

Silane Functionalization of Perfluoroether Oligomers for Reaction Management and Morphology Control of Two-Phase Epoxy Networks

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ABSTRACT: Mixtures of an epoxy resin, hardener, and acid functionalized perfluoroether oligomers will readily undergo phase separation during curing. However, the conditions to bring about the growth of nuclei into microscopic particles have hitherto been found only for systems cured with anhydrides. In the present study perfluoroether oligomers were functionalized by established procedures to introduce both carboxylic acid groups and alkoxy silane groups in sites within the chain extended segments. The presence of alkoxy silane groups together with the preacross step with an excess epoxy resin, prior to the addition of the aromatic amine hardener, induced phase separation by a nucleation-and-growth mechanism. The dual functionality in the perfluoroether oligomer was even more beneficial when the alkoxy silane groups were hydrolyzed prior to the

addition of the amine hardener. Under such circumstances the precipitation of the perfluoroether oligomer occurred quantitatively, as indicated by the complete absence of any plasticization effects in the epoxy matrix. From electron microscopy examinations, thermal analysis, and measurements of mechanical properties it was possible to deduce a plausible mechanism for the formation of the typical core-shell aggregates within the precipitated particles for these systems, which could also be applied to other systems, such as those using carboxylic-acid-terminated butadiene acrylonitrile oligomers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1036–1049, 2005

Key words: macromolecular networks; silane functionality; epoxy resin; phase separation

INTRODUCTION

The methodology for the phase separation of a heterogeneous network in the form of particulate domains through the selective "activation" of one oligomeric component has been known for more than 30 years.^{1–5} These heterophase materials exhibit substantial enhancement in fracture toughness, not only relatively to the parent homogeneously cured resin, but also in comparison to the chemically equivalent bicomponent system where phase separation takes place through the formation of nanostructured interpenetrating networks (IPNs).⁶

Invariably, the morphology of the particulate domains consists of a flocculation of small primary particles (<1 μm) encapsulated in a different network, which binds them to form larger secondary particles (ca. 5–20 μm).⁷

The most widely researched oligomeric morphology modifiers for epoxy resins are α,ω difunctionalized random copolymers of butadiene and acrylonitrile with molecular weight, M_n , in the region of 5000–8000 g mol^{-1} . These are frequently referred to as liquid rubbers⁸ and their composition is tailored to render them miscible with conventional epoxy resins, such as the diglycidyl ether of bisphenol A (DGEBA).^{2–4,9,10} The terminal functionalities are either carboxylic acid or primary amine and the oligomers are known as CTBN and ATBN, respectively. Several other functionalized oligomers have also been used to enhance the fracture toughness of epoxy resins. Notably among these are polysulfones, polyetherimides, poly(butylene terephthalate), and different types of telechelic acrylated oligomers^{11–15}

Mascia et al. have investigated widely the use of telechelic perfluoroether oligomers for the toughening of epoxy resins.^{15–18} These have a molecular weight, M_n , of 2200 g mol^{-1} and are chain extended to introduce terminal carboxylic acid groups and to render them miscible with epoxy resin/hardener mixtures.

One of the reasons for choosing chain extended perfluoroether oligomers for the toughening of epoxy resins is the presumed self-nucleation mechanism for

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the formation of primary particles, owing to the total insolubility of the precursor forming the central block of an A-B-A triblock structure. These are expected to form dispersed micellae rather than a true solution with epoxy resins. The formation of IPN domains, about 7–10 nm, rather than molecularly mixed networks (displaying a single T_g), were observed in such systems by small angle X-ray scattering examinations.¹⁹ The self-nucleation hypothesis is also supported by the findings of Guo et al. in using poly[(ethylene oxide)-copoly(propylene oxide)-copoly(ethylene oxide)] (PEO-PPO-PEO) triblock copolymers as non reactive network modifiers for epoxy resins.²⁰ At concentrations less than 50 wt % of PEO-PPO-PEO the phase-separated domains were in the region of 10–30 nm. Similar results were obtained by Konczol et al. using a polycaprolactone-*co*-polydimethylsiloxane-*co*-polycaprolactone triblock copolymer at concentrations up to 10 wt %.

The use of functionalized perfluoroether oligomers in epoxy resins cured with anhydrides produces heterogeneous networks. The resulting morphology can be controlled, through specific reactions procedures and experimentally determined curing schedules, to form either dispersed particles or IPNs. The low reactivity of anhydrides, toward both the glycidoxyl and the hydroxyl groups of the resin, makes it possible to convert the carboxyl functionality of the perfluoroether oligomer into “active sites” for the subsequent nucleation and growth of particulate soft domains within the fluid reaction medium prior to the onset of gelation of the epoxy resin. The structure of the particles is a typical microclustered agglomerate of very small particles (described earlier). The formation of such microstructures is brought about by reacting the oligomer with an excess of epoxy resin in the presence of small amount of a selective catalyst, such as triphenyl phosphine.

When the prereaction is not carried out, the competing reactions of the hardener and the functionalized oligomer with the resin results in the formation of IPNs.

It has generally been presumed that a microclustered morphology of “rubbery” particles provides a more efficient toughening mechanism. This was supported by previous findings, which showed that the rapid increase in toughness takes place at much lower concentrations of functionalized oligomer when the morphology of the toughening phase was a particulate type.¹⁹

The formation of such clustered particles morphology, however, relies on the careful balance of reactions, which cause chemically induced demixing in appropriate sequences, although the actual mechanism regarding the formation of such agglomerated (microclustered) particles has yet to be established. In view of the difficulties in producing this type of morphology during curing, many researchers have used

preformed core-and-shell particles for the toughening of epoxy resins, following the practice widely used for thermoplastics.^{7,20–22}

Notwithstanding the lack of precise knowledge regarding the mechanism for the formation of clustered particles with functionalized oligomers, it can be expected that the initiation step in the formation of flexible network (rubbery) domains can be preferentially triggered and the subsequent growth of the precipitating particles can be accelerated, if the formation of the two networks (matrix and inclusions) were to take place independently of each other.

The objective of this study was, therefore, to make suitable modifications to the structure of the acid terminated perfluoroether oligomers used in previous work for the toughening of epoxy resins,^{15–19} so that a more effective crosslinking mechanism can operate for the nucleation and growth of soft particulate inclusions, particularly when amine hardeners are used.

A trialkoxysilane coupling agent is to be used as a means of introducing a functionality capable of inducing crosslinking reactions, within the perfluoroether oligomer, through hydrolysis and condensation reactions of the alkoxy functional groups. In principle, this would make the formation of the flexible network completely independent of any reactions with the epoxy resin. A carboxylic acid functionality is also introduced in the oligomer so that reactions with the epoxy resin can still take place, and a strong interfacial bond between the two phases can also be expected.

EXPERIMENTAL

Materials

Rigid network components

The following rigid network components were used:

(a) a low-molecular-weight DGEBA, Epikote 828 (E), manufactured by Shell Chemicals;

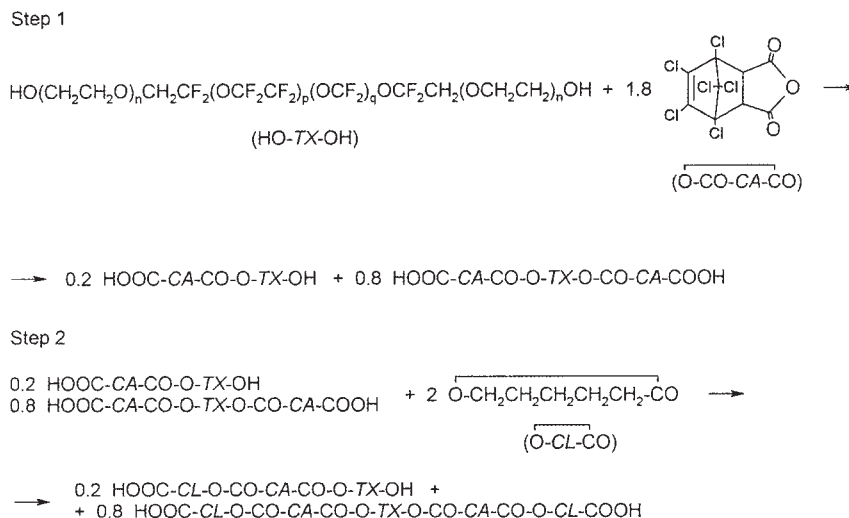
(b) bis (4-amino phenyl) methane (DDM), was used as hardener in the form of a 80% solution in *N,N'*-dimethyl formamide, to facilitate its dissolution in the resin. Both were obtained from Aldrich Chemical.

Reagents for the preparation of the silane functionalized flexible network oligomers

The following reagents were used:

(a) hydroxyl terminated perfluoropolyether (TX); this was a proprietary product, in the form of a viscous liquid, sold under the trade name Fomblin Zdol TX. The chemical structure is shown in Reaction Scheme 1. This oligomer has a number average molecular weight, M_n , equal to 2200 g mol⁻¹;

(b) chlorendic anhydride (CA); this corresponds to hexachloroendomethylene tetraphthalic anhydride, which is a solid with a melting point equal to 335 °C;



Scheme 1

(c) ϵ -caprolactone (CL); this is a liquid with a boiling point equal to 97 °C;

(d) Triphenyl phosphine (TPP); this is a solid with melting point of 80 °C.

Chemicals listed in (b), (c) and (d) were obtained from Aldrich Chemical.

Coupling agents for the functionalization of oligomer TX

γ -Glycidoxyltrimethoxysilane (GOTMS), a liquid reagents with 97% purity, was used as coupling agent and was obtained from Scientific; its structure is shown in Reaction Scheme 1.

Schemes of reactions for the functionalization of perfluoroether oligomer TX and preparation procedures

Chain extended acid functionalization

(a) This preparation has been described elsewhere⁸ according to Reaction Scheme 1.

The reaction was carried out in two steps. In the first step the molar ratio Fomblin Zdol TX : CA was 1 : 1.8. For the purpose of identification this product is designated oligomer TX-CA. The second step of the reaction was carried out with a molar ratio oligomer TX-CA : caprolactone equal to 1 : 2. This product is designated oligomer TX-CA-CL.

The stated molar ratios in both acid functionalization and the subsequent chain extension reaction with caprolactone were found experimentally to provide the best conditions to induce miscibility of the oligomer in the epoxy resin.^{16,17} It should be noted that the use of a lactone for the chain extension step allows the reaction to take place with both OH and COOH terminal groups in the TX-CA oligomer.

(b) Alkoxysilane functionalization

This reaction was carried out in two steps. In the first step the TX oligomer was reacted with CA in equimolar amounts. The first reaction was also carried out in a small, magnetically stirred flask at 150 °C for 20 min according to Reaction Scheme 2.

The product oligomer TX-CA was then reacted, at 90 °C for 1 h, with GOTMS in equimolar amounts so that all the acid groups were converted to trialkoxysilanes, producing an equal number of hydroxyl groups.

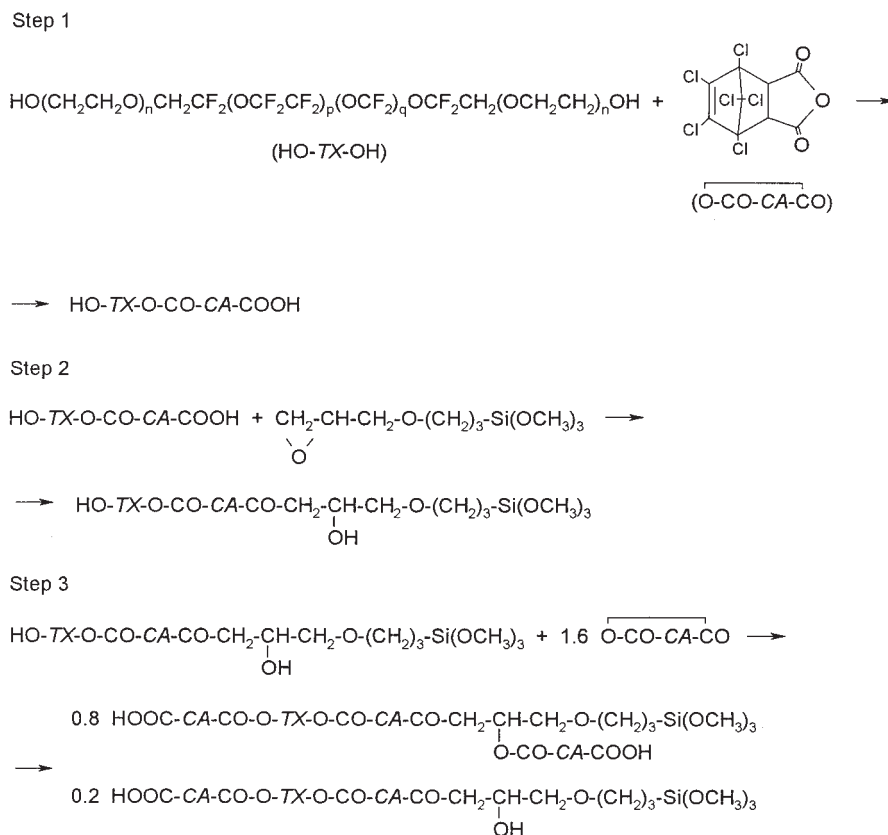
The third step was carried out at 1 : 1.6M quantity of CA at 150 °C. The reaction reached completion within 10 min. This product is designated oligomer TX-CA-GO-CA. The choice of chlorendic anhydride in both steps of the reactions was based on the established high reactivity for these systems.^{7,10}

It is noted that the latter oligomer has dual functionality, respectively, a carboxylic acid functionality to allow it to react with the epoxy resin, and a trialkoxysilane functionality for self-crosslinking.

Nucleation of phase separation

The usual procedure for the nucleation of particles in these systems involves a prereaction of the functionalized oligomer with an excess of epoxy resin. The reaction takes place selectively between the epoxy groups of the resin and the acid groups of the oligomer when carried out in the presence of triphenyl phosphine (TPP). This has the effect of inducing nucleation of the precipitation of soft particles after the hardener has been added and the mixture cured.

In this particular case the resin was first diluted with tetrahydrofuran (THF) and then mixed with the two functionalized oligomers at a molar ratio of 4 : 1,



Scheme 2

respectively, TXCACL and TXCAGOCA, according to Reaction Schemes 3a and b.

The mixture was reacted at 80°C for 15 h in a flask stirred with a magnetic stirrer. The products of the reactions were designated oligomer TX-CA-CL/Ep and oligomer TX-CA-GO-CA/Ep.

Preparation and curing of resin mixtures

The prereacted oligomers were further diluted with the epoxy resin to give different concentrations of the modified perfluoroether oligomer, ranging from 2.5 to 15% w/w.

The hardener was added and mixed at room temperature until a homogeneous (clear) mixture was obtained. The hardener was used in amounts corresponding to weight ratio of 0.25 : 1, which corresponds to a hydrogen equivalent ratio of 0.75 : 1 with respect to the amine hardener. This is the normal stoichiometric requirement for these systems to compensate for the additional crosslinking reactions of the epoxy groups through etherification.

For systems based on the alkoxy silane functionalized oligomers, formulations were also produced in such a manner so that the product of the prereaction of the oligomer with an excess epoxy resin, i.e., oligomer TX-CA-GO-CA/Ep, was first hydrolyzed from a 30

w/w solution in THF with the addition of a 0.5% w/w solution of HCl in water using a large excess over the stoichiometric amount for full hydrolysis. This was carried out for 40 min at room temperature. The amount of acid used is very small in relation to the amount of epoxy groups present in the reaction medium and cannot be expected to have any significant effect on the formation of the epoxy network in the subsequent reactions.

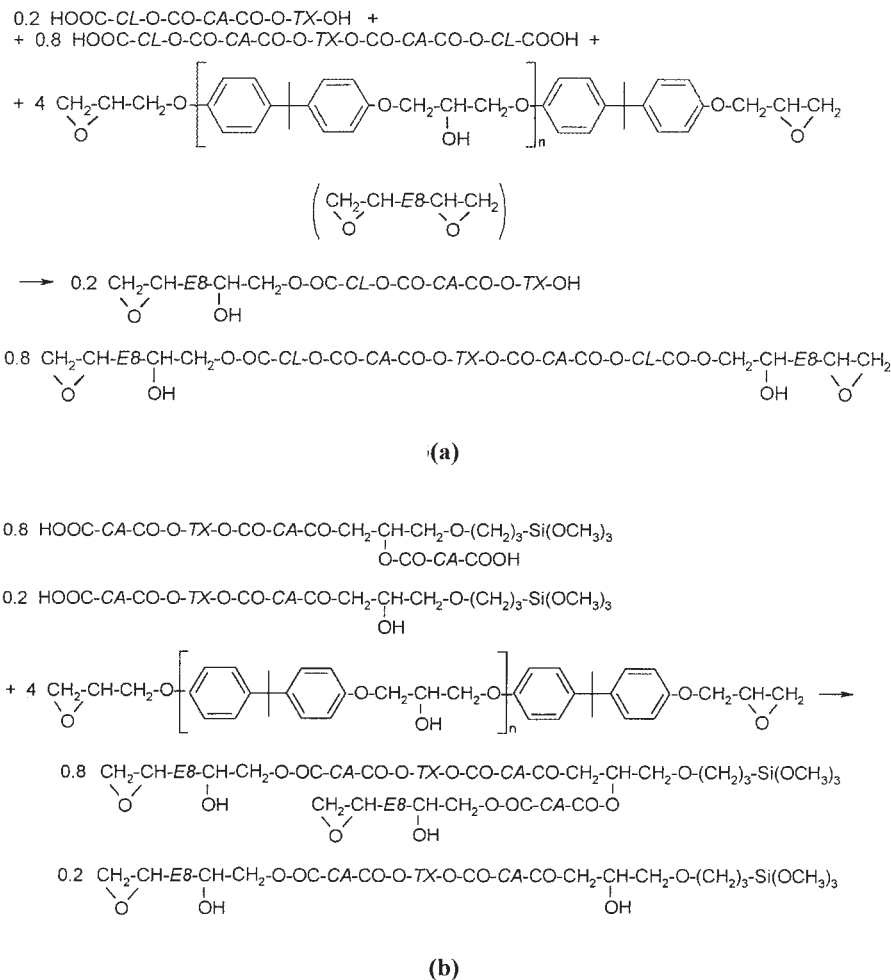
The mixtures were cast into open square PTFE molds (90 × 90 × 5 mm) and cured in a vacuum oven fitted with a solvent trap according to the following schedule:

5 days at room temperature, 18 h at 120 °C, 3 h at 180 °C, and 1 h at 220 °C.

The high temperatures used ensured no residual solvent was left in the cured samples.

Chemical characterization of the reaction products

All functionalization reactions were monitored by infrared spectroscopy in transmission mode, using a Unicam instrument (Mattson 3000 FTIR spectrometer). Samples were placed between sodium chloride disks and spectra were collected with an average of 65 scans. In some cases the samples were also analyzed by proton NMR at 300 MHz in equivolume mixtures



Scheme 3

of deuterated trichloromethane and trichlorotrifluoroethene, using a Varian Unity 300 instrument with the following settings: flip angle 90° , acquisition time 4 s, pulse delay 8 s, and 500 scans. The oligomers were also examined by modulated temperature scanning calorimetry (MTDSC) to measure their glass transition temperature, using a Thermal Analysis apparatus, operated in a nitrogen atmosphere and with a temperature scan of 5 K/min.

Physical characterization of cured samples

The cured samples were examined by scanning electron microscopy (SEM) to determine their morphological structure and by both MTDSC and dynamic mechanical thermal analysis (DMTA) to characterize the networks. Mechanical properties were finally measured to obtain some elucidation of structure/engineering property relationship.

The SEM examinations were performed on specimens fractured in liquid nitrogen using a Jeol 100CX instrument.

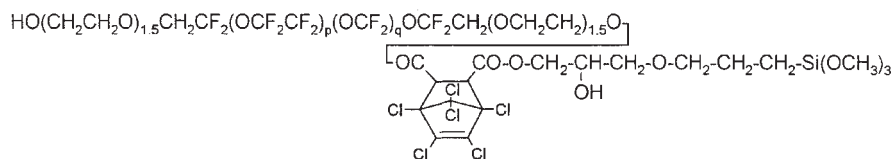
The TMDSC apparatus used was a Thermal Analysis instrument, operated in a nitrogen atmosphere and with a heating scan of 5 K/min, from -100 to 250°C .

The DMTA apparatus was a Polymer Laboratory Mk II instrument operated in a dual cantilever mode. The temperature for each measurement was scanned from -100 to 250°C , under a nitrogen blanket, at a heating rate of 3 K/min and an oscillating frequency of 1 Hz.

Young's modulus was measured in a three-point bending mode (flatwise), with a span to thickness ratio (L/d) of 15 : 1 and a crosshead speed of 2 mm/min.

The gradient of the plot of load, P , versus deflection, Δ , through the origin was used to calculate the modulus (E) from elasticity theory, i.e., $E = P/4\Delta \times L^3/bd^3$, where b is the width. Although the tests were carried out up to fracture the flexural strength was not calculated as the maximum stress due to the absence of distinct yield point.

Fracture toughness was assessed from measurements of the critical stress intensity factor, K_{IC} , in a three-point bending mode and with the load applied



Structure 1 Presumed structure of TXCAGOCA.

edgewise. The specimens were single-edge-notch types, 10 mm wide, and with different notch lengths (a) varying from 1 to 4 mm. The notches were machined to the required length and sharpened with a razor blade. The span to width ratio (L/d) was 4 : 1 and the clamp separation rate used to fracture the specimens was 2 mm/min.

The fracture toughness parameter K_{IC} was calculated from the slope of the plot load to fracture (P_f) recorded for each crack length to width ratio (a/day), taken as the average of six readings, against the reciprocal of the corresponding compliance calibration factor $1/Y$, forced to the origin, in accordance with linear elastic fracture mechanics (LEFM) principles, i.e., $K_{IC} = Y P_f/bW^{0.5}$. The values of Y were obtained from data reported in the literature.²³ In all cases the validity of the LEFM analysis was checked by examining the load/deformation trace produced by the testing equipment and ensuring that large deviations from linearity were absent for deflections up to fracture conditions.

Tests for measurements of Young's modulus and fracture toughness were carried out at room temperature on a J. J. Lloyd tensile testing instrument.

RESULTS AND DISCUSSION

Structure and characteristics of oligomers

The FTIR and $^1\text{H-NMR}$ spectra of the reaction products have confirmed the occurrence of the reactions outlined in Reaction Schemes 1 and 2. The data for oligomer TX-CA-CL and TX-CA-GO have been published elsewhere.²⁴ The results of this analysis were in agreement with the published data. Regarding the oligomer TX-CA-GO-CA the FTIR spectra have revealed that shoulder absorption at 3190 cm^{-1} , corresponding to carboxyl groups, disappears when the product TX-CA is reacted with GOTMS to produce TX-CA-GO. When the latter was subsequently reacted with chlorendic anhydride to produce TX-CA-GO-

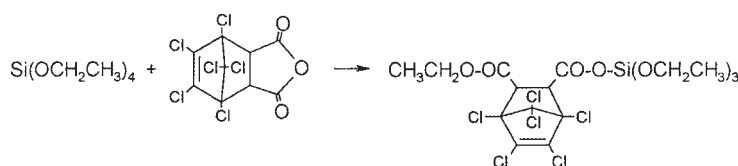
CA, the expected characteristic peak at 3190 cm^{-1} was not evident in the FTIR spectrum, indicating that a substantial amount of CA cannot have reacted with the hydroxyl groups of the GO segment in accordance with the predicted reaction scheme. As there is no possibility of losing CA through volatilization, this was attributed to the occurrence of side reactions.

The $^1\text{H-NMR}$ spectra show that the singlet peak observed at around 4.05 ppm (see "presumed" structure for TX-CA-GO, Structure 1) is due to the protons present in the CA segment of the oligomer and the singlet peak at around 3.50 ppm corresponds to the protons of the methoxysilane groups of the GO segment of the oligomer.

However, the molecular configuration associated with the singlet peak at around 3.75 ppm is not explicable in terms of the presumed structure of TX-CA-GO-CA. To confirm the likelihood of a possible direct ester exchange reaction with the methoxysilane group of the GO segment a comparison was made with the product of the reaction carried out between tetraethoxysilane (TEOS) and chlorendic anhydride at 1 : 1M ratio, where the only possible reaction is an ester exchange type to produce the product TEOS-CA according to Reaction Scheme 4.

TEOS was used in preference to trimethoxysilane because of its much greater stability toward hydrolysis in the atmosphere, thereby eliminating the possibility of side reactions.

The comparison of $^1\text{H-NMR}$ spectra for the product TX-CA-GO-CA and TEOS-CA is shown in Figure 1. The quadruplet at 3.7–3.8 ppm, reported in the insert, can be attributed to the $\text{CH}_3\text{-CH}_2\text{-O-}$ groups directly linked to CA, as shown in Reaction Scheme 4 (note that the chemical shift of the corresponding signal for unreacted TEOS is at 3.8–3.9 ppm). This result can be used to determine the origin of the singlet at 3.75 ppm in Figure 1, which can be attributed to the CH_3O groups directly linked to CA, derived from the reaction between the carboxylic groups of CA and the



Scheme 4

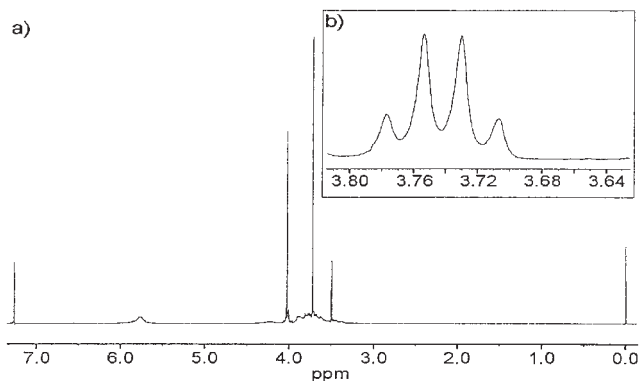


Figure 1 $^1\text{H-NMR}$ spectra of oligomer TXCAGOCA (main diagram) and oligomer TXCA (inset) [both raw products].

methoxy groups of GOTMS. These spectra confirm, therefore, that the third step of the reaction includes the formation, possibly as major product, of siloxane esters with a structure corresponding to TX-CA-GO-CA (Structure 2).

From the intensity of the signal at 3.75 ppm it can be inferred that this reaction predominates over the possible esterification reactions involving the hydroxyl groups from the GOTMS segment and those at the ends of perfluoroether chains, which remained from previous reaction steps due to the unbalanced stoichiometric quantities of reactants used. This can be attributed to the high concentration and ease accessibility of the methoxy groups attached to the silicon.

The $^1\text{H-NMR}$ analysis of the products of the chain extension reaction of TX-CA-GO-CA with an excess epoxy resin (TXCAGOCA/Ep) has indicated that about 38% of the total amount of epoxy resin capable of reacting with the presumed amount of carboxylic acid groups available if the reaction had proceeded according to Reaction Scheme 3(b). This was estimated from a comparison of the integral intensity at around 6.80 and 7.15 ppm, corresponding to the aromatic rings in the epoxy resin (an invariant) with the signals at around 2.75 and 2.90 ppm for the epoxy groups (Fig. 2).

Although one can exclude the likelihood of an etherification reaction occurring between the hydroxyl groups in the oligomer and the epoxy resin, it is presumed that the main reaction has occurred by esterification with the acid groups within the oligomer.

The thermograms obtained by TMDSC for the relevant oligomers are shown as derivatives of the specific

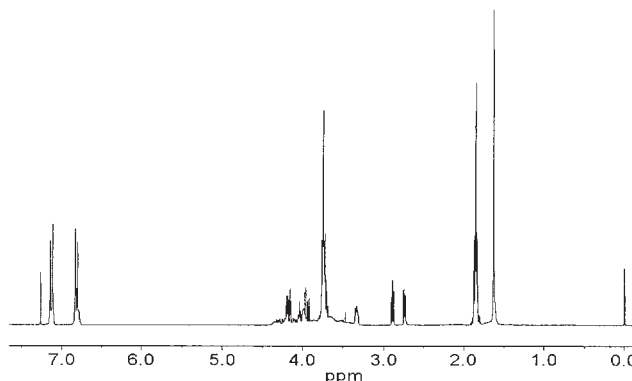


Figure 2 $^1\text{H-NMR}$ spectra of prereacted oligomer TX-CAGOCA/Ep.

heat capacity in Figure 3. These indicate that the glass transition temperature (T_g) of oligomer TX-CA-CL is in the region of $-55\text{ }^\circ\text{C}$ and that of oligomer TX-CA-GO-CA is approximately $-39\text{ }^\circ\text{C}$. The introduction of bulky groups at the chain ends bring about an increase in T_g and a broadening of the glass transition region.

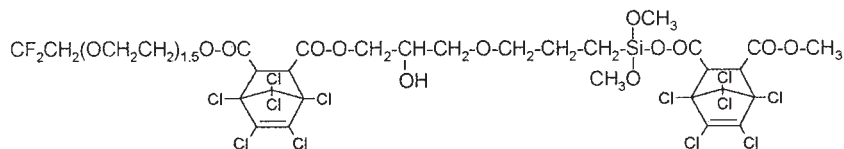
Miscibility of the functionalized oligomers with the epoxy resin

The visual inspection of mixture of functionalized oligomers, TX-CA-CL and TX-CA-GO-CA, and the Epikote 828 resin at weight ratio of 1:2 at room temperature and after heating to $80\text{ }^\circ\text{C}$, indicated that they were only miscible (transparent) at the higher temperature. When the DDM hardener was added to these at a weight ratio of 0.25 : 1 with respect to the epoxy resin, the mixture became fully miscible even at room temperature.

The reaction products of these oligomers with the excess epoxy resin, carried out in the presence of TPP catalyst were homogeneous (transparent) even at room temperature, and remained so after the addition of the hardener.

Microstructure of cured resins and oligomer repartition

Figure 4 shows the SEM micrographs of typical fractured surfaces of specimens of cured epoxy samples produced with the acid functionalized oligomer, TX-CA-CL (produced according to Reaction Scheme 1). From these it is clear that no distinct microstructure is



Structure 2 Actual structure of TX-CA-GO-CA.

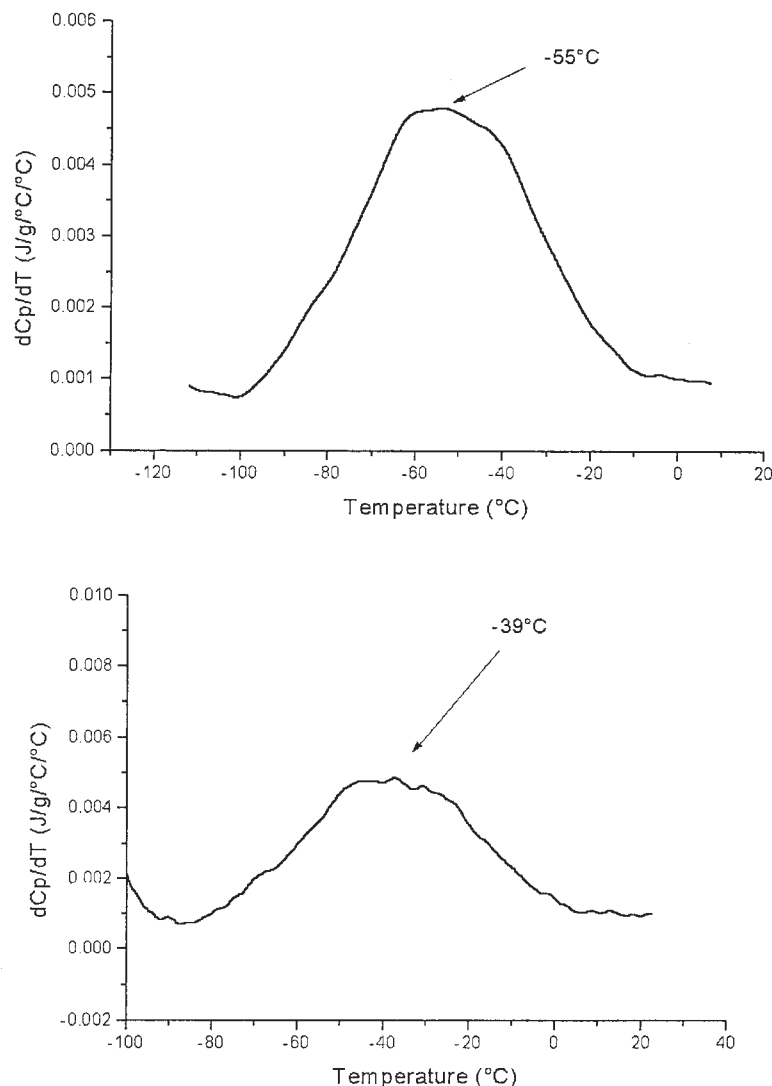


Figure 3 MTDC thermograms, expressed as derivatives of specific heat with respect to temperature. (a) Oligomer TXCACL; (b) oligomer TXCAGOCA.

present in systems produced with the acid functionalized oligomer (TX-CA-CL) apart from a very fine heterogeneity, consisting of finely dispersed primary particles.

The micrographs obtained for systems containing alkoxy silane functionality, in addition to the carboxylic acid functionality, (i.e., TX-CA-GO-CA produced according to Reaction Scheme 2), are shown in Figure 5. (Both samples contain 10% w/w functionalized oligomer.) The silane functionalized oligomer was not prehydrolyzed, but only chain extended with the epoxy resin. These micrographs display the characteristic agglomerated-particle morphology of phase separated epoxy resins^{8,9,14-16} with a broad size distribution, mostly in the region of 5 to 10 μm . Figure 5(b) reveals also a substantial level of coalescence of aggregated particles, which takes place during particle growth. Furthermore, the structure of each particle is internally heterogeneous and more distinctive than

that of the dispersed particles representing the overall morphology of the samples obtained with the acid functionalized oligomer, TX-CA-CL.

For the case where the silane functionalized oligomer, TX-CA-GO-CA, was hydrolyzed after chain extension with the epoxy resin, the cured samples display an overall similar morphology to those produced without the prehydrolysis step (see Fig. 5), but the internal heterogeneity of the particles becomes much more pronounced and the interfacial adhesion appears to have weakened (compare Figs. 5(b) and 6).

This indicates that, while the overall mechanism of particle formation is similar, the prehydrolysis step brings about the formation of more fully developed, and possibly denser, primary particles.

The TMDSC analysis of the cured samples was used to obtain the thermograms of the systems as plots of the derivative of the specific heat as a function of the temperature from which it was possible

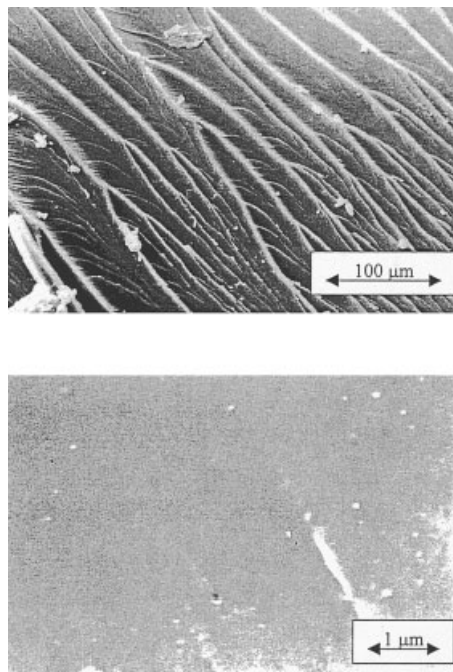


Figure 4 SEM micrograph of a fractured surface of epoxy resin containing 5% w/w oligomer TXCACL. The oligomer was prereacted with excess epoxy resin and subsequently cured with DDM hardener. (a) Low magnification; (b) high magnification.

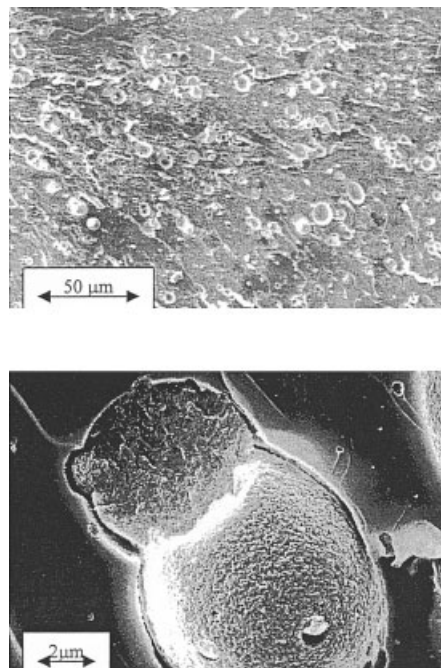


Figure 6 SEM micrograph of a fractured surface of epoxy resin containing 10% w/w prehydrolyzed oligomer TX-CAGOCA. The oligomer was reacted with excess epoxy resin and hydrolyzed before adding DDM hardener. (a) Low magnification; (b) high magnification.

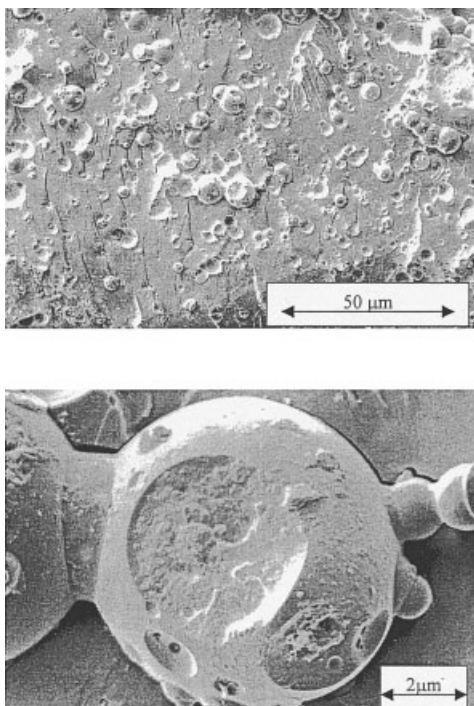


Figure 5 SEM micrograph of a fractured surface of epoxy resin containing 10% w/w oligomer TXCAGOCA. The oligomer was prereacted with excess epoxy resin and subsequently cured with DDM hardener. (a) Low magnification; (b) high magnification.

to get an accurate fingerprint of the secondary transitions.

A typical example is shown in Figure 7, where the glass transition of the major phase (the epoxy network matrix) at 132 °C is shown to be accompanied by a very broad transition at lower temperature, scanning from about -50 °C and merging with the glass transition of the epoxy matrix at the higher temperatures.

Plots of the glass transition of the epoxy network phase against the concentration of functionalized perfluoroether oligomer are shown in Figure 8(a). From these it is clear that there is a substantial and rapid reduction in T_g of the epoxy network for systems based on acid functionalized oligomers (TX-CA-CL) from 156 to about 80 °C and only a very small and gradual drop to 152 °C for systems containing the prehydrolyzed silane functionality. The corresponding system where the silane functionalized oligomer was not prehydrolyzed, on the other hand, showed a gradual reduction in T_g to about 132 °C. The reduction in T_g of the epoxy network is attributed to the plasticization effect of the perfluoroether oligomer, which has entered into the epoxy matrix network rather than separating out with the precipitated particles.

This effect is also reflected in dynamic mechanical properties. Figure 9 shows the variation of elastic component of the dynamic modulus E' as a function of temperature for the three systems examined. A very large reduction in E' values is displayed below the glass transition temperature for the systems contain-

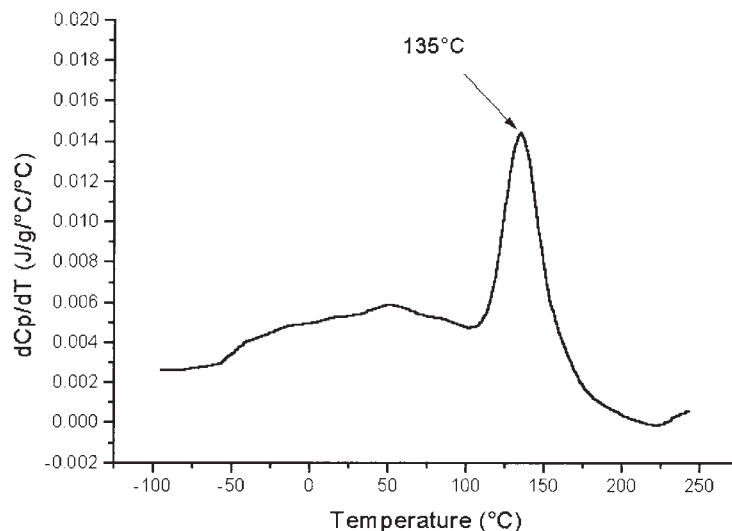


Figure 7 MTDSC thermogram of epoxy resin containing 5% w/w oligomer TXCAGOCA. The oligomer was prereacted with excess epoxy resin and subsequently cured with DDM hardener.

ing the acid functionalized oligomer TX-CA-CL, whereas the systems containing the prehydrolyzed silane functionalized oligomer TX-CA-GO-CA show hardly any difference from the unmodified epoxy resin. The higher E' values just below the T_g may not be significant as there is considerable scatter in these region. Nevertheless, the data are sufficiently accurate to demonstrate that the systems based on the non-hydrolyzed alkoxy functionalized oligomer are much closer to the corresponding composition containing the hydrolyzed oligomer than those based on the oligomer containing only the carboxylic acid functionality (TX-CA-CL).

It is worth noting that the very rapid drop in modulus associated with the glass transition temperature, takes place at temperatures around 100 °C, which is considerably lower than the glass transition temperature revealed by the TMDSC (Fig. 7). The dynamic mechanical spectra for the $\tan \delta$ values, however, show two peaks: one at around 100 °C and another at around 130–150 °C. From this it can be deduced that the large reduction in modulus at the glass/rubber transition would follow a similar trend, but the resolution of the recorded data is not sufficient to detect the second step. It is worth noting that a secondary peak at around 100 °C is also apparent in the thermogram in Figure 7, but this is much less pronounced than the main peak at 135 °C.

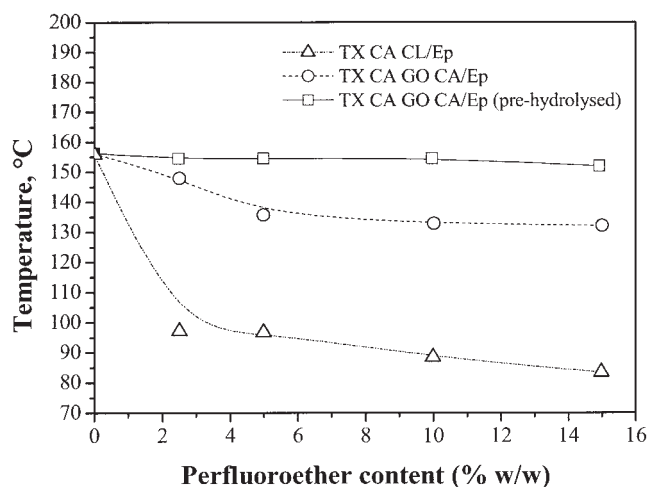


Figure 8 Effect of perfluoroether concentration on the glass temperature of epoxy resin containing different types of functionalized oligomers. All oligomers were prereacted with excess epoxy resin before mixing with DDM hardener. Oligomer systems are TXCAGOCA, TXCACL, and TXCAGOCA [prehydrolyzed].

Mechanical properties

Plots of the Young's modulus from the flexural tests and fracture toughness, K_{IC} , against the concentration of functionalized oligomer are shown in Figure 10. These reveal the expected reduction in modulus with increasing concentration of the added oligomer due to the presence of "soft" (low modulus) particulate inclusions. The largest reduction is experienced with systems containing the acid functionalized oligomer TX-CA-CL while the smallest decrease is achieved with the prehydrolyzed silane modified oligomer (TX-CA-GO-CA). These data follow the trend expected from the plasticization effects of the oligomer remaining within the epoxy network matrix (discussed earlier).

The data in Figure 10, on the other hand, show that all functionalized oligomer systems display an overall similar toughening efficiency, but the acid functionalized oligomer is more efficient at the lower concentrations.

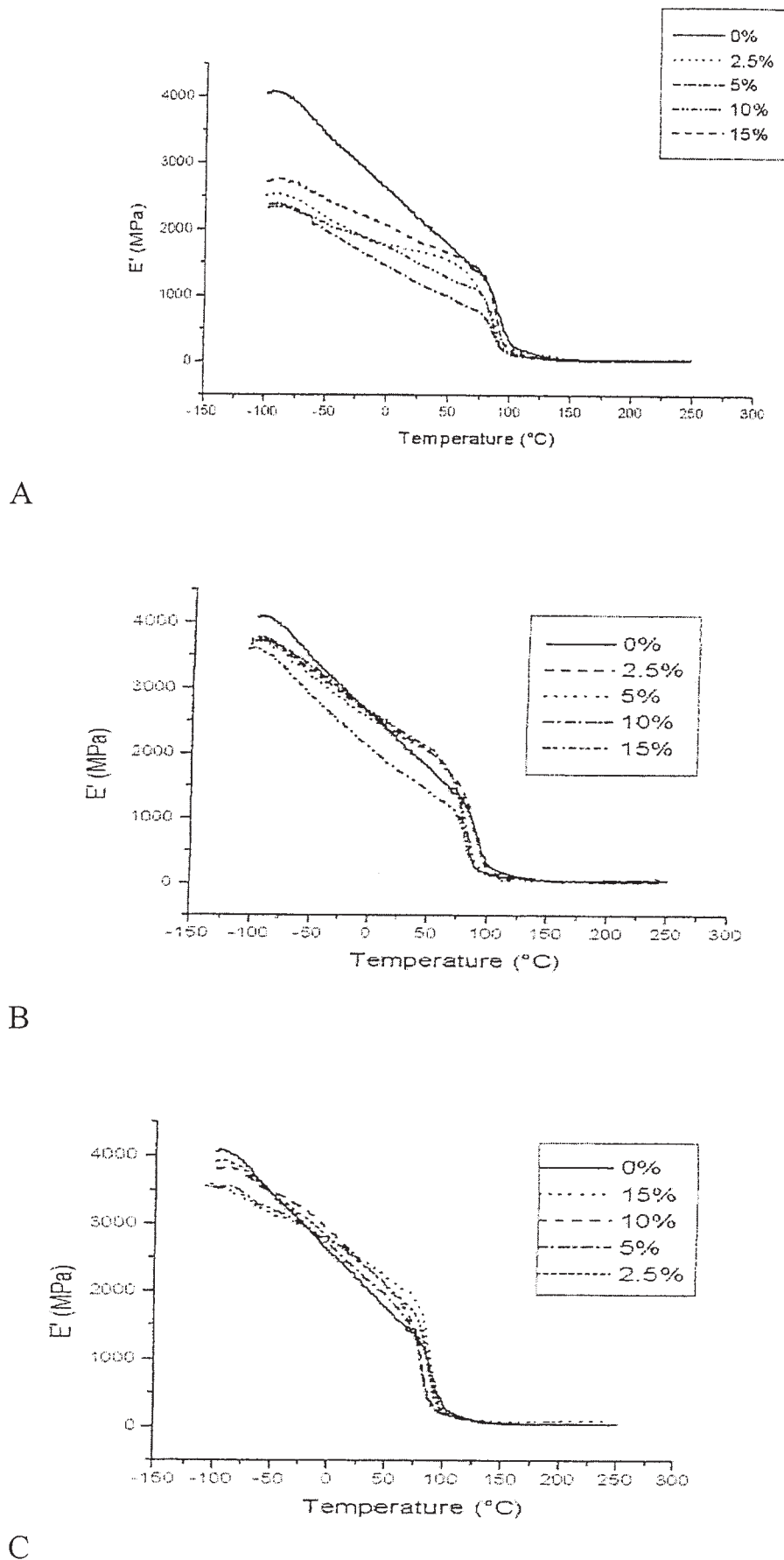


Figure 9 Variation of storage modulus with temperature for epoxy resins containing different types and amounts of perfluoroether oligomers. All oligomers were prereacted with excess epoxy resin before mixing with DDM hardener. (a) TXCAGOCA; (b) TXCACL; and (c) TXCAGOCA [prehydrolyzed].

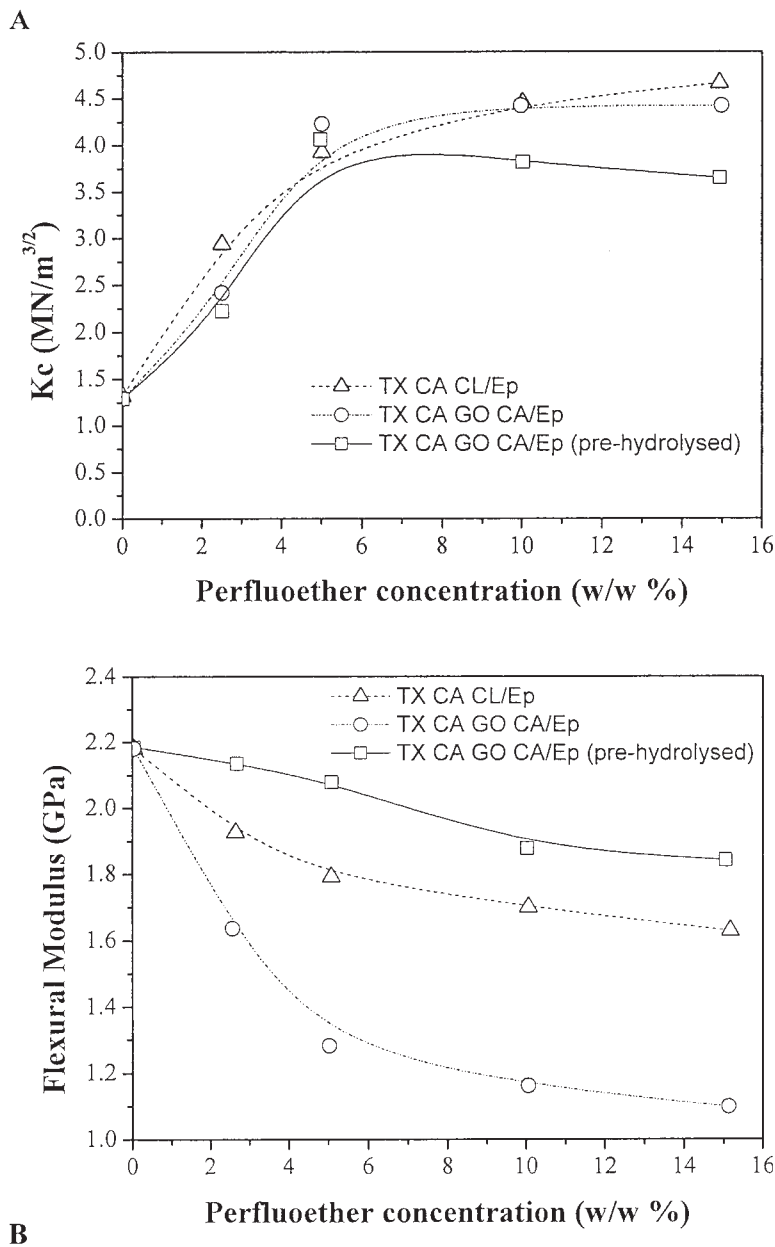


Figure 10 Effect of perfluoroether concentration on mechanical properties of epoxy resin containing different types of functionalized oligomers. All oligomers were prereacted with excess epoxy resin before mixing with DDM hardener. Oligomer systems are TXCAGOCA, TXCACL, and TXCAGOCA [prehydrolyzed]. (a) Flexural modulus; (b) critical stress intensity factor, K_c .

The equivalent systems produced with a longer reaction time show smaller relative increases in K_{IC} (not shown here) at the higher end of the concentrations used. The similarity in the variation of K_{IC} with the concentration of chain extended and functionalized perfluoroether concentration for the three systems suggests that the method used to assess the fracture toughness is not a sufficiently sensitive probe for the fracture characteristics of these systems due to major deviations from linear elastic behavior in approaching fracture conditions. Nevertheless, the lower K_c values displayed by the systems based on prehydrolyzed TXCAGOCA/Ep are signifi-

cant insofar as the corresponding reduction in critical strain energy release rate, G_c , is even higher owing to higher modulus [Fig. 10(b)]. It is possible that this is due to from the reduction a interfacial adhesion between particles and matrix, as indicated by the micrograph in Figure 6(b).

Mechanism for particle nucleation and morphology development

From observations on the morphology of the systems examined in this study, and in previously published

work on anhydride cured resins, it is possible to deduce a possible mechanism for the formation of primary particles (less than 1 μm) and their clustering into secondary particles about 5–15 μm in diameter.

It emerges that there are two steps in the reactions involved. The first is responsible for the precipitation of primary particles through the formation of microgel "nuclei" resulting from the reactions of the hardener at the activated sites of the oligomer chains, which are produced in the preceding chain extension reaction with the epoxy resin in the presence of TPP used as catalyst. These sites originate from the hydroxyl groups formed by ring opening of the epoxy groups and remain associated to TPP molecules via H-bonds resulting from the attractions by the lone electron pair. The polarization of these hydroxyl groups results in the formation of the said activated sites, which trigger the esterification reaction with anhydride hardeners, causing the nucleation of primary particles.

The nuclei so produced are expected to incorporate substantial proportions of both DGEBA segments and anhydride units of the hardener and will, therefore, contain rigid network domains.

The second step in the phase separation consists of further reactions taking place around each primary (core) particle forming "shells" composed of lightly crosslinked species obtained through reactions involving functional groups in the oligomer. For the case of anhydride cured resins, examined in previous studies,^{16–19} the reactions for the formation of the shells take place between the carboxylic acid groups of the oligomer and the epoxy groups of the resin.

As the thickness of the shell around the core particles becomes increasingly larger, the grown particles begin to coalesce to form microclustered agglomerates. When the number of such agglomerates is relatively small they will remain separate and suspended in the surrounding resin, and their morphology is subsequently stabilized through gelation of the resin in the reactions with the hardener.

The distinct interface between the epoxy matrix and secondary particles is formed by the subsequent densification of the surrounding epoxy network through the advancement of the reactions with the hardener. This network cannot diffuse into the shells of the primary particles owing to the lack of sufficient amounts of residual reactive groups. The micrographs in Figures 5 and 6 show clearly the occurrence of interfacial debonding of secondary particles from the matrix. This situation is very different from the corresponding systems using an anhydride hardener, which have been found to display a yield zone around the particles without any sign of interfacial debonding.¹⁸

At very high concentrations of oligomer it may not be possible to form clusters of primary particles suspended in the fluid resin, as there may not be sufficient resin available in the surrounding areas to effectively keeping them separated. In previous work on

epoxy cured with an anhydride hardener it was, indeed, found that the agglomerates particles were not forming above 12–15% w/w oligomer.¹⁸ The actual volume fraction of agglomerates is much higher, possibly double this amount,^{16,17} because of the presence of chain extended units in the perfluoroether oligomer in the prereactions with the epoxy resin and the formation of other adducts in the subsequent curing reactions with the hardener.

When a carboxylic acid terminated oligomer, e.g., TX-CA-CL, is used in amine cured resins, the activated hydroxyl sites that are formed by the reaction of the acid groups in the oligomer with the excess epoxy resin in the presence of TPP are not capable of reacting with the amine hardener and, therefore, nucleation of the primary particles is much more difficult. This will have to take place through reactions of the hardener with the epoxy groups at the end of the chains of the resin segments linked to the perfluoroether oligomer. In this case a mechanism for the formation of the shells, described earlier, is not available, as there are no functional groups in the oligomer chains to react with either the amine groups of the hardener or the epoxy groups of the resin. For this reason, therefore, only primary particles are formed in this situation (see Fig. 4).

The morphological structure identified by SEM examinations provides some evidence for the presumed role of the silane functionalization as a means of inducing an autonucleation mechanism for the formation of primary particles through condensation reactions at the alkoxy silane groups within the oligomer chains. This does not preclude, however, the possibility of a particle nucleation mechanism involving also condensation reactions with the silanol groups in the functionalized perfluoroether oligomer with activated hydroxyl sites in the end of chain epoxide segments, but it is less likely as the substantial difference in solubility parameters would create less favorable conditions.

The hydrolysis of the TX-CA-GO-CA/Ep adduct, prior to mixing with the rest of the epoxy resin and the hardener, ensures that such condensation reactions occur more readily. Since all reactions were carried out in an open flask the initial level of hydrolysis of the alkoxy silane groups required for the condensation reactions brought about by the water vapors entrapped during mixing.

The additional crosslinking mechanism available for the silane functionalized oligomer in the formation of networks in both core particles and shells brings about a more efficient separation of the perfluoroether oligomer from the resin and reduces the extent of plasticization of the surrounding epoxy matrix. Total separation of the perfluoroether oligomer species from the epoxy resin, on the other hand, takes place through the prehydrolysis step, which ensures that sufficient silanol groups are available for the condensation reactions.

CONCLUSIONS

(1) The results of this study provide evidence to support the premise that an alkoxysilane functionality in the perfluoroether oligomer facilitates phase separation in the toughening of epoxy resins cured with amine hardeners and brings about a more complete precipitation of the oligomer into the particulate toughening phase.

(2) For amine cured systems, using the same acid functionalized oligomer TX-CA-CL, the formation of clustered particles is prevented by the lack of a mechanism for the formation of a perfluorooligomer-based network in the shells around primary particles. As a result, an amount of perfluoroether oligomer remains within the resin and participates in the formation of the epoxy matrix network, as indicated by a reduction in the T_g value.

(3) The use of TPP as a catalyst for the chain extension reactions of the functionalized perfluoroether oligomer with an excess epoxy resin has a pronounced effect in the subsequent condensation reactions in the final curing of the resin. Without the use of TPP in any prereactions of the oligomer with the resin, prior to the addition of the hardener, produces only IPN morphologies, similar to the equivalent systems using anhydrides for the curing of the resin.

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