Selective Repartition of *In Situ* Generated Silica Produced During the Evolution of an Epoxide Network from a Homogeneous Precursors Mixture and Effects on Properties

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ABSTRACT: Phase separation of organic networks derived from mixtures of reactive monomers and/or oligomers can take place through the formation of IPNs or precipitation of particles. The latter systems are widely used as a means of increasing the fracture toughness of thermosetting resins, and particularly for products obtained from mixtures of epoxy resins and functionalized aliphatic oligomers. In the present work several mixtures comprised of difunctional epoxy resins, silane functionalized perfluoroether oligomers, prehydrolyzed tetraethoxysilane, and an aromatic amine hardener were examined in a variety of compositions and preparative procedures. The aims were to control the kinetics of phase separation and the repartition of the different components in the two phases, so that the silica domains could be preferentially located within the precipitated soft particles. It was found that the silane functionalization of the perfluoroether oligomer provided an effective mechanism for the localization of the siloxane networks within the precipitated particles. However, phase separation by the precipitation of particles would only take place for systems in which the perfluoroether oligomer could be reacted with an excess of epoxy resin prior to adding the alkoxysilane solution and the hardener. Moreover, it was difficult to achieve the total localization of the siloxane component into the perfluoroether network. The siloxane species remaining dissolved in the resin gave rise to severe embrittlement of the products through reactions with the epoxy chains. Using mixtures of suitably functionalized perfluoroether oligomers it was possible to produce the conditions by which the localization of the silica domains into the precipitated particles could be maximized. This has resulted also in the formation of graded interphase regions and to a global improvement in mechanical properties, manifested as a concomitant increase in modulus, strength, and toughness. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1279–1290, 2004

Key words: organic–inorganic hybrids; epoxy resin; toughness; networks; nanoheterogeneity

INTRODUCTION

The concept of generating silica by the sol-gel method within a macromolecular organic phase (*in situ*) has been widely explored for the production of materials known as organic–inorganic hybrids.[1–6] The organic and inorganic components of these materials are present as cocontinuous phases of a few nanometers in lateral dimensions. The two phases may be bound by H-bonding attractions or may be linked by covalent bonds through the use of suitably functionalized "coupling agents."[7–11] Moreover the organic phase may be composed of discrete oligomeric units chemically bonded to the inorganic oxide network or it may be present as a separate polymeric phase or a macromolecular network.[12,13]

Apart from a few reports concerned with block copolymers, the majority of studies on organic–inorganic hybrids have been concerned only with homogeneous organic components.[14,15] The present investigation represents, therefore, the first study related to the production of organic–inorganic hybrids for two-phase organic network systems, aiming to selectively reinforce one of the phases by the introduction of cocontinuous silica domains. In particular the study seeks to determine the conditions that compel the inorganic domains to be formed within, or intimately connected to, the organic particles as they precipitate out of an epoxy resin mixture. The type of functionalized aliphatic oligomers used to induce the formation of a particulate morphology for the systems examined are those that are normally used for enhancing the fracture toughness of cured epoxy resins.[16]

Some indications of the possibility of inducing a preferential repartition of the inorganic component in two-phase organic networks can be obtained from observations reported in the literature for mixtures of

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epoxy resins and polyethylene glycol, containing a small amount of exfoliated montmorillonite nano-structured particles.[17] Although in these systems the inorganic filler was found to reside in both organic phases, there was an increase in the size of agglomerates of filler particles with increasing concentration of the polyether component in the resin mixture, suggesting that there was a preferential affinity of such a component for the inorganic particles. This type of behavior has also been reported for such mixtures where silica was generated *in situ* by the sol-gel method.[18]

The procedure for the toughening of epoxy resins by the precipitation of "soft/rubbery" particles during the early stages of curing can produce IPN structured interphases, owing to extensive entanglements created by the networks while they undergo phase separation through chemical reactions.[19–21] Such IPNs often form the shells component of primary particles causing them to flocculate into secondary particles agglomerates.[22]

Some authors have also claimed beneficial effects of ductile (semirigid), rather than rubbery, interphases for toughness enhancement.[23–25] Therefore, the preferential location of the silica domains for such systems is expected to be within the precipitated particles and/or in the interphase regions.

The organic networks of this study were produced with the use of difunctional epoxy resins based on bisphenol-A (DGEBA), cured with amine hardeners and modified by the addition of small amounts of suitably functionalized perfluoroether oligomers. These form soft particulate inclusions through reactions with the epoxy functional groups of the resin.

Perfluoroether oligomers are particularly suitable for this study in view of the ease with which their solubility characteristics can be altered through telechelic modifications at the chain ends.[26,27]

The localization of the silica phase within the perfluoroether particles separating from the epoxy matrix during curing is expected to take place by functionalizing the perfluoroether with alkoxysilane coupling agents.

EXPERIMENTAL

Materials

Rigid organic network components

A low molecular weight bisphenol-A resin, Epikote 828 (E), manufactured by Shell Chemical Company was used. Diphenylene methylene diamine (DDM) was used as hardener in the form of a 80% solution in dimethyl formamide (DMF) to facilitate its dissolution in the resin. Both were obtained from Aldrich Chemical Company.

Reagents for the preparation of the silane functionalized flexible network oligomers

Hydroxyl terminated perfluoroether (TX) is a proprietary product, in the form of a viscous liquid, sold under the trade name Fomblin Zdol TX (from Ausimont). The chemical structure is shown in Scheme 1. This oligomer has a number average molecular weight equal to 2,200. Chlorendic anhydride (CA) corresponds to hexachloro-endo-methylene tetraphthalic anhydride. It is a solid with a melting point equal to 335°C (obtained from Aldrich Chemical Company). ε-Caprolactone is a liquid with a boiling point equal to 97°C (obtained from Aldrich Chemical Company). Triphenyl phosphine (TPP) is a solid with melting point of 80°C (obtained from Aldrich Chemical Company). γ-Glycidoxyltrimethoxysilane (GOTMS) is a liquid reagent with 97% purity (obtained from Fisher Scientific). Its structure is shown in Scheme 1.

Reagents for the preparation of the silica component by the sol-gel method

Tetyraethoxysilane (TEOS) with 98% purity was obtained from Aldrich. γ-Glycidoxyltrimethoxysilane (GOTMS) was as specified above. *p*-Toluene sulfonic acid monohydrate (TSA), with 99% purity, and hydrochloric acid (HCl), as a 36.5% solution in water, were obtained from Fisher Scientific. Solvents specified in the text were analytical grades obtained from Aldrich.

Trialkoxy silane functionalization of perfluoroether oligomer TX

Homogeneous fuctionalization

The perfluoroether TX was chain extended to render it miscible with epoxy resins, according to a procedure described elsewhere.[18] This preparation consists of three steps. The first is a reaction with chlorendic anhydride at molar ratio of 1 : 1.8 and the second involves a telechelic extension through a reaction with ε-caprlolactone at molar ratio with respect to acid groups at 1 : 1.1. The products are a statistical mixture of diacid functionalized oligomer (80%) and α-ω hydroxy–carboxylic acid perfluoroether oligomer (20%). For identification purposes this is denoted as oligomer TX-CA-CL.

The molar ratios used in these reactions were experimentally found to provide the best balance of properties for the resulting adducts in terms of miscibility with the epoxy resin components, viscosity, and reaction yields. The silane functionalization was carried out, in the third step, by reacting oligomer TX-CA-CL with GOTMS, at 2 : 1*M* ratio, corresponding to approximately 1 : 1 ratio with respect to the acid groups. In this way the alkoxysilane functionalization takes place at both ends of the oligomer chains and the acid

functionality is totally obliterated. The reaction was carried out using TEOS as solvent in such amount to produce an equivalent silica content of 25% wt/wt, calculated on the basis that all siloxane groups are converted to SiO_2. The reaction was carried out at 90°C for 1 h. The structure of the final product is shown in Scheme 1 and is designated as oligomer TX-CA-CL-GO.

Heterogeneous functionalization

This reaction was also carried out in three steps, according to Scheme 2. In the first step the α-ω hydroxy acid oligomer TX-CA was obtained by reacting at 150°C the two components, using a 1 : 1M ratio, until the solution became clear to indicate the complete disappearance of CA solid particles (normally 20 min). Longer reactions times were avoided to prevent polymerization through condensation reactions between hydrocyl groups and carboxylic acid groups at the chain ends. This was reacted in the second step with GOTMS at molar ratio of 1 : 1 in a small magnetically stirred flask at 90°C for 1 h, to obtain the product designated as TX-CA-GO. In the third step a 1.6 : 1M ratio of CA was used to obtain the product TX-CA-GO-CA. Ideally this oligomer would contain one trialkoxysilane functionality and 1.6 carboxylic acid groups (see below).

The reaction was again carried out at 150°C until the last trace of CA in the form of a solid suspension disappeared (about 10 min). Chlorendic anhydride was used in both steps in view of its high reactivity[7,10] and once more reaction times were kept short to avoid the possible occurrence of side reactions.

Preparation of oligomer TX–silica hybrids

The previously produced oligomer TX-CA-CL-GO as a solution in TEOS was diluted with DMF at weight ratio 1 : 1 with respect to the TEOS content and a water solution of PSA was added in the following molar ratios (with respect to the TEOS content which would give a 25% wt/wt equivalent SiO_2 in the final hybrid): 0.2 : 1 for the PSA and 3:1 for the water. The mixture was stirred vigorously for 15 h at room temperature to fully hydrolyze the TEOS and the trialkoxysilane groups. This mixture is designated as Si-HB sol/TX-CA-CL-GO.

Comparative experiments were carried out using HCl (2% solution, 0.012 : 1 1M ratio with respect to TEOS).[11]

Note that PSA was used as acid catalyst, instead of the more conventional hydrochloric acid, to ensure that there was total hydrolysis of TEOS with very little condensation, thereby delaying the formation of networks.

Comparative experiments were carried out using HCl (2% solution, 0.012 : 1 1M ratio with respect to TEOS).[11]

The PSA was partially removed prior to being mixed with the epoxy resin components by adding ammonium acetate in appropriate stoichiometric amounts from a 32% wt/wt water solution. The precipitated ammonium sulfonate salt was removed from the solution mixture by centrifugation. Its identification was confirmed by DSC analysis by measuring its melting point and heat of fusion. The amount of PSA to be removed from the solution mixture was determined by the gelation characteristics required in subsequent preparation steps. The latter could be effectively carried out when half of the total amount of PSA was removed. An indication of the powerful way the gelation characteristics could be controlled through removal of different amounts of PSA can be obtained from the following observations: The total removal of PSA, which is being replaced by acetic acid thorough the formation of the ammonium toluene sulfonate salt, brings about gelation within about 15 min. Gelation times longer than 18 months were recorded when the PSA was not removed from the precursor solution.

The rationale for varying at will the gelation conditions of the final mixture, not only stems from practical considerations, but also as a way of controlling the diffusion kinetics of the reactants and the repartition of the various components in the different phases formed during curing.

Chemically induced nucleation of the precipitation of particles containing functionalized oligomers TX–silica hybrids

The usual procedure of prereacting the functionalized oligomer with an excess epoxy resin was adopted with the view of inducing nucleation of particles in the early stages of the curing schedule. 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 producing nanoscopic gel particles (nuclei) to initiate the formation and growth of soft particles after the hardener has been added and the mixture cured.

Both oligomer TX-CA-CL (shown in Scheme 1) and oligomer TXCAGOCA (Scheme 2) were prereacted with the epoxy resin in the presence of TPP catalyst, following a procedure already described elsewhere.[26,27] The resin to oligomer molar ratio was 4 : 1. The resin was first diluted with very small amounts (about 5%) of tetrahydrofuran (THF) to enhance the miscibility of the reactants. 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 as oligomers TX-CA-CL/Ep and TXCAGOCA/Ep.

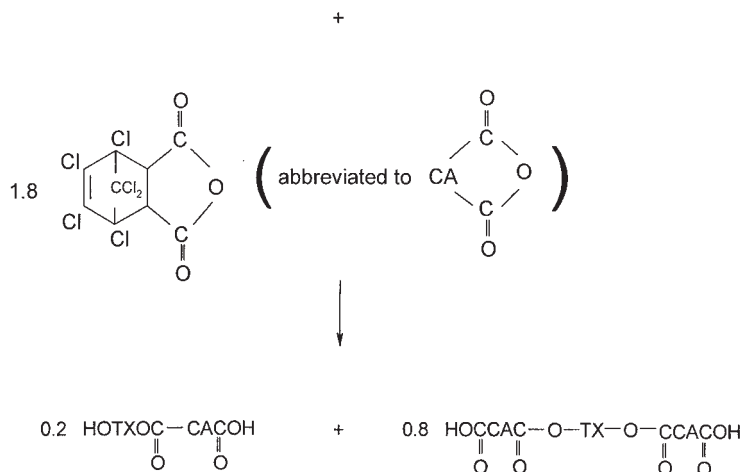**Preparation of resin mixtures for interphase control of precipitated particles**

Both prereacted epoxy/oligomer products, TX-CA-CL/Ep and TXCAGOCA/Ep, were each mixed with

REACTION SCHEME 1:

Homogeneous functionalization of perfluoroether oligomer (abbreviated to HOTXOH, to obtain products coded TXCACLGO.

Step 1
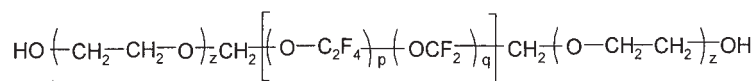
(where p/q = 0.7; z = 1.5, n ≈10)

+

1.8 (abbreviated to CA)

0.2 HOTXOC—CACOH + 0.8 HOCCAC—O—TX—O—CCACOH

Scheme 1 Homogeneous functionalization of perfluoroether oligomer (abbreviated to HOTXOH) to obtain products coded TXCACLGO.
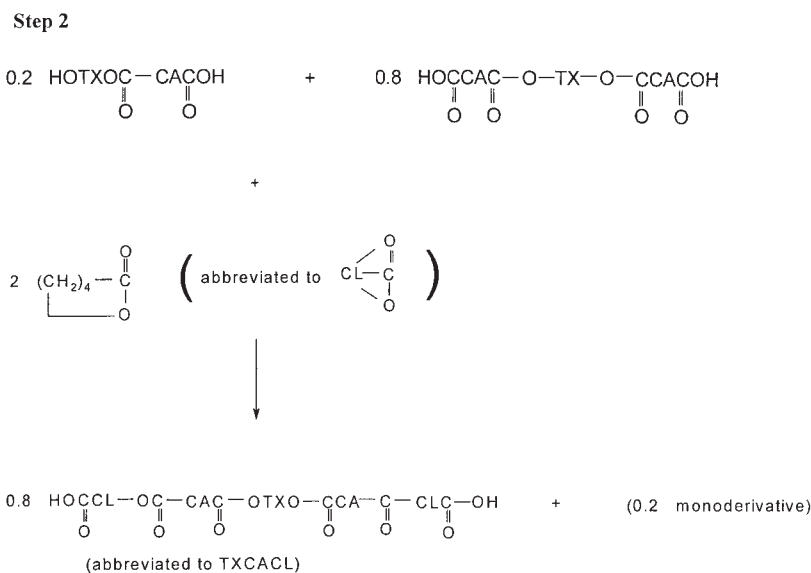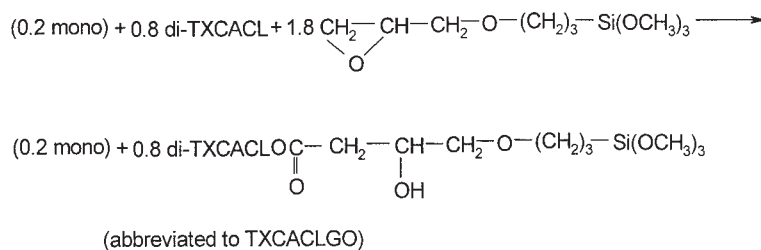
the perfluoroether oligomer-silica precursor solution Si-HB/sol TX-CA-CL-GO (see Preparation of oligomer TX—silica hybrids) in amounts such that the perfluoroether molar ratio of the two systems remained always at 1 : 1 level, while the equivalent SiO_2 content with respect to the total perfluoroether was kept at 25% wt/wt. These mixtures were diluted further with the epoxy resin to give concentrations of perfluoroether oligomer ranging from 2.5 to 15% wt/wt and heated for 4 h at 60°C.

The DDM hardener was added and mixed at room temperature until a homogeneous (clear) mixture was obtained. The hardener was used in amounts corresponding to a molar ratio of 0.75 : 1 (equivalent to weight ratio of 0.25 : 1). It is worth noting that mixtures with TXCACLGO as a single perfluoroether component produced IPN morphology instead of particle precipitation.

To determine the extent to which the resulting changes in properties were due to the presence of the *in situ* generated silica, a series of "control mixtures" were produced, in which the epoxy-extended oligomers TXCACL/Ep and TXCAGOCA/Ep (prehydrolyzed) were cured directly by the addition of the

hardener and diluted with the appropriate amount of epoxy resin to reduce the concentration of perfluoroether oligomer to the desired level without mixing with the alkoxysilane precursor solution SiHB/sol TX CACLGO. A comparison with the corresponding silica hybrids makes it possible to obtain an estimate of the relative effects of the silica and perfluoroether components on properties. The oligomer TX-CA-GO-CA/Ep was first hydrolyzed from a 30% wt/wt solution in THF with the addition of a 0.5% wt/wt 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 mm × 90 mm × 5 mm) and cured 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 for curing ensured no residual solvent was left in the cured samples.

Step 2

0.2 HOTXOC—CACOH   +   0.8 HOCCAC—O—TX—O—CCACOH

+

2 (CH₂)₄ — C (abbreviated to CL—C)

0.8 HOCCL—OC—CAC—OTXO—CCA—C—CLC—OH   +   (0.2 monoderivative)

(abbreviated to TXCACL)

Step 3

(0.2 mono) + 0.8 di-TXCACL + 1.8 CH₂—CH—CH₂—O—(CH₂)₃—Si(OCH₃)₃ ⟶

(0.2 mono) + 0.8 di-TXCACLOC— CH₂—CH—CH₂—O—(CH₂)₃—Si(OCH₃)₃

(abbreviated to TXCACLGO)

Scheme 1 (*Continued from the previous page*)

Control experiments to determine the effects of small quantities of prehydrolyzed alxoxysilane solution were also performed. These consisted of preparing a TEOS/GOTMS mixture at the usual molar ratio of 1 : 0.12 and adding 0.2 mol of PSA solution in water, keeping the molar ratio of H_2O : TEOS at 3 : 1, using the same conditions described in Preparation of oligomer TX—silica hybrids and the sample preparation and curing procedure described above.

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 disk 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 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°C/min. A modulated period of 60 s and a temperature amplitude of 0.5 K.

Physical characterization of cured samples

The cured samples were examined by scanning electron microscopy (SEM) to obtain an assessment of 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.

REACTION SCHEME 2:

*Heterogeneous functionalization of perfluoroether oligomer, (abbreviated to HOTXOH –
see* reaction scheme 1*), to obtain products coded TXCAGOCA.*

Step 1
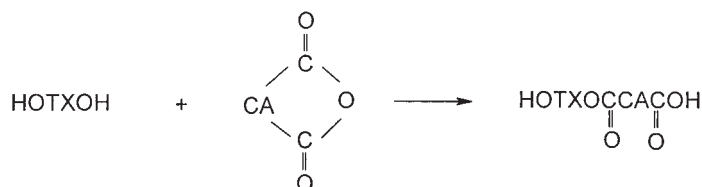
Step 2
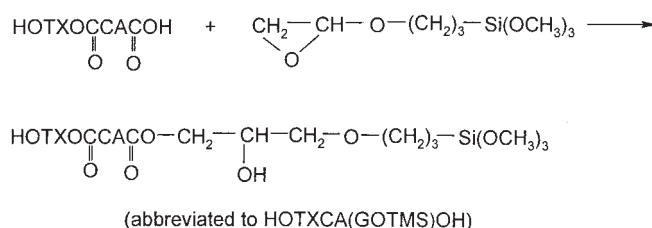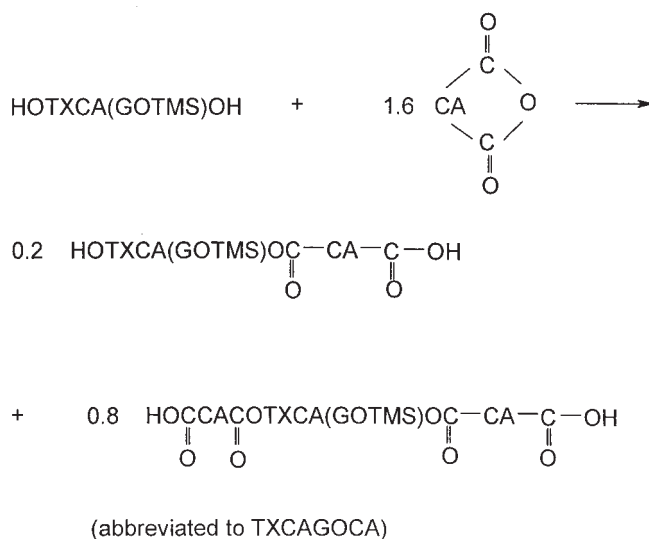
(abbreviated to HOTXCA(GOTMS)OH)

Step 3

(abbreviated to TXCAGOCA)

Scheme 2 Heterogeneous functionalization of perfluoroether oligomer (abbreviated to HOTXOH, see Scheme 1) to obtain products coded TXCAGOCA.

The TMDSC apparatus used was a Thermal Analysis instrument, operated in a nitrogen atmosphere and with a heating scan of 5°C/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 +0250°C, under a nitrogen blanket, at a heating rate of 3°C/min and an oscillating frequency of 1 Hz.

The Young's modulus and flexural strength were measured in a three-point bending mode with a span to thickness ratio (L/day) of 15 : 1 and a cross-head speed of 2 mm/min.

The gradient of the plot load P versus deflection Δ through the origin was used to calculate the modulus (E) and fracture stress (σ_B) from elasticity theory, i.e., $E = P/4D \times L^3/bd^3$ and $\sigma_B = 1.5 \, P_f L/bd^2$, where b is the specimen thickness and P_f is the recorded load at fracture.

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

$$--CF_2CH_2(OCH_2CH_2)_{1.5}O-OC \quad CO-O-CH_2-CH-CH_2-O-CH_2-CH_2-CH_2-Si-O-OC \quad CO-O-CH_3$$
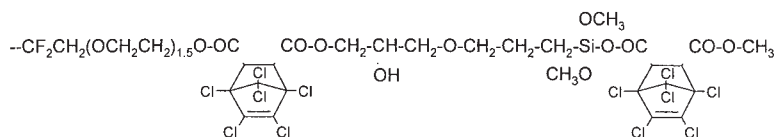
Scheme 3

edgewise. The specimens were single-edge-notch (SEN) 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 thickness ratio (*L/b*) 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 thickness ratio (*a/b*), 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, which yields the following relationship between fracture parameters specimen geometrical factors, $K_{IC} = YP_f/bW^{0.5}$. The values of Y were obtained from data reported in the literature.[22] In all case the validity of the LEFM analysis was checked by examining the load/deformation trace produced by the testing equipment and ensuring that linearity existed up to the point of fracture or very close to the fracture load. Tests were carried out at room temperature on a J.J. Lloyd tensile testing instrument.

RESULTS AND DISCUSSION

Analysis of the products of functionalization and chain extension reactions

Both FTIR and ^{1}H-NMR analyses have confirmed that the expected reactions, shown in Scheme 1, have taken place. The evidence and interpretation of the data have been published elsewhere.[13,15]

The NMR spectra of the products of the reaction for the preparation of epoxy-extended oligomer TX-CAGOCA/Ep indicated that only about 38% of the amount that would have reacted with nominally available acid groups were actually consumed. The NMR spectra of the precursor oligomer TXCAGOCA confirmed that the structure does not correspond entirely to that shown in Scheme 1, but substantial amounts of secondary products were obtained through side reactions between chlorendic anhydride and the methoxysilane functional groups giving products with the structure shown in Scheme 3.

Morphology of cured products

The micrograph in Figure 1 shows the fractographic morphology of the cured products obtained by mixing

simultaneously all the components, respectively, epoxy resin, hardener, perfluoroether oligomer TX-CACL, and the prehydrolyzed alkoxysilane. These depict the typical IPN morphology associated with these types of systems when phase separation does not take place.[26,27]

In Figure 2 are shown the SEM micrographs of hybrids produced by mixing (1 : 1 ratio) the homogeneous silane-functionalized perfluoroether oligomer TX-CA-CL-GO with the dicarboxylic acid functionalized oligomer TXCACL (chain extended with epoxy resin). In this case it can be clearly seen that the prereaction of the perfluoroether components with the epoxy resin brings about the precipitation of microscopic particles, comprising large quantities of agglomerated primary particles.

The energy disperse X-rays (EXD) analysis showed that the Cl and Si were concentrated in the precipitated particles, thereby confirming that both the silica and the perfluoroether components are repartitioned in the manner that was aimed by the study.

The micrographs in Figure 3 show the structure of precipitated particles for systems produced from 1 : 1 mixtures of homogeneously functionalized perfluoroligomer TXCACLGO and the heterogeneously functionalized oligomer TXCAGOCA (prereacted with epoxy resin) with additional amounts of epoxy resin and appropriate amounts of hardener to make the final compositions. These reveal the presence of large spherical particles (about 1–5 μm in diameter) made up of a very large number of clustered nanoparticles. An amount of slightly larger particles are also found,
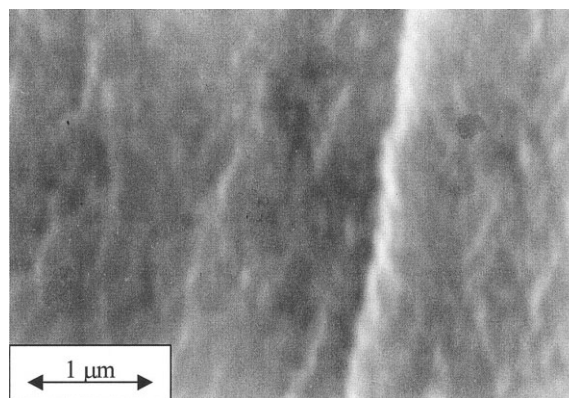

Figure 1 SEM micrograph of epoxy–perfluoroether–silica hybrids obtained by mixing simultaneously all components, respectively: epoxy resin, hardener, perfluoroether oligomer TXCACL (10% wt/wt), and prehydrolyzed TEOS (1.25%).
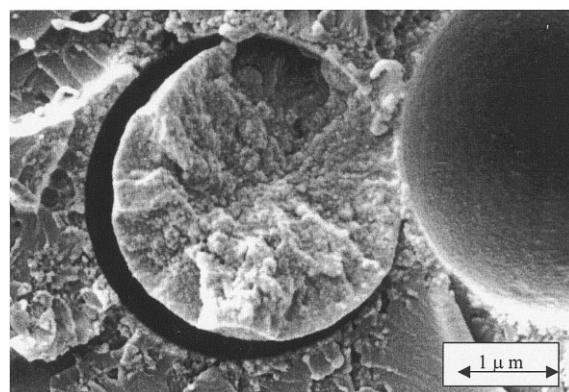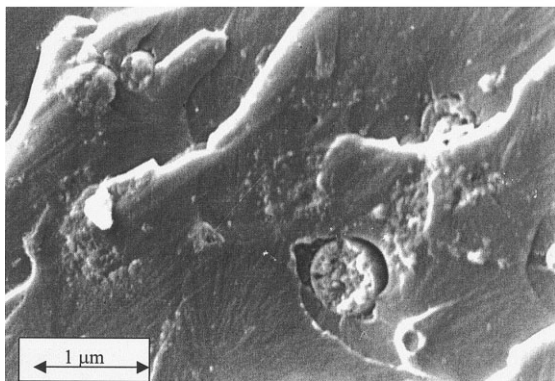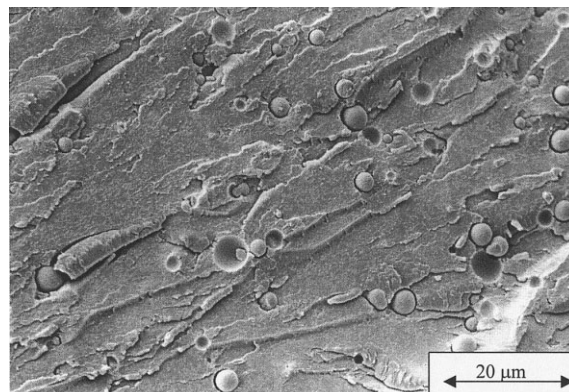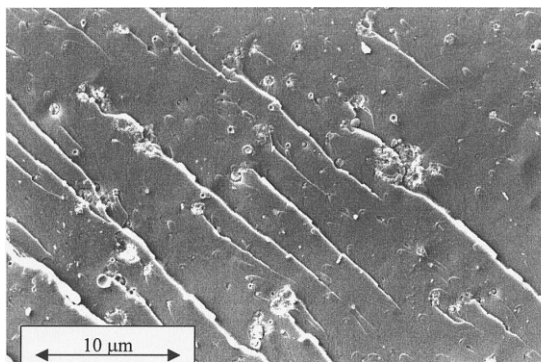
Figure 2 SEM micrographs of epoxy–perfluoroether–silica hybrids obtained by mixing (1 : 1 weight ratio) homogeneous silane functionalized perfluoroether TXCACLGO with dicarboxylic acid functionalized perfluoroether oligomer TXCACL (chain extended with epoxy resin). Total perfluoroether content = 5% wt/wt. (a) Low magnification; (b) high magnification.

Figure 3 SEM micrographs of epoxy–perfluoroether–silica hybrids. Composition same as in Figure 2. Total perfluoroether content = 5% wt/wt. (a) Low magnification; (b) high magnification.

randomly placed, on the outer surface of the larger spherical particles forming an irregular interphase with the matrix. The micrograph in Figure 4 shows that the amount of interfacial particles increase with increasing the perfluoroether (and equivalent silica) content.

The localized EDX analysis was used to confirm that the silica and perfluoroether oligomer were the primary constituents of the agglomerated particles, but the field area covered is too large to differentiate the composition of the primary particles within the agglomerates from those in the interphase regions.

A clearer picture of the microstructure of the precipitated particles was revealed by the TEM examinations. The micrographs in Figure 5 reveal the presence of a uniform layer surrounding the spherical particles below the irregular interphase zone. The existence of such an interlayer may also account for the debonding of the particle agglomerates from the heterogeneous interphase regions shown in Figures 3 and 4.

Note that none of the formulations containing either perfluoroether oligomer as a single component lead to the formation of a particulate morphological structure even when the TXCACL oligomer was prereacted
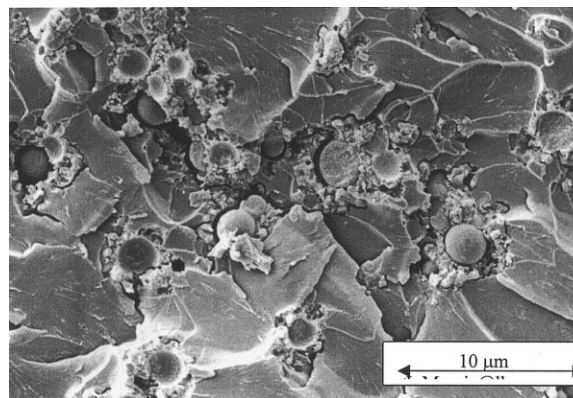

Figure 4 SEM micrograph of epoxy—perfluoroether–silica hybrids. Composition is the same as for Figure 2. Total perfluoroether content = 10% wt/wt.
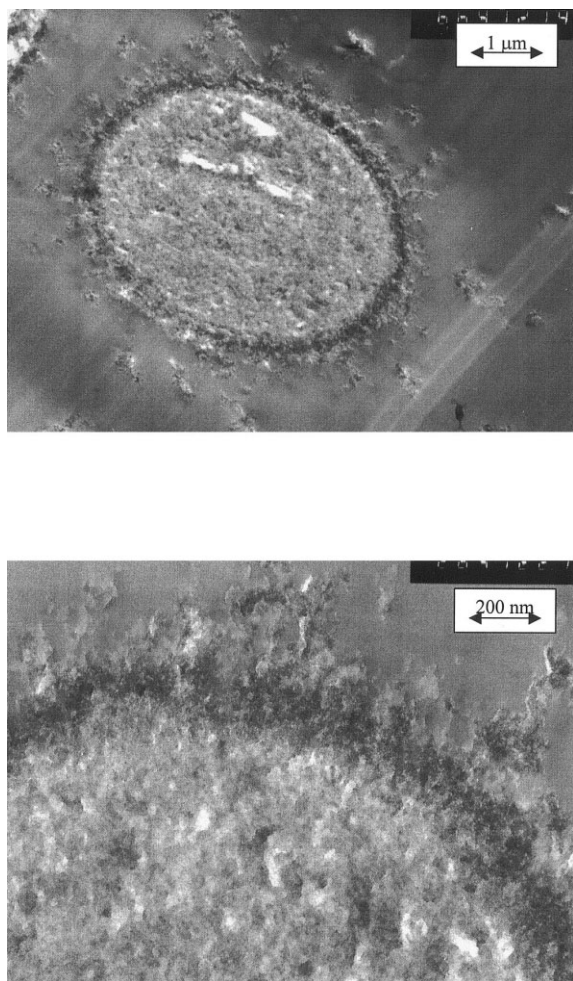
Figure 5 TEM micrographs of epoxy—perfluoroether–silica hybrids obtained. Composition is the same as in Figure 2. Total perfluoroether content = 10% wt/wt. (a) Low magnification; (b) high magnification.

with the epoxy resin. In these cases some very fine particles were apparent in the SEM micrographs, indicating that the subsequent reactions of the perfluoroether oligomer produced species that remained dissolved within the epoxy matrix rather than continuing the growth of existing nuclei particles.

Furthermore, when HCl was used as catalyst for the hydrolysis of TEOS, particulated microstructures were never observed and the final products were always very brittle.

Dynamic mechanical spectra

The majority of the silica hybrids produced by the previously described procedures were very brittle and unsuitable for mechanical tests. However, the samples obtained from formulations containing 1 : 1 mixtures of homogeneously and heterogeneously silane functionalized perfluoroether oligomers, respectively, TX-CACLGO and TXCAGOCA. (prereacted with epoxy

resin), were more suitable for evaluation of the mechanical properties.

The dynamic mechanical spectra, in the form of plots of elastic modulus (E') and tan δ against temperature, are shown in Figure 6 for compositions with varying contents of "mixed" functionalized perfluoroether oligomer. In all cases the silica content is 25% wt/wt with respect to the perfluoroether.

In common with the control epoxy resin sample (DGEBA/DDM) all formulations exhibited two glass transitions, one at around 100°C and the other at around 150°C.

The presence of the particulate perfluoroether component containing the *in situ* generated silica brings about a small reduction in the lower T_g values and a concomitant small increase in the upper T_g. The intensity of the peak relaxations associated with the latter transition became more pronounced with increasing the content of perfluoroether/silica particles.

The reduction in the lower glass transition temperature can be associated with the presence of residual (dissolved) perfluoroether oligomer in the epoxy matrix, thereby producing a plasticization effect. The enhanced relaxations at the upper transition temperature, on the other hand, can only be attributed to the structure heterogeneity in the interphase regions, which were described earlier. An indication of the causes for the small increase in the upper glass transition temperature may be obtained from observations related to the plot of the T_g of the epoxy resin against the concentration of equivalent silica, shown in Figure 7, with respect to formulations that do not contain any functionalized perfluoroether oligomer. The thermograms in this figure reveal the occurrence of a very large increase in the T_g of the epoxy network even with very low amounts of sol-gel generated silica. The T_g values shown on the thermograms were computed by the dedicated software of the apparatus.

Note that the measurements of the T_g of these systems had to be made by MTDSC because the samples were too brittle to be handled for DMTA tests.

Although the thermal analysis by DSC was not sufficiently sensitive to reveal the occurrence of the additional glass transition at around 145–150°C, the data show that the main glass transition increases very rapidly with the addition of small amounts of TEOS prehydrolyzed with PSA. Moreover the main glass transition becomes less distinctive and the relaxations are suppressed to a very large extent. This type of behavior has also been associated with embrittlement for amine cured amine epoxy nanocomposites.[28] Although the possibility of residual TSA forming salts with the amine hardener, or reacting directly with the epoxy resin, cannot be excluded, these reactions would have a minor influence on properties for stoichiometric reasons. Moreover both events would be
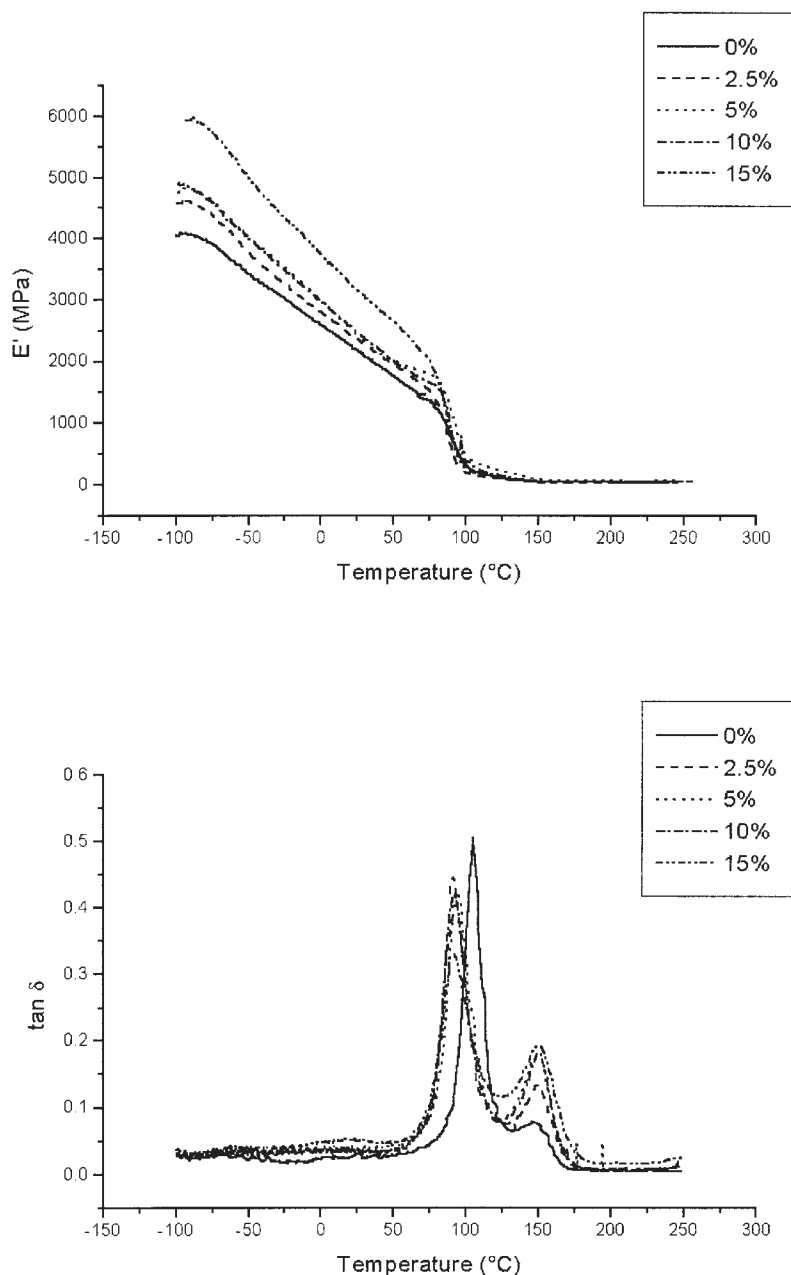
Figure 6 Dynamic mechanical spectra of epoxy–perfluoroether–silica hybrids. Composition is the same as in Figure 2. Polyether oligomer content was varied from 0 to 15% wt/wt. (a) Elastic modulus, E'; b) loss factor, tan δ

expected to cause a reduction, rather than an increase in the T_g of the cured resin.

From these observations it can be inferred that, although the prereaction of the oligomer TXCACL with the epoxy resin induces the precipitation of soft particles containing large amounts of perfluorooligomer and polysiloxane domains, a small amount of soluble siloxane low molecular weight species is likely to remain dissolved in the epoxy resin.

The hydrolysis of TEOS in the presence of TSA has been found to produce only alkoxysilane species with molecular weights in the region of 1,300 and signifi-

cant amounts of cyclic products.[29] Accordingly, while any residual perflouoroether remaining in the epoxy resin would cause plasticization and reduce the T_g (in this case the lower T_g), the soluble siloxanes can undergo condensation reactions with the hydroxyl groups in the chains of epoxy resin to produce small regions of highly crosslinked domains or clusters capable of increasing the T_g and to depress the relaxations within these transitions.[28] These would also account for the observed severe embrittlement for samples obtained from the majority of the formulations examined, and in particular those catalyzed with
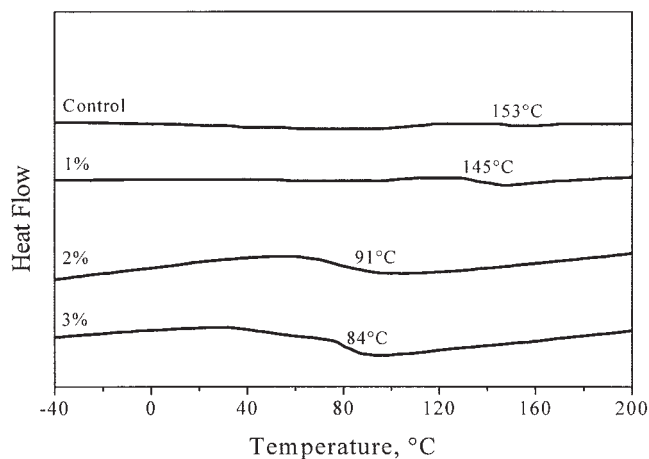
Figure 7 TMDSC thermograms for epoxy–silica hybrids. The nominal silica content was varied from 0 to 3% wt/wt.

Figure 8 Effects of perfluoroether content on mechanical properties of epoxy–perfluoroether–silica hybrids. Composition is the same as in Figure 2. (a) Flexural modulus; (b) flexural strength.

HCl. The contrast in morphology and properties observed with the use of TSA relative to HCl as catalysts is related to the propensity of the resulting siloxane species remaining dissolved within the epoxy resin/hardner mixture. By suppressing the condensation reactions through the use of TSA, the highly hydrolyzed low molecular weight siloxane species produced will be in a state of strong H-bonded associations within the functionalized perfluoroether and will undergo condensation reactions to form localized microclusters.

Systems produced with HCl as catalyst, on the other hand, will form highly dispersed branched siloxanes containing large quantities of low molecular weight species in a low state of association, which allows them to diffuse readily and react with the hydroxyl groups of the epoxy resin, rather than participating in the condensation reactions for the formation of silica domains.

It is in the light of these observations the higher intensity of the peak relaxations for the upper transition temperature, for formulations exhibiting the morphology depicted in Figure 5, has to be associated with the heterogeneity in the interphase regions rather than molecular relaxations within the adjacent networks. These observations provide also a plausible explanation for the increase in E' within the glassy state with increasing concentration of perfluoroether content [Fig. 6(a)], which is substantiated by the consideration of the higher amounts of particles deposited in the interphase regions, as shown by the micrograph in Figure 4.

Mechanical properties and interdependence on structural features

The data obtained from the measurements of mechanical properties show that the occurrence of the events
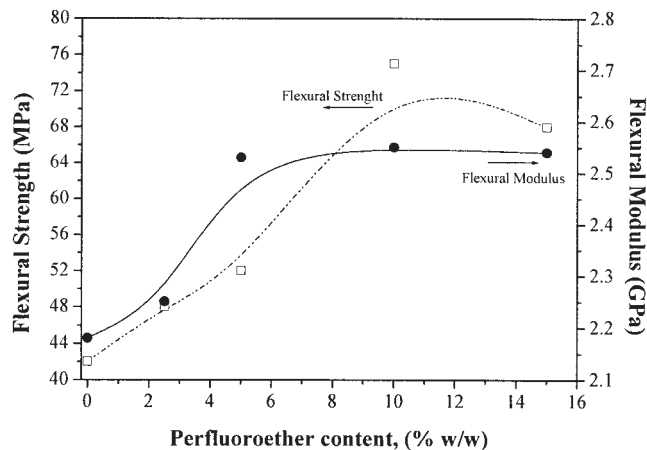
described, with respect to the samples exhibiting the morphology depicted in Figure 3, can have beneficial effects. This is illustrated by the plots in Figures 8 and 9, which show that all the important engineering properties, flexural modulus and strength, and fracture toughness parameters K_C and G_C increase with increasing the content of silica reinforced perfluoroether particles. Although the fracture toughness enhancement is relatively small in comparison to previously reported data for systems without silica reinforcement, the balance of properties displayed by the epoxy compositions of this study is unique. Usually, improvements in toughness are achieved at the expense of a reduction in modulus and, often, also in flexural strength. The flexural strength values recorded for the systems with a heterogeneous inter-
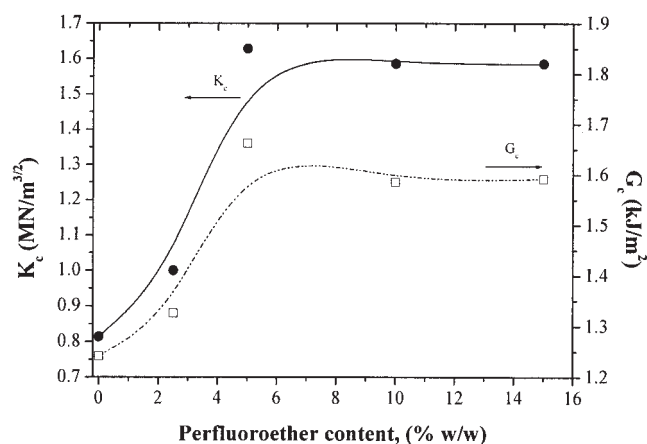

Figure 9 Effects of perfluoroether content on mechanical properties of epoxy–perfluoroether–silica hybrids. Composition is the same as in Figure 2. (a) Critical stress intensity factor, K_C; (b) critical strain energy release rate, G_C.

phase are indeed remarkably high. Together with the concomitant increase in modulus the systems and procedures described could constitute a viable route for further enhancement of properties through optimization of the formulations used.

The coarser structure of the particles in the interphase regions compared to the particulate domains within the main particles [see Figs. 3(b) and 4] suggests that they are formed subsequently to the precipitation of the heterogeneously functionalized oligomer TXCAGOCA, owing to its higher molecular weight and more branched nature that the dicarboxylic acid functionalized oligomer TXCACL. This will be followed by the precipitation of TXCAC, as it is linked to epoxy chains, and form the uniform interlayer identified in the TEM micrograph in Figure 5. The homogenously functionalized oligomer TXCACLGO is expected to be the last perfluoroether component to precipitate, bringing down the rest of the siloxane species through condensation reactions with the alkoxysilane/silanol functionality. These will form the particles on the outer surface to produce uneven outer regions with some detached particles, as indicated by the SEM micrographs in Figures 3 and 4. Obviously the events described have to be considered within the context of morphological confinements and are expected to take place in a cascading fashion, rather than as distinct sequential processes, and each stage of the process will involve the participation of all reactants, but at different levels.

CONCLUSION

From the results of this study and related discussion it is possible to draw the following main conclusions:

1. Functionalization of telechelic-modified perfluorooligomers with alkoxysilanes and a chain extension reaction with epoxy resin is required to bring about the precipitation of particles containing occluded silica domains, when an amine hardener is used to crosslink the resin.
2. Acid prehydrolyzed alkoxysilane precursors for the formation of silica domains by the sol-gel method can produce resin soluble siloxane species capable of forming highly crosslinked clusters in the epoxy matrix, which will cause severe embrittlement of the cured products.
3. The use of a mixture of a silane-functionalized telechelic perfluoroether and diacid functionalised perfluoroether, previously extended by a

catalyzed reaction with the epoxy resin, provides the required conditions for the cascading precipitation of toughening particles containing occluded silica domains and surrounded by an irregular interphase region. The unique combination of increased modulus, strength, and fracture toughness is attributed to the synergistic effect of the morphological features of the products and a more quantitative precipitation of both siloxanes and perfluoroether components of resin mixture.

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