (CTBN or ATBN) dissolved in the epoxy resin and cured at a controlled rate to avoid the formation of monophase products consisting of flexibilised networks.[17-21]

The main weakness of epoxy resins toughened with butadiene-based telechelic oligomers is their poor resistance to oxidative environments caused by the deterioration of the elastomeric properties of the precipitated particles that ultimately become rigid and brittle as a consequence of the simultaneous occurrence of chain scission and cross-linking reactions.

It is for this reason that many attempts have been made to replace CTBN and ATBN with more stable oligomers. An example of these is to be found in the work on Banthia et al.[22] who have used various carboxy-terminated elastomeric acrylate oligomers in diglycidyl ether of bisphenol A. A two-phase precipitated particles morphology was obtained, and for the case of ethylhexyl acrylate oligomers the cured castings exhibited enhancements in impact strength comparable to similar systems based on ATBN. The search for functionalised oligomers for the production of toughened epoxy resins suitable for high temperature applications has also been the focus of attention of research workers in this area. For example Takahashi et al.[23] examined several amine-terminated silicone oligomers as toughening agents for epoxidised Novolac resins for use as incapsulants for semiconductor integrated circuit devices. For these applications siloxane oligomers offer other advantages, such as a much lower T_g for the dispersed rubbery particles and a reduction in thermal expansion of the cured resin.

The solubility of the silicone oligomers was found to increase when increasing the ratio of phenyl methyl siloxane units relative to dimethyl siloxane units in statistical copolymers. Total solubility in the epoxy resin was achieved, however, only in the case of phenyl methyl siloxane homopolymers that produced transparent, monophase, cured products. For other siloxane oligomers a two-phase morphology was observed in every case, but the dispersed particles became extremely small (i.e., about 0.01 μm) when the silicone oligomers were added to the resin as solutions in toluene.

The use of reactive perfluoroether oligomers by Rosser et al.,[16] mentioned earlier, illustrates the difficulty of achieving an initially monophase resin mixture when the solubility parameters of the oligomer and resin are considerably different, even if the two are forced to react with each other in solution. It is important to note that the increase in toughness obtained with these oligomers was relatively small, in the region of 30–70%. This can only be attributed

to the relatively low energy absorption character-istics of the dispersed particles, either because they did not have the opportunity to react fully with the epoxy resin or because once precipitated out of the solution, after evaporation of the solvent, they were not able to react with the Di-amino diphenyl sulphone (DDS) hardener to develop the required mechanical properties.

Another approach that has been frequently used to enhance the toughness of cross-linked polymers or to improve their damping characteristics, is through the formation of interpenetrating networks (IPN).

Sperling and Sarge[24] and Touhsaent et al.[25] simultaneously polymerised acrylate monomers by free radical initiation and epoxy resins by reactions with conventional curatives from an initially homogeneous mixture. They found that a two-phase morphology emerged, consisting of co-continuous dispersed rubbery domains, about 0.1–0.5 μm) within the epoxy resin that constituted the major phase. The dimensions of the dispersed rubber domains and the extent of molecular mixing between the two components were found to depend on the relative reaction rates in relation to the rate of phase separation. Better mechanical properties resulted when the extent of molecular mixing was minimised and a two-phase co-continuous morphology was obtained instead. Such dual continuity morphologies are often referred to as IPNs to denote the existence of fine interpenetrating phases.

From the foregoing discussion and, in particular, from the findings of Rosser et al.[16] it can be inferred that great benefits are to be expected by chain extending fluoroligomers to render them fully miscible and reactive with epoxy resins.

The aims of the present work were, therefore, to establish the nature and amount of chain extension required to achieve miscible systems and to determine the effects on the properties of cured epoxy resins.
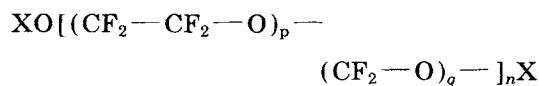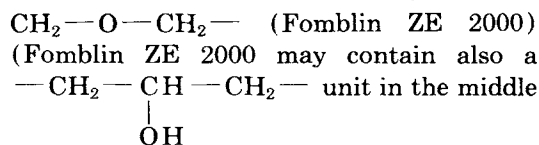
EXPERIMENTAL

Materials

The main materials used in this study were:

1. Functionalised fluoroalkeneoxide oligomers (available commercially under the trade name of Fomblin Z from Ausimont), whose

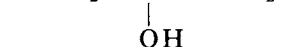chemical composition can be represented with the following formula:

$$XO[(CF_2 - CF_2 - O)_p -$$

$$(CF_2 - O)_q -]_nX$$

where X is either —CH$_2$OH (Fomblin ZDOL), (O — CH$_2$ — CH$_2$)$_{1-3}$ — OH (Fomblin ZDOL-TX), or $\begin{smallmatrix} CH_2 - CH_2 - \\ \backslash \quad / \\ O \end{smallmatrix}$

CH$_2$—O—CH$_2$— (Fomblin ZE 2000) (Fomblin ZE 2000 may contain also a —CH$_2$— CH —CH$_2$— unit in the middle $\;\;\;\;\;\;\;\;\;\;\;$ | $\;\;\;\;\;\;\;\;\;\;\;$ OH

of the chain); p/q molar ratio is approximately 1; n is in the region of 10–12, giving a number average molecular weight of approximately 2000.

2. Bisphenol-A epoxy resin, Epikote 828, manufactured by Shell Chemicals, having a molecular weight of approximately 370 and an average number of central —CH$_2$— CH —CH$_2$— $\;\;\;\;\;\;\;\;\;\;\;$ | $\;\;\;\;\;\;\;\;\;\;\;$ OH units in the region

of 0.13–0.15.

3. Hardener/catalyst system. An anhydride curing system was chosen to provide relatively slow cross-linking reactions, which could be accelerated by the addition of a tertiary amine catalyst. The hardener was hexahydrophthalic anhydride (HT 907, supplied by Ciba Geigy) and the catalyst was benzyldimethylaniline, obtained from Aldrich Chemicals.

Assessment of Miscibility of Fluoroalkene Oxide Oligomers in Epoxy Resins

A preliminary study was carried out to assess the miscibility of the fluoroalkene oxide oligomers under examination with different types of epoxy resins namely diglycidyl ether of bisphenol A (Epikote 828), cycloaliphatic resin (Araldite CY 179, supplied by Ciba Geigy), and tetraglycidyl diamino diphenyl methane (Araldite MY720, supplied by Ciba Geigy). The diglycidyl ether terminated fluoroligomer (Fomblin ZE2000) was chosen for this preliminary examination because it was expected to exert the greatest level of miscibility with the epoxy resins.
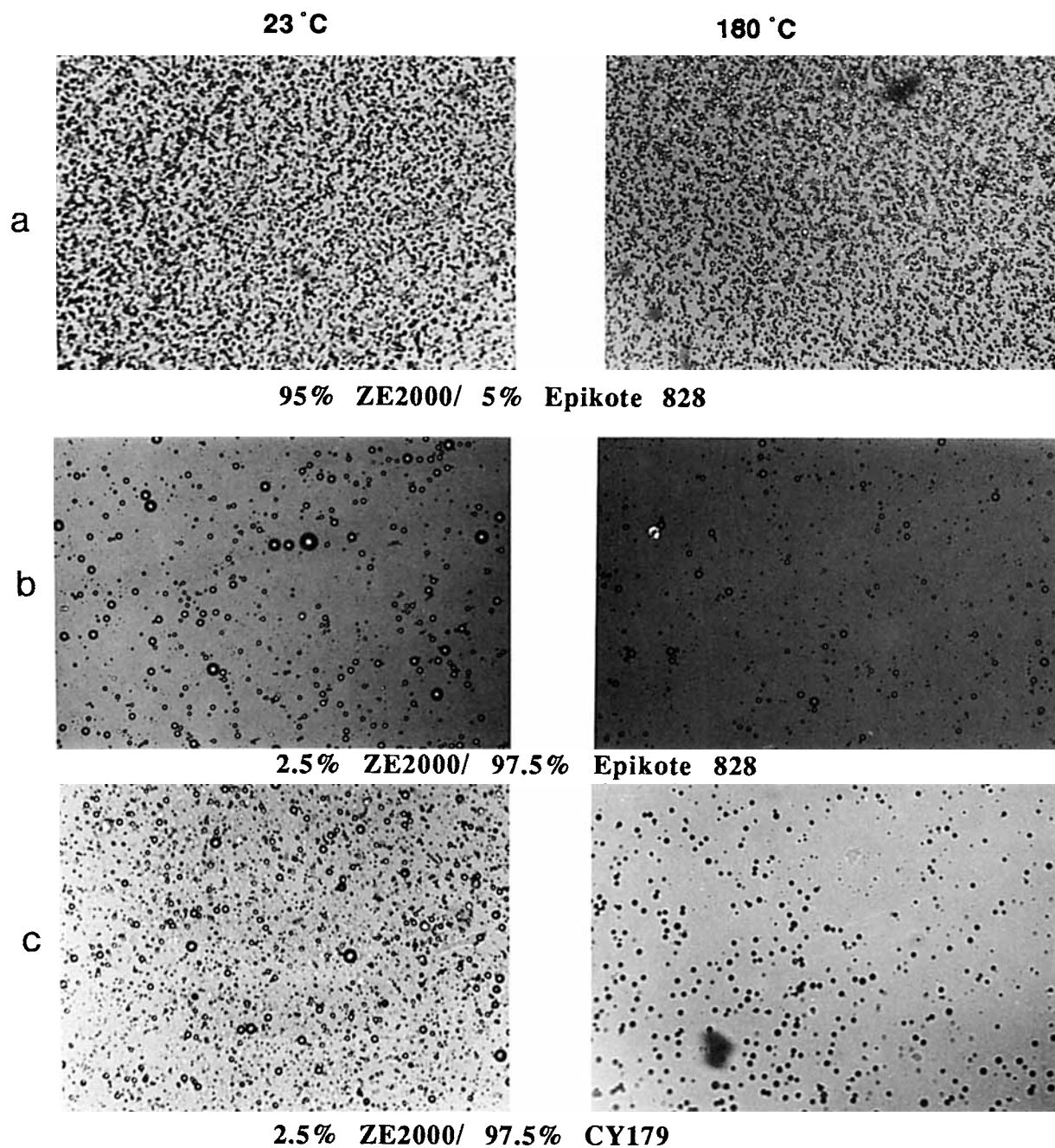
23 °C **180 °C**

95% ZE2000/ 5% Epikote 828

2.5% ZE2000/ 97.5% Epikote 828

2.5% ZE2000/ 97.5% CY179

Figure 1 Optical micrographs of mixtures of Fomblin ZE2000 and epoxy resins, taken at 23 and 180°C.

Binary mixtures were produced at the two extreme composition ranges, namely 2.5–5.0% and 95.0–97.5%, respectively, and were examined visually under a hot-stage optical microscope from room temperature to 180°C. These tests confirmed the total immiscibility of the fluoroligomers described earlier with conventional epoxy resins (Fig. 1).

Modification of Fluoroalkene Oxide Oligomers to Induce Miscibility in Epoxy Resins

In order to miscibilise the fluoroligomers in question with epoxy resins, a reaction scheme was devised to extend the oligomer chains with soluble telechelic segments. The scheme consisted of first reacting the fluoroligomer with an anhydride and then with ε-

caprolactone, in the eventuality that the first step alone would be insufficient to induce total miscibility. The reactions were to be carried out in bulk in order to avoid the use of chlorofluorocarbons that are normally required to dissolve the fluoroligomers in question.

The other advantages that arise from the scheme are: the elimination of the need to remove any residual (unreacted) anhydride from the modified oligomer because it would subsequently act as a hardener for the epoxy resin; and the relatively low boiling point of ε-caprolactone that allows it to be easily removed by vacuum extraction.

The anhydrides chosen for the end-capping reactions in the first step were chlorendic anhydride (i.e., 1,4,5,6,7,7'-hexachloro-5-norborene 2,3-dicarboxylic anhydride) and cis-hexahydrophthalic anhydride (both obtained from Aldrich Chemicals), as well as eutectic mixtures of the two anhydrides.

Chlorendic anhydride (CA) was chosen because of its high reactivity but it was presumed to be difficult to solubilise in view of its very high melting point (330°C). Such a difficulty would have been alleviated with the use of lower melting point eutectic mixtures with hexahydrophthalic anhydride (HHPA), which at 75% CA by weight were found to have a melting point in the region of 60°C.

Binary and ternary mixtures of the fluoroligomer and anhydrides were produced over a wide range of compositions and reacted by continuous stirring in an oil heated flask at 150°C for up to 9 h. Their appearance was examined visually at different time intervals, both at the reaction temperature and after cooling to room temperature. Those mixtures that were homogeneous, that is, completely transparent over the entire temperature range, were chosen to be tested for miscibility in mixtures of bisphenol A epoxy resin and HHPA and for subsequent chain extension reactions with ε-caprolactone. The latter reactions were carried out at 120°C under reflux conditions for various periods up to 6 h, followed by vacuum distillation to remove the residual (unreacted) ε-caprolactone. The production of "adducts" in the first step was made with molar ratios of fluoroligomer to anhydride of 1 : 1, 1 : 1.5, and 1 : 2, while for the production of the so-called "prepolymers" in the second step, the molar ratio of the fluoroligomer to ε-caprolactone was kept at 1 : 2, using a 10% excess ε-caprolactone. The viscosity of the reaction mixtures was measured with the aid of a Haake (Rhotovisco) cone-and-plate viscometer, over a range of shear rates at 60°C, in order to monitor the increase in molecular weight during the

course of the reaction, aiming to achieve total miscibility with epoxy resin/anhydride mixtures with the lowest possible increase in molecular weight of the fluoroligomer. The course of the reaction in the first step was also monitored by examining the FTIR spectra, focusing attention on the disappearance of OH groups and the appearance of ester groups.

Evaluation of Network Characteristics and Morphological Features of Systems of Epoxy/HHPA/Fluoroalkeneoxide Prepolymer

A series of transparent formulations containing different amounts of fluoroalkeneoxide prepolymer were produced at 120°C by mixing the prepolymer first with the epoxy resins and then with the HHPA component. The mixtures were cooled to room temperature and 1 phr catalyst Benzyldimethylaniline (BDMA) added and stirred for about 10 min. The mixture was degassed in a vacuum oven at 80°C for 30 min to remove the entrapped air and then cast into the cavities of a Polytetrafluoroethylene (PTFE) mould to produce specimens $150 \times 12 \times 2.5$ mm thick. The resin mixtures were then cured for 24 h at 120°C and postcured for 3 h at 150°C and 1 h at 180°C.

Similar formulations were also used to produce opaque, dispersed particle systems following the procedure normally used for epoxy/CTBN systems.

Mixtures of bisphenol-A epoxy resin and prepolymer, at 2 : 1 and 4 : 1 weight ratios, containing 1 phr triphenylphosphine (TPP) as catalyst, were heated at 85°C for different times up to 6 h to produce epoxy-extended prepolymers. These two-phase, particle dispersed formulations are referred to as System A.

In an attempt to facilitate the nucleation of the dispersed particles during curing the prepolymer was first reacted with the maximum possible amount of glycidoxyfluoroalkene oxide oligomer (Fomblin ZE 2000), corresponding to 20% of the total prepolymer, without impairing its solubility in the epoxy/anhydride mixture. The mixture of the glycidoxyfluoroligomer and the prepolymer was mixed with 1 phr TPP and heated for various periods of time prior to the addition of the epoxy resin for the preparation of the epoxy-extended prepolymer. These nucleation enhanced formulations are referred to as System B.

The course of the reaction was again followed by measuring the viscosity at 60°C and by visual examination to observe the development of cloudiness or major precipitations through cross-linking reactions. Samples of the reaction mixtures were taken

Table I   Appearance of Hydroxy-Terminated Fluoroligomer/Anhydride Mixtures (1 : 1.5 Molar Ratio) at 150 and 25°C After Different Reaction Times at 150°C

Reaction Time	0 min	10 min		30 min		1 h		6 h	
Temperature (°C)	25	150	25	150	25	150	25	150	25
Fomblin ZDOLTX/hexahydrophthalic anhydride	O	T	T	T	T	T	T	CL	CL
Fomblin ZDOL/hexhydrophthalic anhydride	O	O	O	O	O	T	O	T	T
Fomblin ZDOLTX/chlorendic anhydride	O	O	O	O	O	T	T	T	T
Fomblin ZDOL/chlorendic anhydride	O	O	O	O	O	O	O	O	O
Fomblin ZDOL/(75% chlorendic anhydride + 25% hexahydrophthalic anhydride)[a]	O	O	O	O	O	O	O	O	CL

O, opaque (dispersed particles morphology); T, transparent (fine co-continuous morphology); CL, cloudy (some particle precipitation).
[a] *Note:* The system became transparent at both 150 and 25°C after 9 h.

at different time intervals and mixed at 120°C with HHPA and additional quantities of epoxy resin to obtain the desired concentration of fluoroalkene oxide prepolymer in the final mixture.

Following the same procedure used for the production of transparent systems, the mixtures were catalysed with 1 phr BDMA and cured in PTFE moulds to produce suitable testing specimens, followed by two postcuring steps outlined previously.

The course of particle formation and growth during curing was followed using a hot-stage optical microscope at 120°C, with the samples placed between glass slides; the gelation reactions were studied by performing isothermal scans using DSC at the same temperature.

The morphology of both transparent and opaque cured formulations was examined on fractured surfaces using a Cambridge (360 Model) stereoscan electron microscope (SEM). An energy dispersive X-ray analysis was performed during the SEM examination in an attempt to determine the distribution of fluorine in the two phases. The micrographs were subsequently used to analyse the mor-

phology, the fracture characteristics, and the domain dimension of the dispersed phase, as well as their volume fraction.

Using a Riechart MeF2 instrument, fitted with a standard 136° face angle indentor, the Vickers microhardness was measured on the fractured surfaces of the specimens to record values for both matrix and dispersed domains, wherever applicable and possible.

Physical Properties of the Cured Systems

In order to establish the relationships between composition, morphology, and physical properties, several tests were performed to separate the effects related to chemical modifications of the network of the epoxy resin from those resulting from morphological differences.

Surface Energy Measurements

The surface energy of cured systems was obtained from measurements of the contact angle formed with

Table II   Physical Appearance of Hydroxy-Terminated Fluoroligomer Acid Anhydride Reaction Mixtures After 6 h at 150°C

Fluoroligomer/Anhydride Molar Ratio	1 : 1		1 : 1.5		1 : 2	
Temperature (°C)	25	150	25	150	25	150
Fomblin ZDOL + chlorendic anhydride	O	T	O	O	O	O
Fomblin ZDOLTX + chlorendic anhydride	T	T	T	T	O	T[a]
Fomblin ZDOL + chlorendic anhydride (75%) + hexahydrophthalic anhydride (25%)	T	T	T	T	O	O

O, opaque, T, transparent.
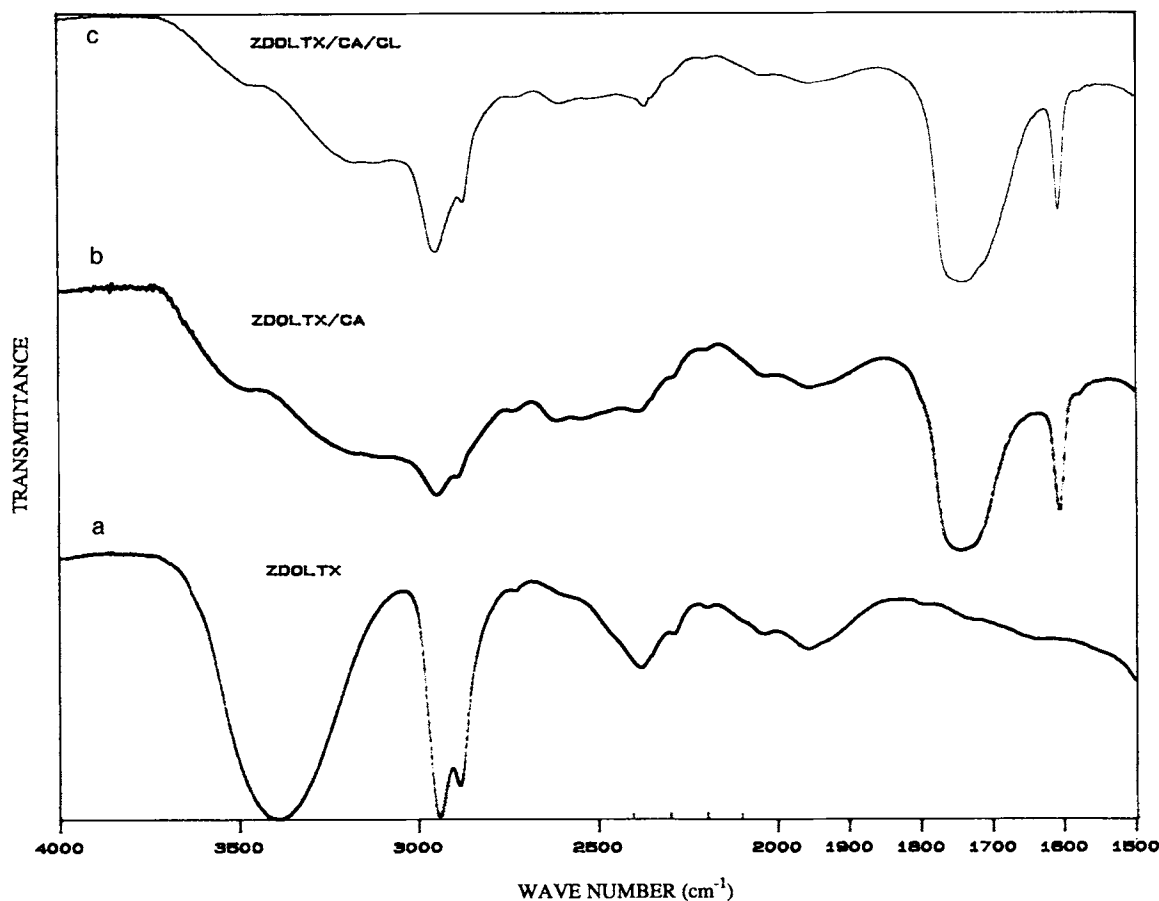[a] Turns cloudy as it cools down to room temperature.

Figure 2 FTIR spectra for the telechelic fluoroligomer: (a) initially (ZDOLTX); (b) after reaction with chlorendic anhydride (ZDOLTX/CA); (c) after subsequent reaction with ε-caprolactone (ZDOLTX/CA/CL).

the surface of the solid specimens by the sessile drop of a series of pure liquids of known surface tension, using the Krauss G40 goniometer.

The liquids used were, respectively: triple distilled water; ethane 1,2 diol; dimethyl sulphoxide; and dimethyl formamide. The surface energy was obtained by Zisman plots, that is, cosine of the equilibrium contact angle against surface energy of the liquid. The extrapolated value for the surface energy of the liquid for contact angle equal to zero (i.e., cos θ = 1), corresponding to thorough wetting conditions was taken as being equal to the surface energy of the solid substrate.

To find out whether surface energy changes resulted from bulk modification of the structure or from surface enrichment phenomena through migration of unreacted fluoroligomer fractions, contact angle measurements were made on both outer surfaces, air/solid and PTFE/solid, and on a sectioned surface from the middle, solid/solid.

Water Diffusion Measurements

Sorption isotherms were constructed by measuring the water uptake of specimens, 25 × 12 × 2.5 mm, immersed in distilled water at 85°C up to saturation. The diffusion coefficient, D, was calculated from the initial slope (K) of the plots of water uptake (percent weight increase) against square root of immersion time (hours), that is,

$$D = \frac{\pi}{3600} \left(\frac{bK}{4W_\infty} \right)^2$$

where b = thickness of the specimen (cm), W_∞ = percent weight increase of specimen at saturation, D = diffusion coefficient (cm^2/s).

Dynamic Mechanical Spectra Determinations

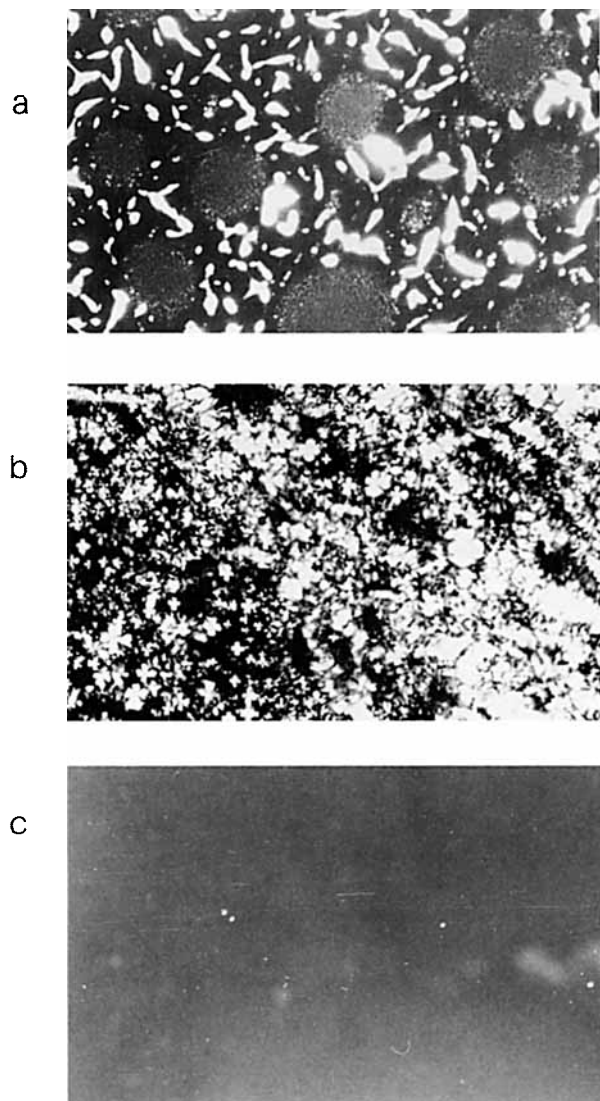Dynamic mechanical tests were performed with the aid of a Du Pont DMA-983 instrument, over the

Figure 3 Optical micrographs of reaction mixture for the preparation of prepolymer 'Prep TX' (i.e., 1 ZDOLTX/1.5 CA/2 CL) at different stages: (a) initially; (b) after 1 h at 150°C; (c) after 6 h at 150°C.

temperature range −100 to +180°C with a temperature ramp of 10°C/min at a test frequency of 1 Hz, using specimens 25 × 12 × 2.5 mm. The traces obtained for the loss modulus against temperature were used to analyse the molecular relaxations for the microstructural entities of the material under examination.

Flexural Tests

Flexural strength, modulus, and strain at break for the cured samples were measured at room temper-

ature with the aid of a J. J. Lloyd tensile testing instrument, using specimens 60 × 12 × 2.5 mm, freely supported in a three-point bending jig with span:thickness ratio of 16 : 1 and a crosshead speed of 10 mm/min in accordance with the ASTM D790 procedure. No corrections were made for excessive deflections that may have caused deviations from the standard formulae used for elastic behaviour.

Adhesion Tests

The strength of the bond of the modified epoxy resins to mild steel was measured, in accordance with the ASTM D897 procedure, by using flat-end cylindrical specimens, 25 mm in diameter, joined together with the resin cured under the same conditions as the cast specimens. Ballotini spheres, 0.2 mm in diameter, were added to the resin at 2% concentration as a means of achieving constant thickness for the adhesive layer. The joint between the cylindrical adherents was stressed to rupture in tension using an Instron universal testing machine (model TT-DM). The bond strength was calculated from the ratio of the breaking force to the cross-sectional area of the adherent.

RESULTS AND DISCUSSION

Reactivity of Hydroxyl-Terminated Fluoroalkeneoxide Oligomers with Anhydrides

The visual appearance of HHPA, CA, and 25/75 eutectic mixtures of the two anhydrides after reacting with the two hydroxy-terminated fluoroalkeneoxide oligomers under examination (i.e., Fomblin ZDOL and Fomblin ZDOL-TX) for different periods of time at 150°C is shown in Tables I and II. The results indicate that the most soluble combinations are Fomblin ZDOL-TX with HHPA and the most insoluble systems are the combinations Fomblin ZDOL with CA. The eutectic mixtures of the two anhydrides exhibit an intermediate behaviour. The extent of reaction between the different combinations of anhydride/hydroxy-terminated fluoroligomer could not be quantified but in all cases the FTIR spectra revealed clearly a depression of the absorption band at 3400–3500 cm^{-1} corresponding to free OH groups and the appearance of a band at 3000–3200 cm^{-1} corresponding to the stretching of OH bonds from the newly formed COOH groups (Fig.

Table III Composition of Prepolymers Based on Hydroxyl-Terminated Fluoroalkene Oxide Oligomers (Fomblin, ZDOLTX, and ZDOL)

| | Prepolymer Formulations (wt %) | | | |
| | Based on Fomblin ZDOLTX | | Based on Fomblin ZDOL | |
Ingredients	Prep 1	Prep 2	Prep 3	Prep 4
Fomblin ZDOLTX	71.93	81.33	—	—
Fomblin ZDOL	—	—	81.33	74.15
Chlorendic anhydride	19.85	—	—	—
Hexahydrophthalic anhydride (HHPA)	—	9.39	9.39	—
75% CA/25% HHPA	—	—	—	17.48
ε-Caprolactone	8.20	9.27	9.27	8.44

Note: These "prepolymers" were produced by making first the "adduct" with molar ratio Fomblin/anhydride 1/1.5 and then reacting the "adduct" with ε-caprolactone, so that the final molar ratios were Fomblin 1/anhydride 1.5/ε-caprolactone 2.

2). The ratio of the height of the absorption peak at 2390 cm^{-1} (an invariant peak) to that at 3400 cm^{-1} was found to decrease from the original value of 2.3 for the unmodified fluoroligomer to 0.87 after the reaction with CA and then to 0.78 after the subsequent reaction with ε-caprolactone. The latter confirmed that the reaction with CA at molar ratio of 1 : 1 and 1 : 1.5 had reached completion. The reaction mixture at 1 : 2 molar ratio, on the other hand, becomes opaque on cooling due to the precipitation of unreacted CA (Table II).

When the above anhydride adducts were mixed with the bisphenol A epoxy resin only those based on combinations of ZDOL-TX with CA were found to be soluble after prolonged heating at 150°C. This indicated that solubilisation occurred through chemical reactions of the terminal acid groups with the epoxy resin, often resulting in cross-linked products before achieving complete solubilisation.

Characteristics of Fluoroalkeneoxide Prepolymers Produced Through Chain Extension of Adducts with ε-Caprolactone

Figure 3 illustrates the gradual solubilisation of ε-caprolactone in the adduct (1 ZDOL-TX : 1.5 CA) with increasing time of reaction.

Table IV Compatibility of Prepolymers With Epoxy Resin (Epikote 828) at Room Temperature

| | Reaction Time[a] (h) | | | | | | |
| | Prep 1 | | Prep 2 | | Prep 3 | | Prep 4 |
Prepolymer/Epoxy Resin Ratio	1 + 1	1 + 6	1 + 1	1 + 6	1 + 1	1 + 6	6 + 6
10/90	C	C	NC	C	NC	C	C*
20/80	C	C	NC	NC	NC	NC	C*
30/70	C	C	NC	NC	NC	NC	C*
40/60	C	C	NC	NC	NC	NC	C*
50/50	C	C	NC	NC	NC	NC	C*
60/40	C	C	NC	NC	NC	NC	NC
70/30	C	C	NC	NC	NC	NC	NC
80/20	C	C	NC	NC	NC	NC	NC
90/10	C	C	NC	NC	NC	NC	NC

C, compatible; NC, noncompatible; C*, compatibility at high shearing. Prepolymers as described in Table III.

[a] $X + Y$ hours, means X hours reaction time for the adduct (i.e., Fomblin with anhydride) and Y hours reaction time for the prepolymer (i.e., adduct with ε-caprolactone).
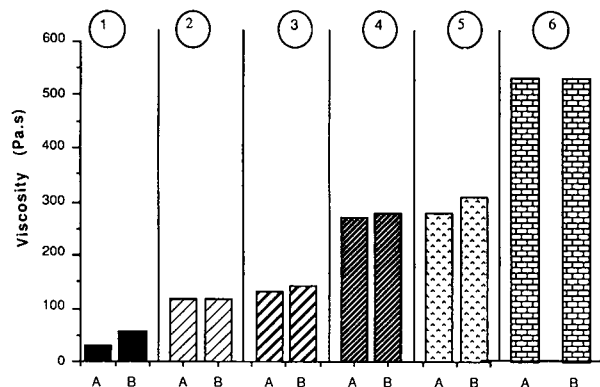
Figure 4 Viscosity of various reaction mixtures (a) fluoroalkene oxide oligomer/chlorendic anhydride (TX/CA) and (b) subsequently reacted with ε-caprolactone (TX/CA/CL). ①1 TX/1 CA; ②1 TX/1 CA/2 CL; ③1 TX/1.5 CA; ④1 TX/1.5 CA/2 CL; ⑤1 TX/2 CA; ⑥1 TX/2 CA/2 CL. A, after 6 h at 150°C; B, after 6 h at 150°C and subsequently stored for 3 months at room temperature.

The composition of four prepolymers produced from various adducts at molar ratio fluoroligomer/anhydride 1 : 1.5 and adduct/ε-caprolactone 1 : 2 is shown in Table III. Their respective miscibility in the bisphenol A epoxy resin is shown in Table IV for two different reaction times used in the preparation of the adduct and subsequent prepolymer.

From the observations in Table IV it is clear that only the prepolymers produced from CA-based adducts were completely miscible with epoxy resins at room temperature. The partial replacement of CA with HHPA in the 75/25 eutectic mixture considerably reduced the solubility of the resulting prepolymer.

Combining these observations with the qualitative interpretation of the FTIR spectra it is inferred that only CA has sufficient reactivity for the esterification of the terminal OH groups of the fluoroalkeneoxide oligomers and that, in particular, the extension of the methylol ligament at the chain end with short ethylene oxide segments assists the solubilisation of the surface layers of the CA particles to speed up the reaction.

The data in Figure 4 show that increasing the molar ratio of fluoroligomer/CA from 1 : 1 to 1 : 2 produces the expected increase in molecular weight and that the subsequent reaction with ε-caprolactone results in a further two-fold increase in viscosity, which corresponds to an approximate equivalent increase in molecular weight. (Note that viscosities were essentially Newtonian.)

Attempts to obtain a more accurate estimate of molecular weights by GPC measurements were aborted to avoid running the risk of clogging up the column with insoluble fluoroligomer tails that may have been present in the reaction mixture.

The loss of weight after vacuum distillation at the end of the reaction was in the region of about 5–10% of the total amount of ε-caprolactone used and, therefore, it can be assumed that the reaction went almost to completion.
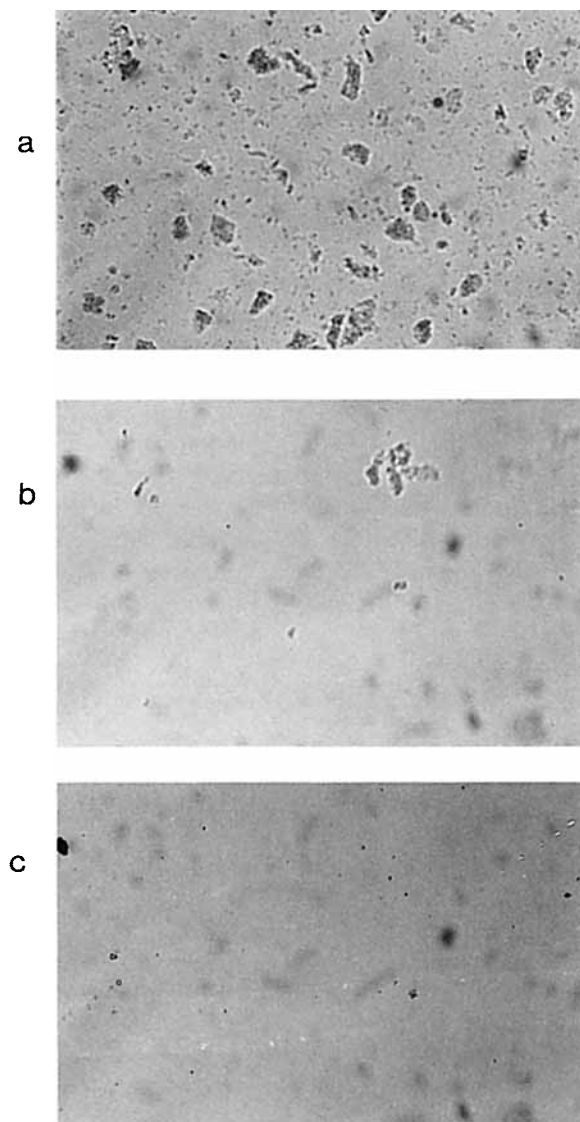

Figure 5 Optical micrographs for transparent formulations at various stages: (a) initially at room temperature; (b) after 2 min at 120°C (still fluid); (c) after 4 min at 120°C (gelled).
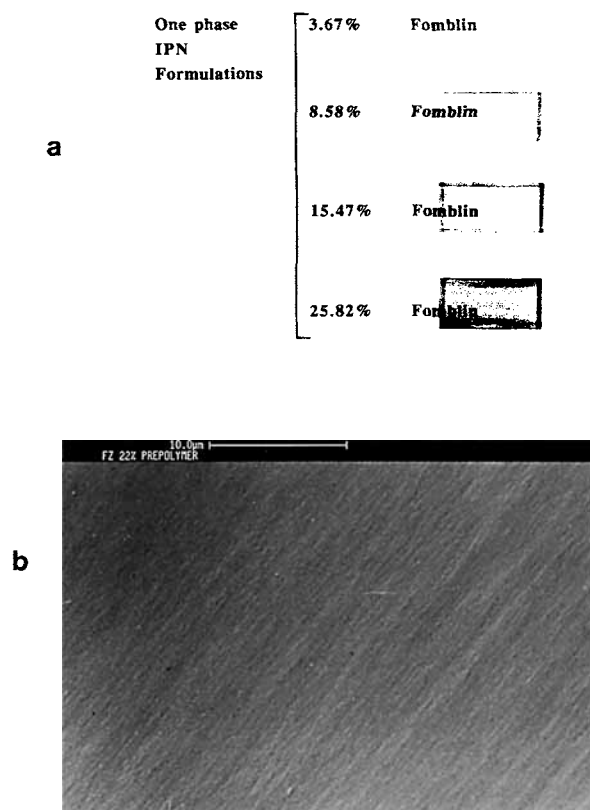
One phase
IPN
Formulations

3.67%   Fomblin

8.58%   Fomblin

15.47%   Fomblin

25.82%   For...

a

b

Figure 6 Appearance of transparent co-continuous phases formulations: (a) photograph of specimens (24 × 12 × 2 mm); (b) SEM micrograph of formulation containing 22% prepolymer 'Prep TX'.

The absence of any changes in viscosity of the prepolymers after 3 months storage at room temperature (see Fig. 4) provided further evidence that the reactions were advanced to their equilibrium conditions.

Because there are on average approximately 25% free OH groups left over in the first reaction (for the preparation of the adduct), the nearly two-fold increase in molecular weight obtained in the second reaction (for the preparation or the prepolymer) suggests that both OH and COOH groups take part in the reaction with ε-caprolactone and that the approximately two-fold increase in molecular weight results from reactions of the COOH groups of the monoesterified CA with the OH groups of the hydroxy caproic ester segments at the other end of the fluoroligomer chains. This is supported by the further suppression of the absorption band associated with free OH groups in the second reaction (Fig. 2).

The failure to miscibilise the prepolymers obtained from mixtures with HHPA in the epoxy resin is, therefore, due to the low reactivity of HHPA to-

wards the OH end groups in the fluoroligomer, thereby preventing the formation of the required ligaments for the ε-caprolactone in the second reaction.

Morphology Development During Curing

The micrographs in Figure 5 obtained with the use of the hot-stage optical microscope for transparent formulations, that is, simultaneous reactions of the hardener and prepolymer with the epoxy resin, have revealed the presence of substantial quantities of crystalline HHPA in the mixture. Upon heating to the curing temperature the HHPA crystals redissolved almost completely in the resin apart from some diffused microdomains that remained entrapped as the resin gelled. On subsequent curing these microdomains were no longer visible and were replaced by extremely fine lamellae that appear to have resulted from a spinodal separation of the fluoroligomer component (Fig. 6).

The mixture of epoxy-extended prepolymer with HHPA and additional amounts of epoxy resin, on the other hand, displayed a very large number of nuclei that grew in size and new ones were formed as the reactions reached gelation (Fig. 7). The precipitated particles assumed a distinct heterogeneous morphology similar to W/O/W (water/oil/water) systems observed in multiple emulsions[26] (see Figs. 7(d), 8). The energy dispersive X-ray analysis on fracture surfaces confirmed that the fluoroligomer resided primarily within the precipitated particles (Fig. 9).

It is postulated that the formation of the fine microdomains within the primary particles is the result of further precipitation of the less soluble fluoroligomer fractions present in the prepolymer, which is being accelerated by the inward diffusion of HHPA hardener from the surrounding matrix in order to minimise the concentration differential between the two phases. It is envisaged that the migration of HHPA molecules into the particles causes the gelation of unreacted epoxy resin thereby promoting a further spinodal decomposition within the particles. The outer migration of the fluoroligomer species from the precipitated particles into the matrix is prevented, on the other hand, by their rather low diffusivity because they are present in the form of highly branched/lightly cross-linked species. The sharp boundary between matrix and precipitated particles arises from the vast difference in surface energy between the two phases. The distribution of white dots in Figure 9 provides direct evidence for the predominance of fluorine in the dispersed par-
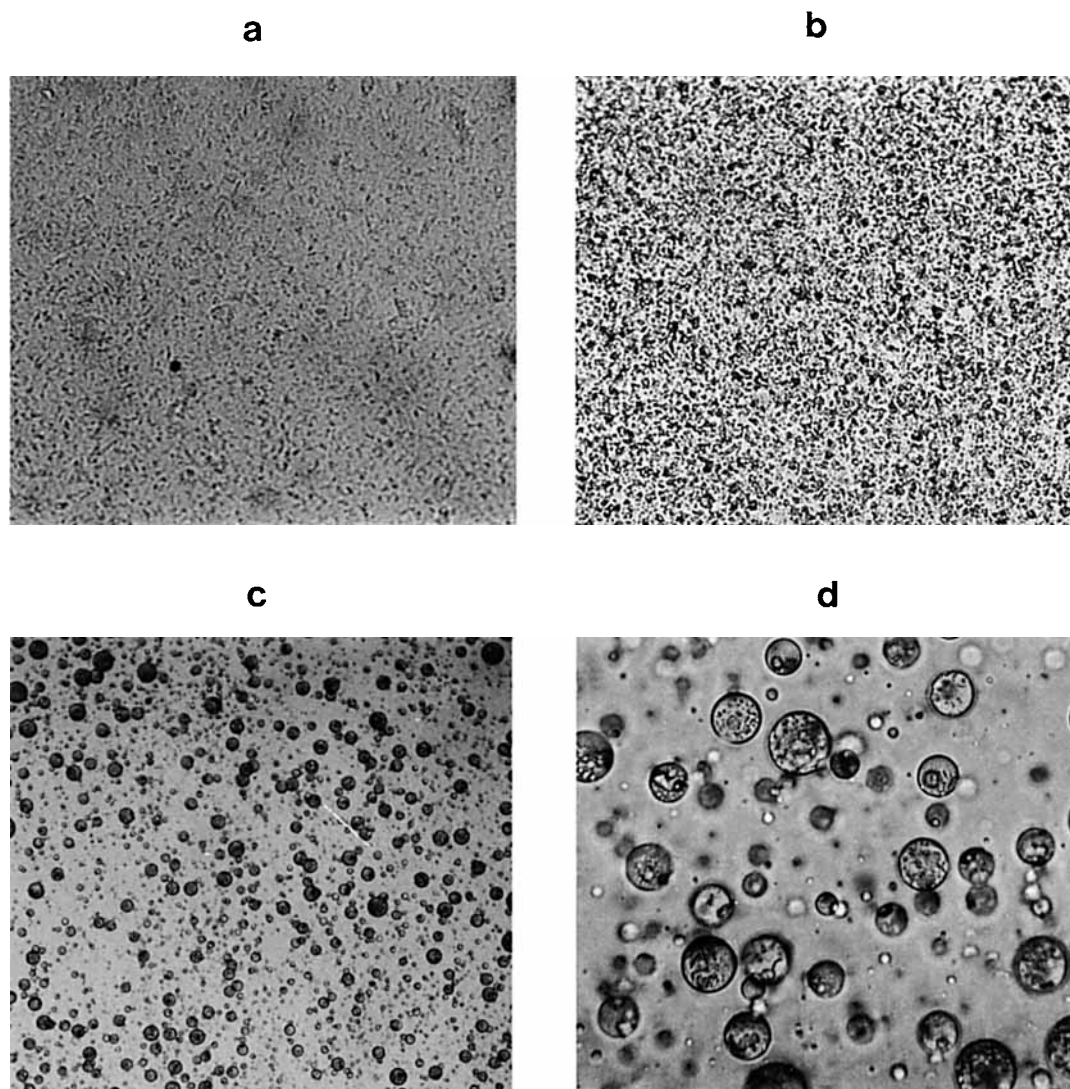
a

b

c

d

Figure 7 Optical micrographs of particulate morphology formulations showing the nucleation and growth of the dispersed phase (System A, containing prepolymer 'Prep TX' with 3.67% Fomblin ZDOLTX): (a) initially at room temperature (×400); (b) after 2 min at 120°C; fluid system (×400); (c) after 4 min at 120°C; gelled system (×400); (d) after 4 min at 120°C; gelled system (×800).

ticles and reveals the existence of a high concentration of fluorine in the outer layers of the primary particles. This is indicative of a thermodynamic drive for the fluoroligomer species to diffuse out of the precipitated particles against unfavourable kinetic conditions. The more diffuse presence of fluorine in the areas surrounding the main particles is believed to be associated with the dispersive X-ray emission from smaller particles and from those below the surface examined.

Microhardness measurements (see Fig. 10) have shown that the matrix exhibits the same Vickers

Hardness value as the control samples, that is those not containing the fluoroligomer prepolymer, but for the dispersed particles the hardness is about half the value exhibited by the surrounding matrix (i.e., approximately 200 and 100 N/mm^2, respectively). These data and the permanent microindentation imprinted on the particles (Fig. 10) confirm that the dispersed phase is not elastomeric in nature but it exhibits a substantially lower cross-linking density than the surrounding matrix. An approximate estimate of the volume fraction, based on the cross-sectional area of the fractured particles, indicates
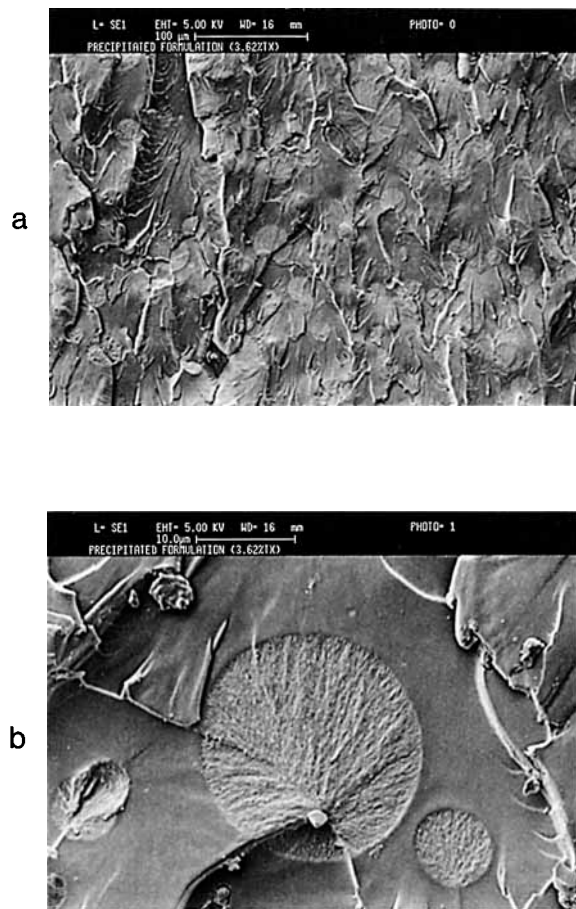
Figure 8 SEM micrographs of fractured surfaces of cured opaque particulate morphology formulations (System A, containing prepolymer 'Prep TX' with 3.62% Fomblin ZDOLTX).

that this is about 50–75% higher than the amount of prepolymer used in the formulation, thereby confirming the presence of large amounts of epoxy resin and HHPA in the precipitated phase.

In examining the micrographs of the dispersed particles of System B formulations, one notes that the addition of higher molecular weight and less soluble fluoroligomer produces a finer microstructure (Fig. 11).

Surface Energy and Water Diffusion

The surface energy values calculated from the advancing contact angle for both co-continuous phases (transparent) and precipitated particles (opaque) systems are reported in Table IV. A very large reduction in surface energy is observed for both systems containing the miscibilised fluoroligomer. It is

evident that this does not result from the possible migration of the fluoroligomer to the surface. Furthermore it is to be noted that this is achieved even with small amounts of fluoroligomer (i.e., 3.5% corresponding to ca. 5% chain extended prepolymer) and that the reduction in surface energy is greater for particle precipitated systems than for co-continuous morphology formulations. This is surprising and may be related to the heterogeneous nature of the surface of the samples with a particulate morphology.

Pilati et al.[27] have shown, however, that block copolyesters based on similar telechelic fluoroligomers exhibited considerable enrichment of fluorinated species in the outer layers of the samples. The extent of such an occurrence was found to depend on the amount of unreacted fluoroligomer present in the sample.

The water diffusion coefficients at 85°C shown in Table VI appear to confirm the same trend as for surface energy data, that is, the particle dispersed systems exhibit slightly lower diffusion rates. These data are affected, however, by differences in network density and are not very accurate in view of the considerable deviation from Fickian behaviour, which was noted particularly for the particle dispersed systems.

Mechanical Properties

The results of the flexural tests are shown in Table VII. These show that the addition of up to about 15% fluoroligomer, corresponding to about 20% prepolymer, reduces the flexular modulus by a maximum of about 20% while the flexural strength increases substantially, up to about 80% in some cases. It is noted that the transparent co-continuous phase systems exhibit overall higher flexural strength and modulus than the opaque particulate morphology systems. The largest benefits resulting from the addition of the miscibilised fluoroligomer are derived with respect to ductility, the particulate morphology systems showing the largest increase in strain at break. The higher values shown for System B in Table VII are underestimated because the specimens did not fail and the values shown correspond to the bending strain experienced by the specimen as they were forced through the support without breaking.

Dynamic Mechanical Spectra

The DMA traces for the variation of the loss modulus with temperature for the transparent co-con-
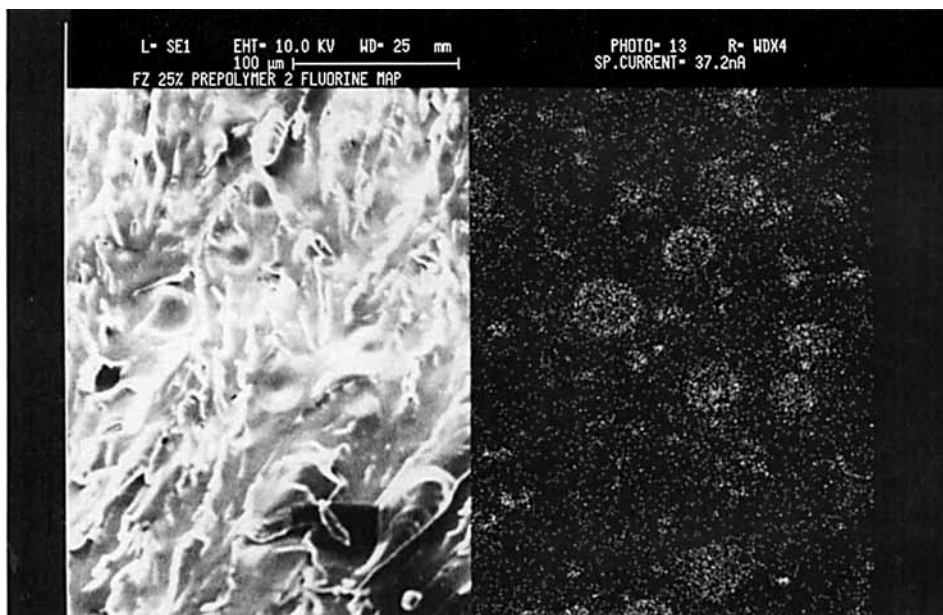
Figure 9 Energy dispersive X-ray analysis of a fractured surface of a two-phase formulation (System A, 5.67% Fomblin ZDOLTX), showing the distribution of fluorine.

tinuous morphology and the opaque particle dispersed systems are shown in Figures 12 and 13, respectively. The traces for both particle precipitated systems A and B were quite similar, hence only one is being shown. An examination of these spectra reveals a large reduction in the height of the α-peak with increasing concentration of fluoroligomer for the co-continuous morphology systems, and small downward shift in the α-transition temperature for the particle dispersed systems without any appreciable changes in the height of the peaks. A small increase in the α-transition temperature is observed for the co-continuous morphology systems at low concentrations of fluoroligomer. These findings are

in good agreement with the observations reported for similar systems that have been referred to as IPNs.[28] In particular it is worth noting that the microheterogeneity of these systems is the main cause for the broadening of the damping peaks that are, in turn, responsible for their enhanced energy absorption characteristics.

A comparison of the change in the height of the α-peak with concentration of fluoroligomer for both systems is shown in Figure 14, and the corresponding variation of the glass transition temperature (T_g) is

Figure 10 SEM micrographs of the fractured surface of a typical opaque particulate morphology formulation (System B) after microhardness measurements.
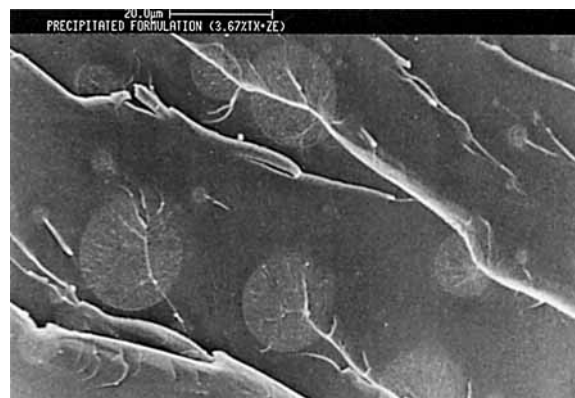

Figure 11 SEM micrographs of fractured surfaces of cured opaque particulate morphology formulations (System B, containing glycidoxyfluoroalkene in the prepolymer, 3.67% total fluoroligomer content).

Table V   Surface Energy of Epoxy Resin (Control) and Fluoroligomer Modified Cured Formulations

	Fomblin Content (wt %)	Surface Energy (mN/m²)
Control	0	30.3
Co-continuous morphology systems	3.5	20.8
	25.8	16.7
Particulate morphology, System A	3.5ᵃ	15.1
	3.5ᵇ	14.9
	3.5ᶜ	15.5

ᵃ Measurements on the top surface of the casting.
ᵇ Measurements on the bottom surface of the casting.
ᶜ Measurements on the ininer surface of sectioned casting.

shown in Figure 15 as are the theoretical T_g values calculated according to the Gordon–Taylor equation for fully miscible mixtures. The much larger T_g values found in all cases over those expected from plasticised networks provide strong evidence for the heterogeneous nature of both systems. The larger reduction in T_g for the precipitated particles systems in relation to co-continuous morphology systems could arise from differences in the repartition of the BDMA catalyst, which would affect the epoxide network density, and from the possible solubilisation of some oligomeric species. In other words the precipitation of particles of epoxy-extended prepolymer in the particulate morphology system could drag behind substantial amounts of BDMA through associations with the activated species in the prepolymer.

It is remarkable, on the other hand, that very little difference was revealed in the mechanical spectra of the two systems at temperatures below the α-transition. Both systems were found to exhibit a large increase in loss modulus without any obvious changes in the position of the very broad β-transition. This type of behaviour has been attributed by Takahama and Geil[29] to the presence of microheterogeneities.

CONCLUSIONS

From the results and discussion in the foregoing sections, the following main conclusions can be derived:

1. Hydroxy-terminated fluoroalkeneoxide oligomers can be readily miscibilised with epoxy resins through esterification reactions with chlorendic anhydride and subsequent chain extension with ε-caprolactone to produce carboxy-terminated prepolymers.
2. These chain extended prepolymers are only capable of forming aggregate solutions in epoxy resins and, therefore, will produce a fine co-continuous morphology in cured products.
3. Particulate morphologies by particle precipitation and growth can be produced by conventional procedures involving catalysed prereactions of the carboxy-terminated fluorinated prepolymer with an excess epoxy resin.
4. Particle dispersed two-phase systems exhibit lower surface energies than equivalent co-continuous morphology systems, such a dif-

Table VI   Summary of Water Absorption Data for Epoxy Resin (Control) and Fluoroligomer Modified Cured Formulations

	Fomblin Content (wt %)	W (%)	k (% h^{1/2})	D (×10⁸ cm²/s)
Control	0	1.07	0.135	0.43
Co-continuous morphology systems	3.65	1.11	0.148	0.45
	8.58	1.05	0.164	0.53
	15.47	1.03	0.163	0.53
	25.82	1.04	0.150	0.49
Particulate morphology, System A	3.66	1.27	0.141	0.37
	5.63	1.26	0.141	0.38
Particulate morphology, System B	3.65	1.36	0.153	0.38
	5.60	1.37	0.158	0.39

W, weight gain after 466 h; k, initial slope of graph W versus $t^{1/2}$, that is, up to 17 h; D, diffusion coefficient.

Table VII Mechanical Properties of Cocontinuous and Particulate Morphology Epoxy Formulations

	Modulus at 1% Strain (GPa)	Flexural Strength (MPa)	Flexural Strain at Break (%)
Control	3.37 ± 0.25	76.1 ± 3.9	2.654 ± 0.30
Co-continuous phases formulations			
3.65% fluoroligomer	2.31 ± 0.16	131.7 ± 15.1	2.90 ± 0.50
8.58% fluoroligomer	2.71 ± 0.41	127.6 ± 20.7	3.60 ± 0.60
15.47% fluoroligomer	2.80 ± 0.20	107.6 ± 10.1	3.00 ± 0.10
Particulate morphology formulations			
3.65% fluoroligomer			
System A	2.50 ± 0.25	94.1 ± 6.5	5.08 ± 1.12
System B	2.40 ± 0.33	133.2 ± 3.5	8.09 ± 1.30
5.63% fluoroligomer			
System A	2.16 ± 0.17	98.4 ± 13.5	7.37 ± 1.7
System B	2.27 ± 0.18	105.0 ± 6.8	6.88 ± 1.0

ference also being reflected in their water diffusion behaviour.

5. Both co-continuous phase systems and particle-dispersed formulations exhibit higher flexural strength and ductility than the equivalent unmodified resins. Similar improvements are observed also with respect to the adhesive bonding against mild steel, despite the lower surface energy of the modified resins.
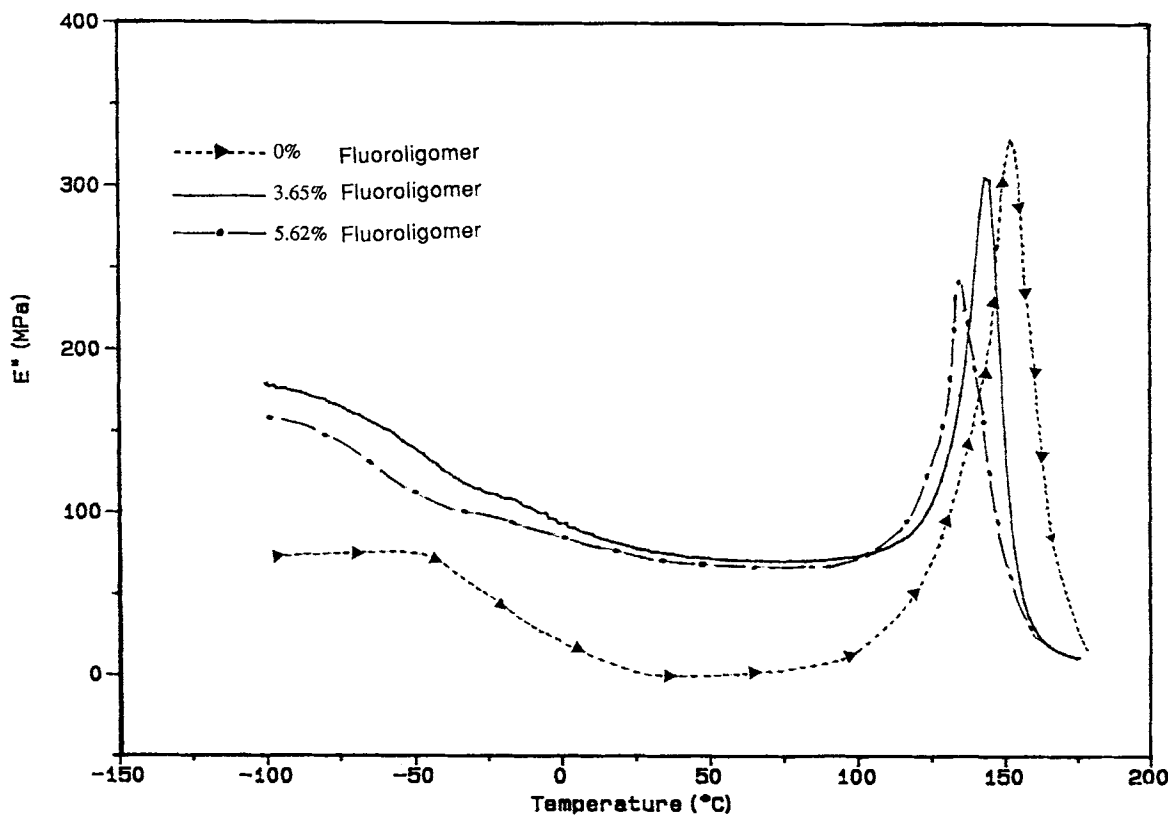

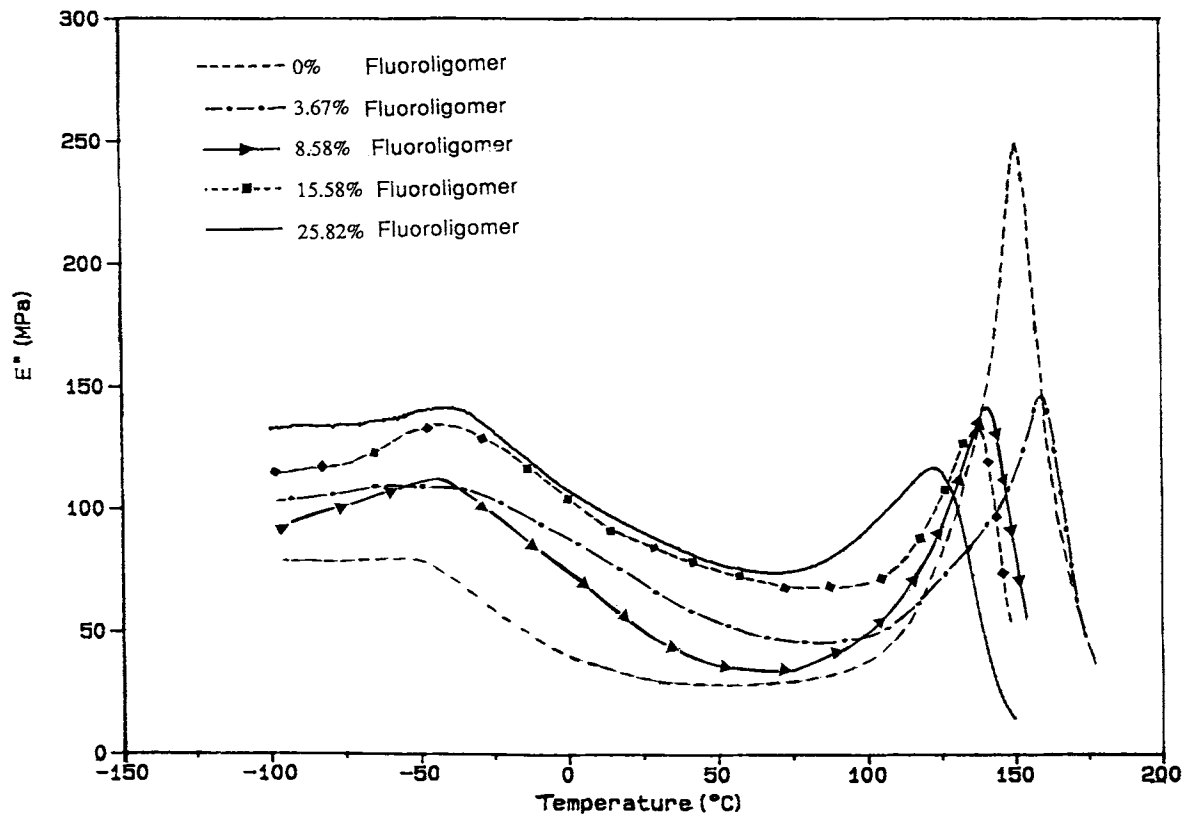**Figure 12** Dynamic mechanical spectra of opaque particulate morphology formulations (System A).

Figure 13 Dynamic mechanical spectra of transparent co-continuous morphology formulations.
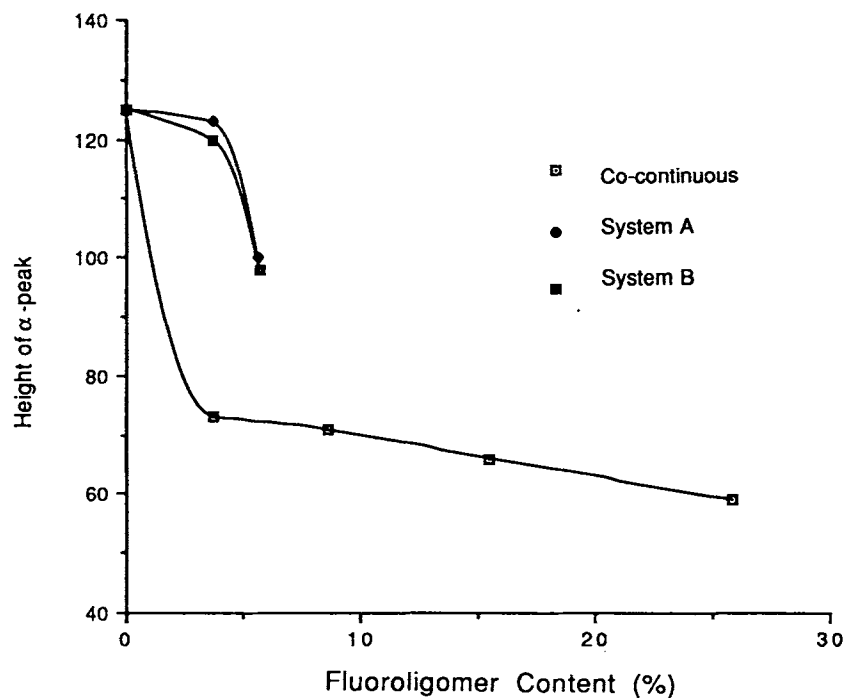

Figure 14 Comparison of the height of the peaks of the E'' curves at the glass-transition temperature for co-continuous and particulate morphology formulations.
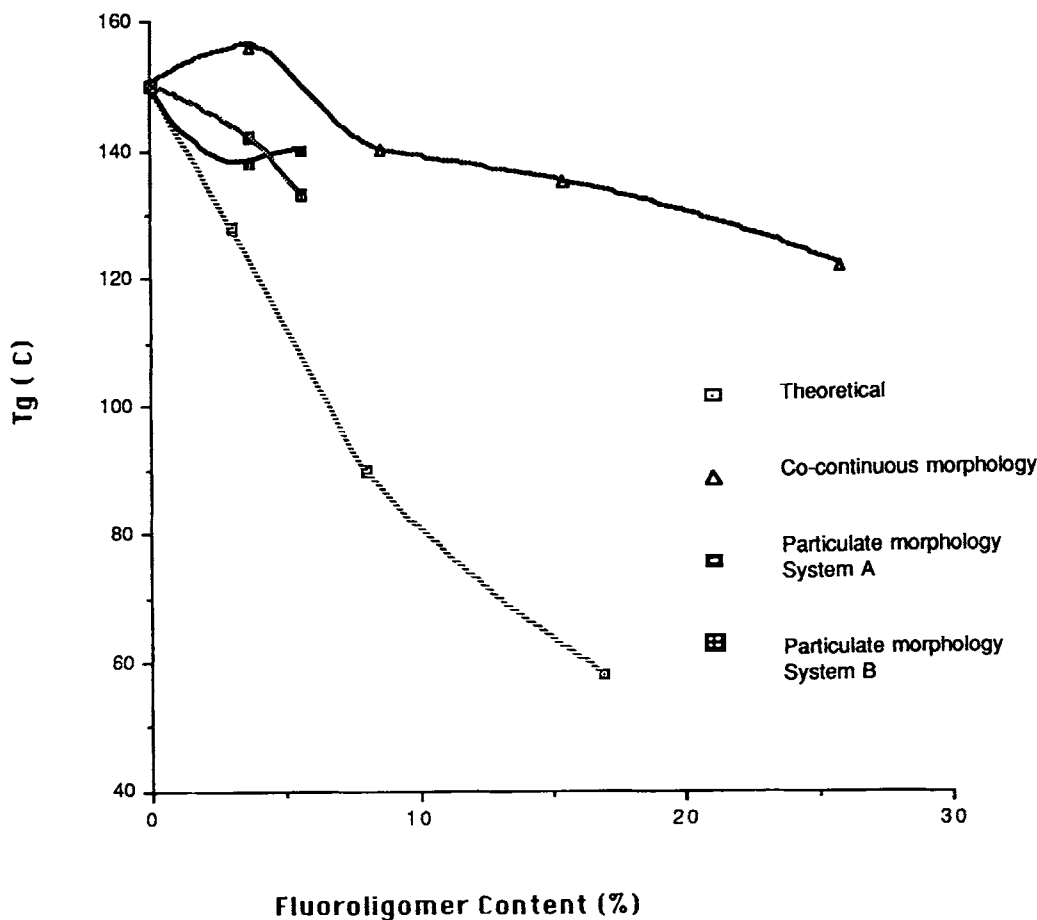
Figure 15 Glass-transition temperature as function of fluoroligomer content for co-continuous and particulate morphology formulations, compared to theoretical values for fully soluble systems.

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