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Investigation of properties of fiber/matrix interphase formed due to the glass fiber sizings

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Sizings on glass fibers consist of a silane-based network that is chemically bound to the fiber and other compounds that are adsorbed onto the glass surface. Formation of interphase involves dissolution of adsorbed species and inter-diffusion of these compounds and resin monomers into the interphase region and chemical reaction of available functional groups. All these phenomena occur at the presence of the silane-based network. In this study, the effects of the silane-based network on the properties of the interphase region are investigated for an epoxy/amine resin system and compatible sized glass fibers. The composition of the sizing material bound to glass was determined using nuclear magnetic resonance (NMR) spectroscopy. Based on this information, model interphase materials were synthesized that were a blend of an epoxy/amine matrix and inclusions. The inclusions consist of an interpenetrating network of silane-based polymer and epoxy/amine thermoset that represents the interphase material formed during processing. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) techniques were used to characterize the glass transition temperature and flexural modulus of the model materials. The properties of the model interphase material were obtained using the DMA results and established micromechanics models. The results show that the glass transition temperature of the model interphase is about -5°C, and its flexural storage modulus at room temperature is about 50% of that of the bulk matrix. This work has also shown that a reduction in the cross-link density of the bound network might significantly reduce the modulus within the interphase region by a factor of 5 to 8.

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1. Introduction

A typical polymeric matrix composite is made of reinforcing fibers such as glass, carbon, and aramid, and a polymeric matrix, either thermoplastic or thermoset. For thermosetting composites, theoretical and experimental studies have shown that an interphase region between the fiber and the matrix may form that has distinct properties [1–9]. Mechanisms for interphase formation include (1) preferential adsorption of one reacting resin species onto the fiber surface [10, 11] and (2) the presence of sizings applied to the fiber surface during manufacturing [12–17]. The properties of the interphase and the degree of adhesion to the fiber surface govern load transfer between the constituents of the composite. Previous investigations have shown that interphase properties significantly affect the strength, toughness, ballistic resistance, and durability of composites [2, 3, 18–23]. Much of this work has focused on optimizing fiber-matrix adhesion and durability using a variety of approaches [12–17, 24–30]. In this work, we focus on gaining a better understanding of the structure and properties of the network polymers formed at the glass fiber/epoxy-amine interphase.

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During commercial manufacturing of fibers (carbon or glass), an aqueous emulsion of sizing material is applied to the fibers as they are formed [31]. The sizing serves several purposes, such as improving ease of handling, facilitating storage of the fibers, and enhancing compatibility with the matrix resin in terms of both processing and mechanical behavior.

Typically, carbon fiber sizings are composed mainly of low molecular weight epoxy resins such as diglycidyl ether of bisphenol-A (DGEBA). In most applications, it has been suggested that the sizing material dissolve into the matrix during the manufacture of carbon/epoxy composites [1, 5, 6]. For an epoxy-amine resin system and unsized carbon fibers, Palmese and McCullough [1, 32] showed calculations that there is preferential adsorption of one of the reacting species onto the carbon fibers. This phenomenon results in an off-stoichiometric composition of epoxy and amine at the interphase region that exhibits significantly different properties (e.g.: glass transition temperature and mechanical properties) from those of the bulk matrix. Skourlis later validated their predictions by showing that the T_g of the interphase was indeed lower than the matrix T_g due to the off-stoichiometry network [11].

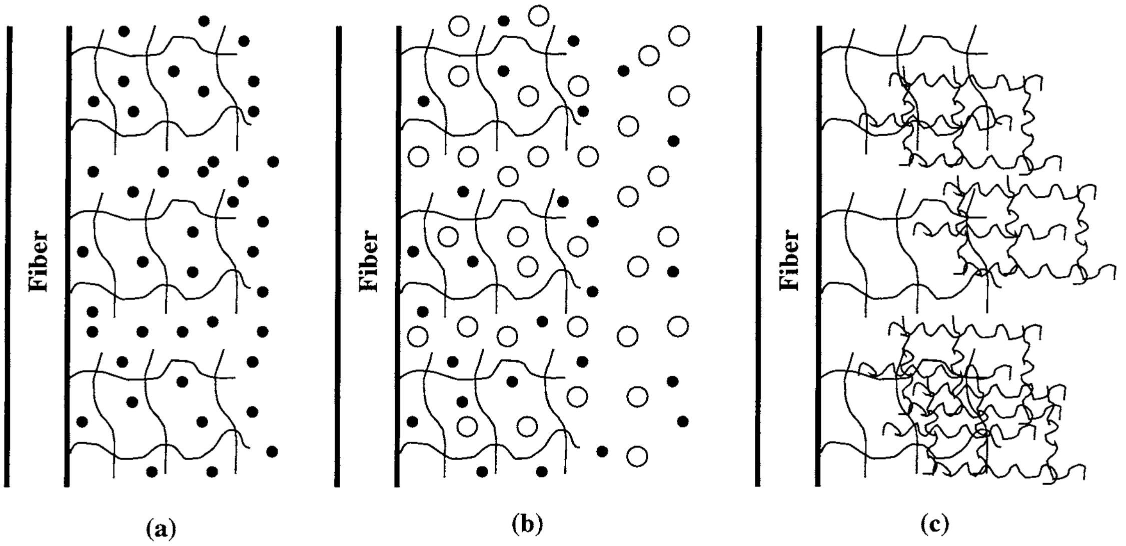
In glass fiber systems, the sizing material is more complex. It is often an aqueous emulsion. Its solid fraction consists primarily of a film former, a surfactant, and a silane coupling agent. Small amounts of lubricant and anti-static agent are also used. The film former is typically a low molecular weight compound identical to or strongly compatible with one of the resin components. The silane coupling agent of most commercial glass fibers has three alkoxy functional groups. These groups allow the silanes to react with each other and with the glass to form a multi-layer network on the glass surface. Therefore, the sizing on the glass is a blend of high molecular weight polymers, including a silane-based network and surfactant, as well as low molecular weight materials such as film former. The size and network structure of the polymeric phase could affect the equilibrium composition of the low molecular weight compounds in this phase. The silane coupling agent also has a functional group on its organic tail that can be designed to react with the matrix resin. Silanes that can react with the resin system are termed “compatible” and those that do not are termed “incompatible” with the resin system. In this way, the term *compatibility* is used differently than it is used in the field of polymer blends. Numerous studies have shown that the treatment of glass surfaces with silane coupling agents improves the interfacial strength and hygrothermal durability between the fiber and the matrix due to both chemical bond and physical interaction between the silane-based and matrix networks [29, 30, 33–35]. Less research has been devoted to study of the network polymer structure at the interphase.

Several researchers have studied various glass fiber sizings to understand their effects on the formation of the interphase and composite mechanical behavior [2, 3]. It is well known that upon wetting of the glass fibers by resin, a fraction of the sizing dissolves into the matrix while the rest remains bound to the fiber surface [3]. Published works have shown that diffusion of the extractable species into the matrix can alter the matrix properties dramatically [2–4]. These researchers made model interphase compounds to simulate the material at the interphase region.

Drown *et al.* [2] assumed that the interphase could be represented by a blend of sizing and matrix. Their model interphase specimens consisted of matrix resin mixed with 5 to 25 wt.% of commercial sizing, which contained film former, surfactant, silane coupling agent, antistatic agent, and lubricant. This approach investigates the effects of a non-bound sizing component on resin properties. The effects of the alkoxy silane hydrolysis and subsequent condensation were not considered. The matrix resin was a stoichiometric mixture of DGEBA (DER 383, Dow Corning) resin and diaminocyclohexane (DACH, Aldrich Chemical) hardener. The thermophysical and mechanical properties of these samples were determined. The authors reported that the T_g of the samples decreases monotonically with increasing sizing content. It was explained that the decrease in the T_g was caused by reduction of the crosslink density due to the presence of mobile silanes and other ingredients in the sizing blend. They also reported that the tensile modulus, storage modulus, and tensile strength of the samples increased with increasing sizing content, and was attributed to an antiplasticization effect below the T_g.

Thomason [3] argued that if the soluble portion of the sizing remains at the vicinity of the fiber, then the interphase properties are mainly affected by this soluble portion. He used acetone extraction technique to remove the soluble portion of several commercially available sized glass fibers and showed the percentage of soluble sizing to be about 75%. He used nuclear magnetic resonance (NMR) spectroscopy and elemental analysis to show that the soluble part consists of approximately 70% film former and 30% surfactant. No silane was detected in the acetone wash. The extracted materials were subsequently dried and mixed in different concentrations (up to 20 wt.%) with stoichiometric ratio of a DGEBA resin (Epikote 828EL, Shell) and amine hardener (Epikure 113, Shell). The amount of amine was not adjusted for complete reaction of the epoxide groups of the film former. The results from DMA and DSC experiments showed that the T_g of these model interphase specimens decreased with increased concentration of the extract. On the other hand, it was found that the DMA-measured storage modulus values of the blends displayed a maximum at around 2-wt.% sizing extract. This behavior was explained as the outcome of two competing effects: (1) flexibilization of the matrix by the sizing and (2) stiffening due to the reduced free volume of the matrix with low cross-link density resulting from the addition of extra epoxy molecules. It was also found that the interfacial shear strength of composites fabricated using these sized-fiber/epoxy-matrix systems is directly related to the amount of non-extractable sizing.

While the previous studies have shown the extractable components can affect resin properties, less



Network represents bound material. Filled circles represent unbound material.

Open circles represent resin constituents. Inter-diffusion of unbound sizing and resin materials occur.

An interpenetrating network between bound sizing and the matrix is created.

Figure 1 Schematic illustrating the sizing material on glass fiber at different stages of the process: (a) before the resin is applied, (b) after the resin wets the fiber, and (c) after the resin is cured.

work has been devoted to understanding the structure and properties of the interpenetrating network (IPN) that is formed from the bound functionalized silane layer and the reactive resin. This is most likely due to the difficulty involved in preparing "model" specimens that are representative of the true interphase structure. However, the sequential IPN that is formed by silane condensation on the fiber surface followed by resin diffusion and subsequent crosslinking should have a pronounced effect on interphase properties. This work focuses on characterization and analysis of this type of material. Fig. 1 clarifies this approach. Fig. 1a shows the glass fiber covered with the sizing. Upon wetting of the fiber by resin, the soluble portion of the sizing and the resin constituents interdiffuse into the interphase region (Fig. 1b). At this stage, the thermodynamics of mixing and kinetics of diffusion mainly govern the equilibrium concentration and the rate of diffusion. The chemical reaction between epoxide and amine groups leads to formation of an interpenetrating network as shown in Fig. 1c. In this work, it is proposed that the composition and network structure of the bound sizing may have significant effects on the formation of this interpenetrating network. Thus, in this work a three-part methodology has been developed and implemented to understand the properties of the interphase in sized glass fiber epoxy systems. This methodology includes (a) determination of the composition of bound sizing, (b) synthesis of materials that replicate the interpenetrating network between bound sizing and matrix (based on the above composition determination), and (c) evaluation of the T_g and flexural modulus of these model interphase specimens to gain a better understanding of interphase behavior.

The sizing on glass fibers was first analyzed to determine the composition of the extractable and bound phases. The sizing was comprised solely of epoxy film former, surfactant, and silane coupling agent. Using burnout and acetone extraction experiments, an overall mass balance of the extractable and bound portions of the sizing on glass fibers was performed. NMR spectroscopy was then used to determine the composition of the extractable phase.

Using these results, model interphase materials were synthesized that simulated the composition and the structure of the actual interphase. This involved three main steps: (1) bulk hydrolysis and condensation of silane coupling agent in the presence of only film former and surfactant, (2) separation of the silane-rich network and its chemical analysis, and (3) synthesis of model interphase samples using silane-based network, epoxy resin, and amine curing agent. The aqueous solution of film former and surfactant used by Owens Corning was also provided by the company.

These model specimens were characterized using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) to obtain the thermophysical properties of the model interphase materials. The T_g of the interphase was obtained from the subambient DSC measurements. The modulus of the interphase was derived from the DMA measurements of the model composite using an established self-consistent micromechanics model that considers the properties of rubbery inclusions (silane-rich network) embedded in a glassy matrix (epoxy-amine) phase.

2. Experimental procedure and results

2.1. Materials

The resin system used in this study was an epoxy-amine thermoset system. The epoxy resin was DGEBA, Epon-828, purchased from Shell. The amine was bis (*p*-amino cyclohexyl) methane, PACM-20, purchased from Air Products. The average molecular weight of Epon-828 is 370 g/mol. A stoichiometric amount of

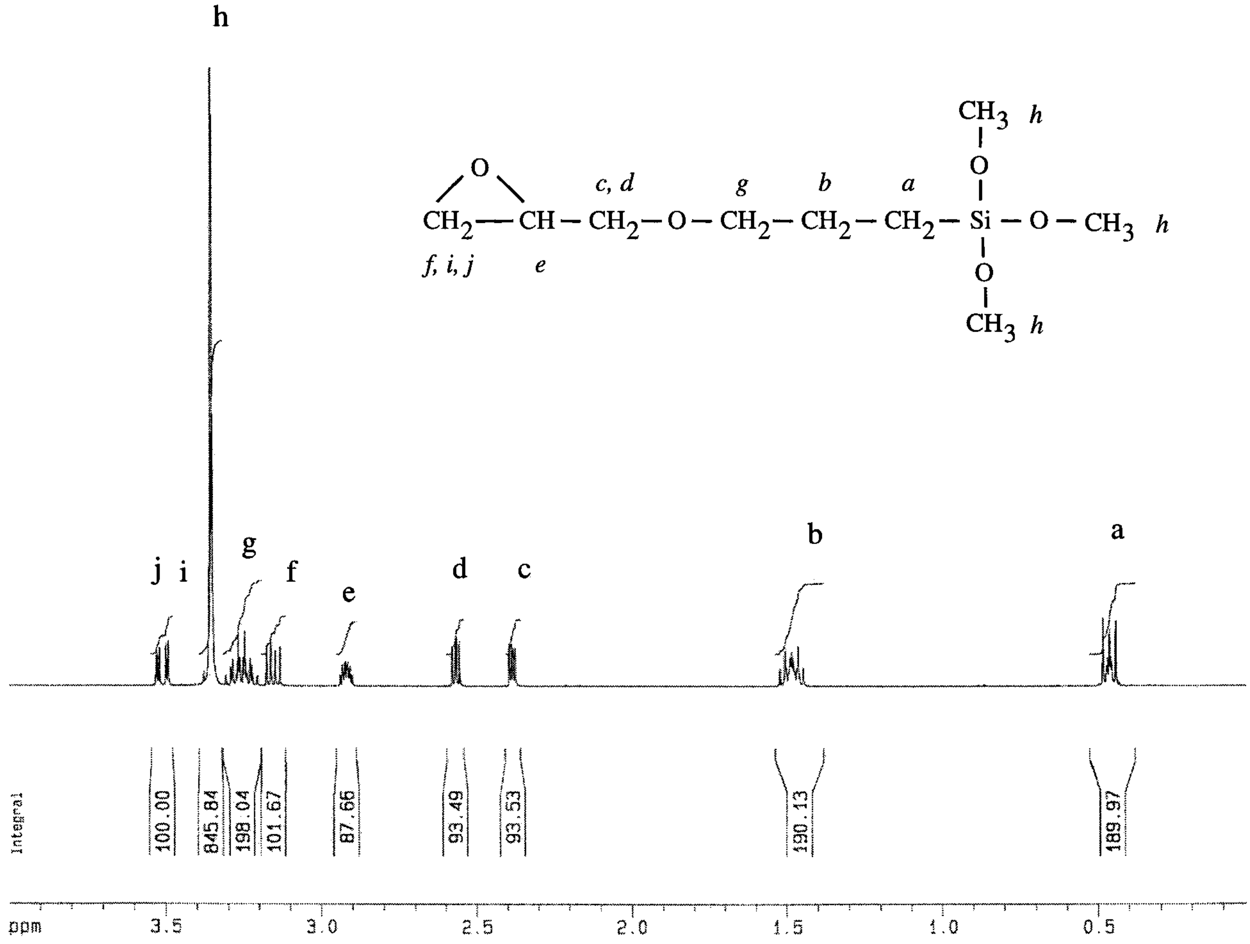


Figure 2 Proton NMR spectrum of glycidoxy propyl trimethoxy silane, its chemical structure, integration of peaks, and peak assignments.

amine was used for all samples made in this study. This includes epoxide groups of the DGEBA resin and that of silane compound as determined from NMR. All samples were cured at 80°C for 2 hours and post-cured at 160°C for 2 hours.

The silane coupling agent was glycidoxy propyl trimethoxy silane. This compound was purchased from Dow Corning Corporation under the commercial name of Z-6040. The silane was 99.8% pure and was used as received. Fig. 2 shows the proton NMR spectrum of the silane. The chemical structure of silane and the peak assignments are also given in Fig. 2. The peak assignments will be used in what follows to detect the concentration of silane.

Epoxy-amine compatible sized E-glass fibers were custom made for this work by Owens Corning Corporation. The sizing contains three components: epoxy film former, surfactant, and silane coupling agent. The film former was DGEBA. The surfactant was a triblock ethylene oxide and propylene oxide copolymer. The silane coupling agent was glycidoxy propyl trimethoxy silane.

The sizing is an aqueous emulsion of film former, surfactant, and silane. This mixture is rolled onto the glass fiber and dried at about 140°C overnight. To make a mixture similar to the commercial sizing, we obtained an aqueous emulsion of film former and surfactant from Owens Corning. The water content of this emulsion is 43.1% by weight. The average molecular weight and mass fraction of the film former were calculated using the proton NMR spectrum of the dried emulsion (see Fig. 3). This calculation is briefly explained in the following paragraph. The chemical structure of epoxy film former and surfactant, the peak assignment, and their corresponding areas are also shown in Fig. 3.

Two pieces of information can be obtained from the NMR analysis: the average molecular weight of the epoxy film former and the mass fraction of film former and surfactant in the emulsion. The molecular weight can be calculated from the ratio of areas for the aromatic protons (peaks at 6.8 and 7.1 ppm) to the areas for the methylene protons of the epoxide groups (peaks at 2.7 and 2.9 ppm). The mass fraction of surfactant and film former was calculated as follows. First, the NMR peaks for the methyl group (CH_3-) of propylene oxide at 1.2 ppm and methylene group (-CH_2-) of ethylene oxide at 3.7 ppm and the epoxide methylene group of the film former at 2.7–2.9 ppm were normalized with respect to their corresponding number of protons. Second, the mole fraction of ethylene oxide, propylene oxide, and film former was calculated. Third, the mass fraction of film former and surfactant was calculated using the molecular weight of film former, ethylene oxide, and propylene oxide repeat units. Details of the calculations are beyond the scope of this paper and are shown elsewhere [36]. Such calculations yield an average molecular weight of 497 g/mol for the film former and a composition of 78.6 wt.% film former and 21.4 wt.% surfactant for the emulsion. This value is close to the 70% film former reported by Thomason [3].

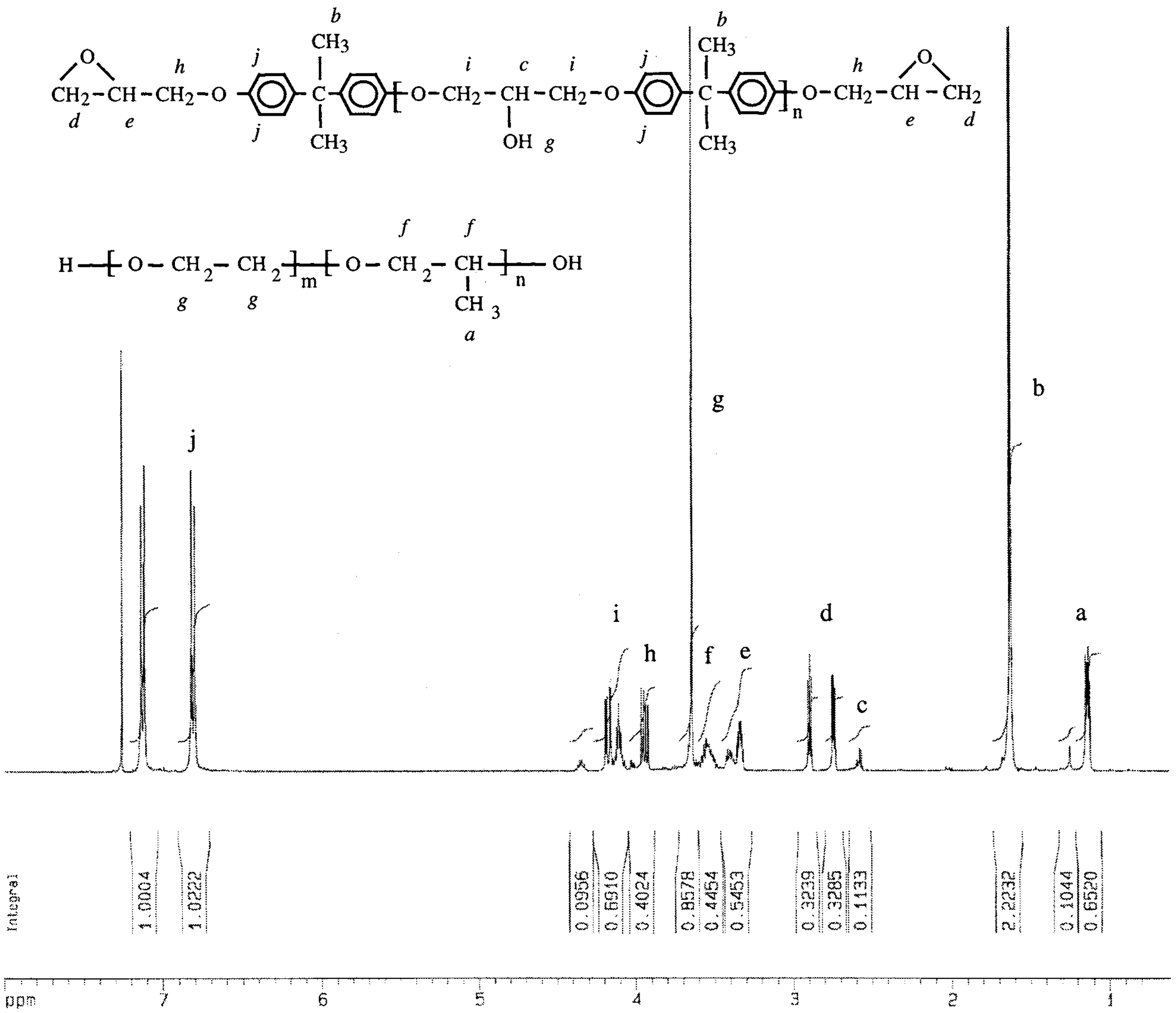


Figure 3 Proton NMR spectrum of the emulsion provided by Owens Corning Corporation. The emulsion contains film-former (diglycidyl ether of bisphenol-A (DGEBA)) and surfactant (Poly (Ethylene Oxide – co – Propylene Oxide)). Chemical structures of film former and surfactant and peak assignments are also shown.

2.2. Acetone extraction and burnout experiments

Acetone extraction and burnout experiments were used to determine the amount of bound and extractable sizing. For the burnout test, as-received fibers were dried in a vacuum oven at −100 KPa and room temperature to reach a constant mass. The mass loss was less than 0.1 wt.%. The fibers were placed in a dry crucible and left in a furnace at 620°C for 35–40 minutes. The samples were then cooled to room temperature under vacuum and weighed. The fibers were further heated for an additional 10 minutes at 620°C to ensure that weight loss was stabilized. There was no further change in the mass. The results showed that 0.60 ± 0.01 wt.% of the fibers as received are the sizing.

To determine the fraction of extractable sizing, acetone extraction was performed. The main assumption for this analysis is that the fraction of sizing that is able to diffuse into the matrix is equal to the fraction that is soluble in acetone. In this experiment, a known quantity of fiber was dried, weighed, and soaked in boiling acetone for 5–6 hours. The fibers were then rinsed with acetone and dried to constant mass. The dried fibers were burned in a furnace at 620°C for 35–40 minutes. The burned fibers were weighed. The acetone solution was also dried to a constant mass. The results are summarized in Table I. The fraction of soluble sizing is $83 \pm 2\%$. The values in the first two rows of Table I are within the standard deviation of each other and therefore equal. The thickness of the bound and initial sizing is calculated from Equations 1–3, assuming even coverage of the fiber by the sizing material.

$$r_s = \sqrt{\frac{m_s}{\pi \rho_s L_f} + r_f^2} \qquad (1)$$

TABLE I Acetone extraction and burnout experimental results showing the percentage of extractable and bound sizing. The number in the second row was calculated from a mass balance using the results from burnout tests of washed fibers

Mass Percentage of:	%
Sizing from burnout of fibers as received	0.60 ± 0.01
Sizing from acetone extraction and burnout of washed fibers	0.59 ± 0.01
Extractable sizing	82.5 ± 1.9
Bound sizing	17.5 ± 1.9

TABLE II Calculated thickness of extractable and bound sizing for sized glass fibers

Sizing	Thickness (nm)
Initial (before acetone wash)	64 ± 2
Bound (after acetone wash)	11 ± 2

$$L_\mathrm{f} = \frac{m_\mathrm{f}}{\pi \rho_\mathrm{f} r_\mathrm{f}^2} \tag{2}$$

$$t_\mathrm{s} = r_\mathrm{s} - r_\mathrm{f} \tag{3}$$

where r, m, t, L and ρ represent the radius, mass, thickness, length, and density, while the subscripts "s" and "f" stand for the sizing and fiber, respectively. The average fiber radius (r_f) was measured to be 11.5 μm using scanning electron microscopy (SEM). The value of ρ_f is 2.54 gr/cm^3 [37]. The density of the sizing (ρ_s) was estimated from the density of pure component and a mass fraction mixing rule. Using the initial mass of sizing, the extractable portion, and Equations 1–3, the thickness of the sizing before and after the acetone extraction was calculated to be 64 ± 2 and 11 ± 2 nm, respectively (see Table II).

2.3. Determination of the composition of the bound sizing

The composition of the bound sizing was determined from overall and component mass balances of the initial and extractable sizing. The composition of the as-applied sizing on the glass fibers is 67% film former, 18% surfactant, and 15% silane coupling agent. These values were provided by Owens Corning Corporation. The mass fraction of film former, surfactant, and silane in the extractable sizing was obtained using the NMR spectrum of the acetone extract given in Fig. 4. From these results, the average molecular weight of the film former was calculated to be 515 g/mol. This molecular weight is about 4% different from the molecular weight obtained from the emulsion sample (497 g/mol). The difference is within a nominal 5% variation in the NMR peak integration. Comparison of the silane NMR spectrum in Fig. 2 and the spectrum of the extract reveals no detectable amount of silane in the acetone extract. Therefore, we can conclude that almost all the silane remains at the glass surface. Using the spectrum in Fig. 4, the weight fractions of film former and the surfactant in the extractable sizing were calculated to be 81% and 19%, respectively. The composition of the bound portion was calculated to be 87% silane and 13% surfactant. The results in Fig. 5 show that practically all

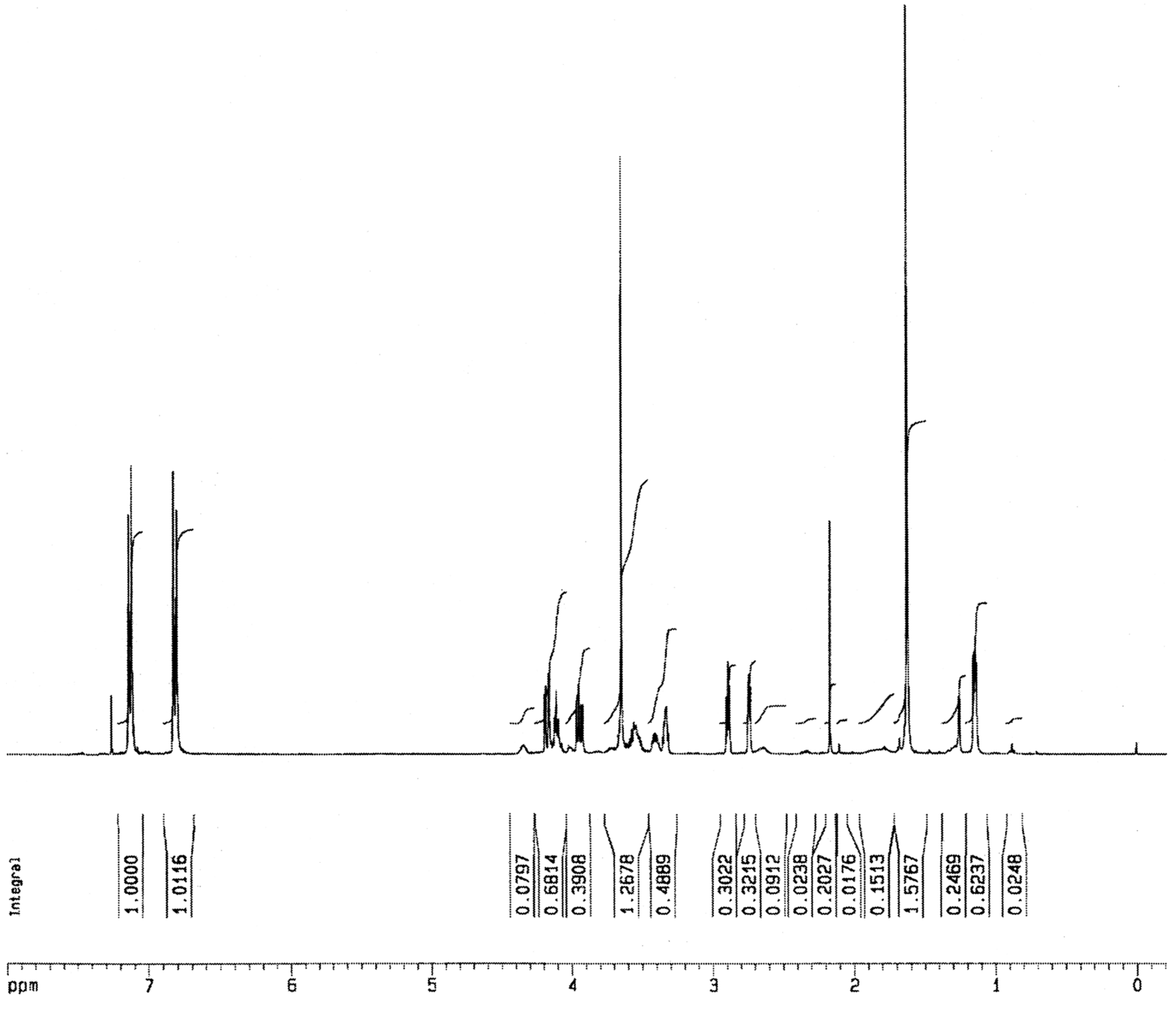


Figure 4 Proton NMR spectrum of glass fiber sizing extracted in acetone and integration of peaks.

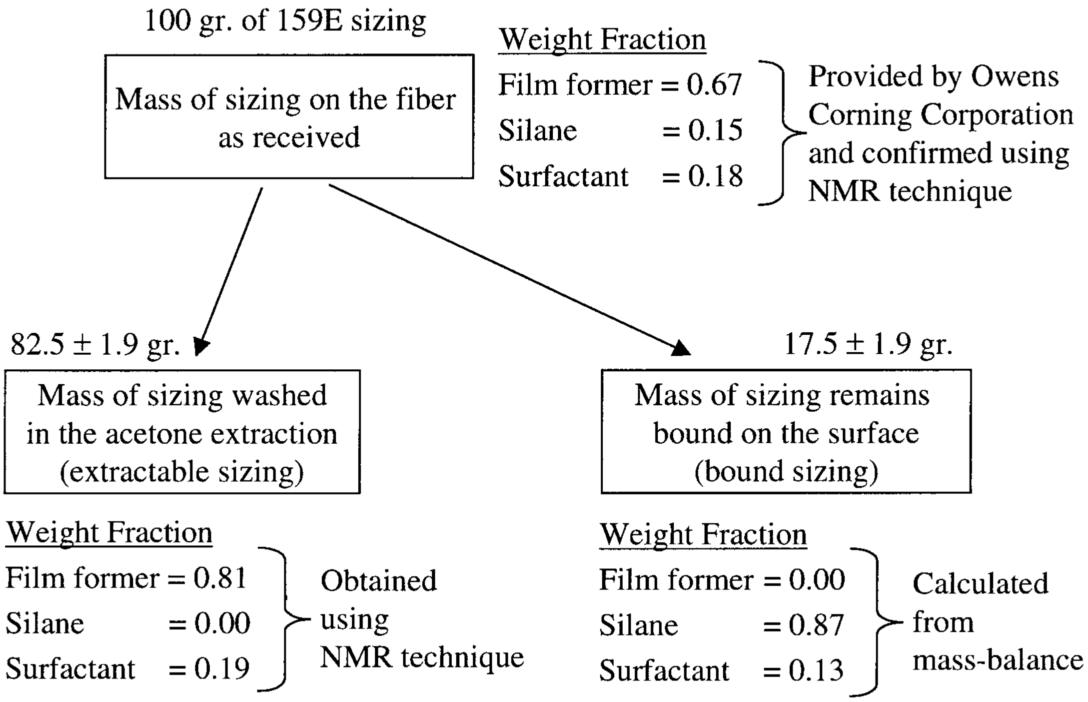


Figure 5 Schematic illustrating the overall and component mass balance of the sizing compound on the glass fiber. All values have a standard deviation of ±3%.

silane molecules have condensed into the network that is bound to the fiber.

2.4. Synthesis of model interphase materials

Preparation of samples from which the properties of the actual interphase are estimated is explained in this section. In this part of the work, silane is reacted to condense in the presence of film former and surfactant but in the absence of a glass surface. The condensed silane was washed with acetone to remove any unreacted compound. This silane-based material is considered representative of the bound portion of sizing found on glass fiber. It was then mixed with epoxy and amine at stoichiometric ratio and cured. This sample is referred to as the *blend sample*; it has a silane-rich domain and an epoxy-amine matrix. The silane-rich phase of this sample is the model interphase material, and its properties are determined in the following section. The schematic shown in Fig. 6 summarizes the processing steps. Sample preparation started with hydrolysis of the glycidoxy propyl trimethoxy silane. A mixture of 10-wt.% silane coupling agent in acidified de-ionized water, with a pH of 3.5 was prepared. The solution was allowed to mix for 30 minutes. Known amounts of this solution and emulsion were mixed together to prepare a mixture of 15-wt.% silane dry basis. The mixture was well stirred and poured onto a Teflon sheet and dried to a constant mass in a vacuum oven at −100 KPa and 65°C for two days. The final material consisted of two phases: clear liquid (sol), and white particulate material (gel). Both gel and sol phases were washed with acetone and filtered several times. The powder was not soluble in acetone or any common organic solvent to an appreciable degree. The acetone wash was collected and dried, as was the gel phase. The composition of the sol phase was determined using the NMR technique, and the composition of the gel phase was calculated from overall and component mass balance. The sol contained 81% film former and 19% surfactant by weight. The gel is 73% silane, 8% film former, and 19% surfactant. Almost all the silane remained in the gel. This result is identical to that obtained from acetone extraction of the glass fibers (in Section 2.3), where our analyses showed that all silane is incorporated into the bound network.

The particle size and distribution of the gel phase were quantified using a particle size distribution analyzer (Horiba Instruments, Inc., Model LA-900) and scanning electron microscope (SEM, Joel 804). The SEM micrograph of the gel phase is shown in Fig. 7. The largest inclusion diameter was measured to be about 5 micron from SEM. The results from particle analysis are shown in Fig. 8. The mean particle diameter was found to be 2.902 micron. The thermophysical analysis of the pure powdery gel was conducted, and results are given later in this paper. This dried gel was further powdered to micron size using a mortar and pestle for inclusion in an epoxy-amine network.

A 40% mixture of powder with Epon-828 and PACM-20 was prepared. Enough amine was added to react with the epoxide groups of Epon-828 and silane. The solution was well mixed, degassed, cured at 80°C for 2 hours, and post-cured at 160°C for 2 hours. The blend sample was white after curing. Diffusion calculations were performed to verify the assumption that enough time was allowed for the amine monomers to diffuse into silane-rich particles and reach equilibrium before the diffusion became limited by the kinetics of cure [36]. It was shown that for the measured particle sizes amine can fully diffuse into the particulate gel phase within the vitrification time of the system (1100 sec [5, 6]) for diffusion constant values ranging from 1×10^{-8} to 1×10^{-10} cm^2/sec. This suggests that

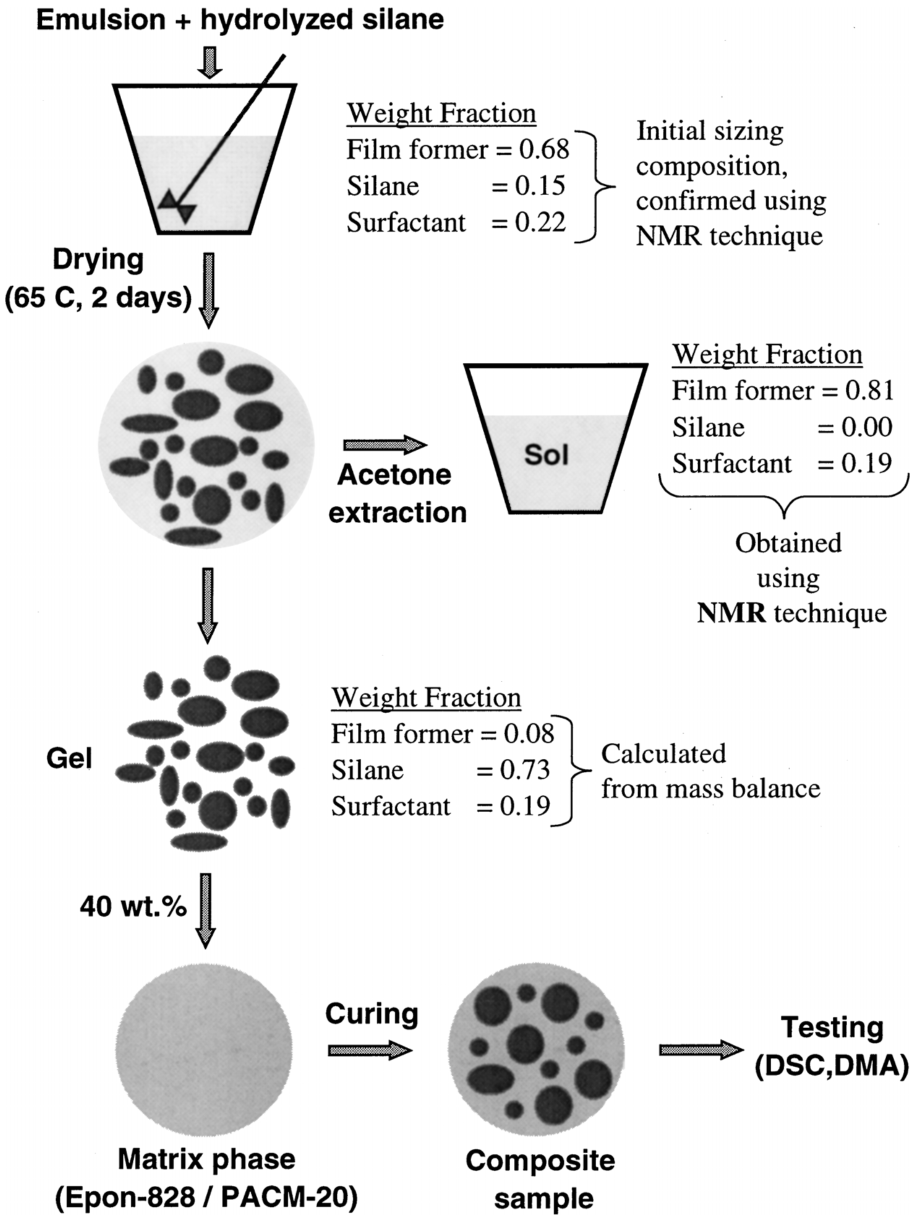


Figure 6 Schematic illustrating the processing steps for synthesis of model interphase material.

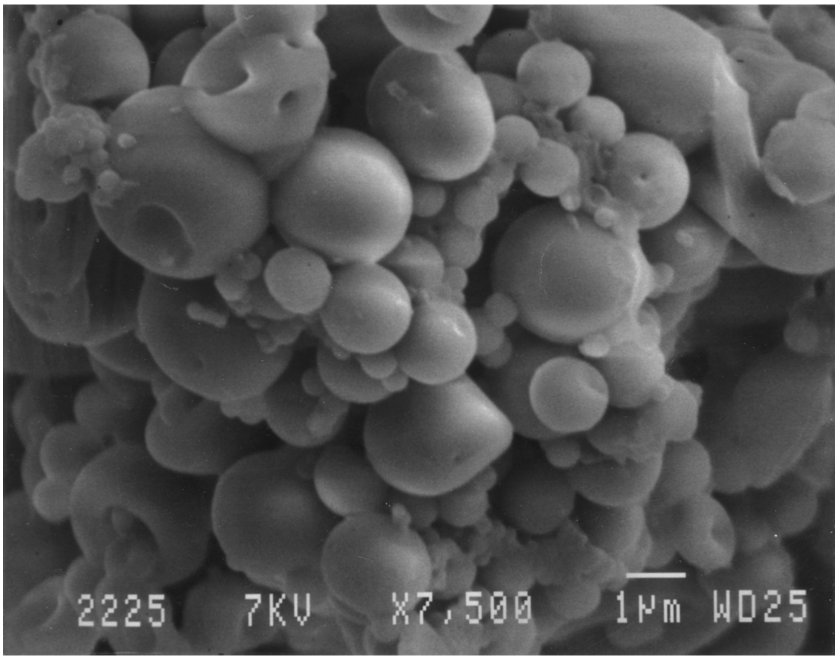


Figure 7 SEM micrographs showing the particulate gel phase after acetone extraction.

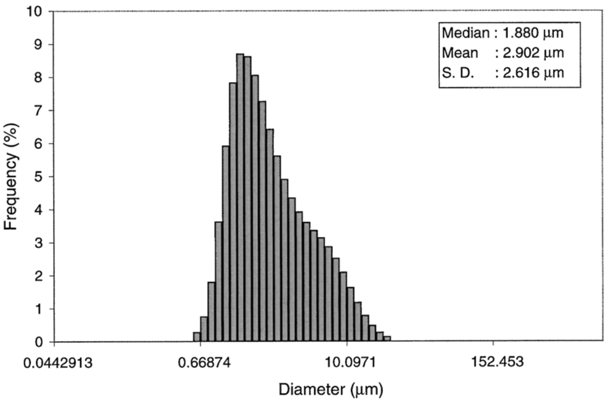


Figure 8 Particulate gel phase size distribution measured using laser scattering particle size distribution analyzer.

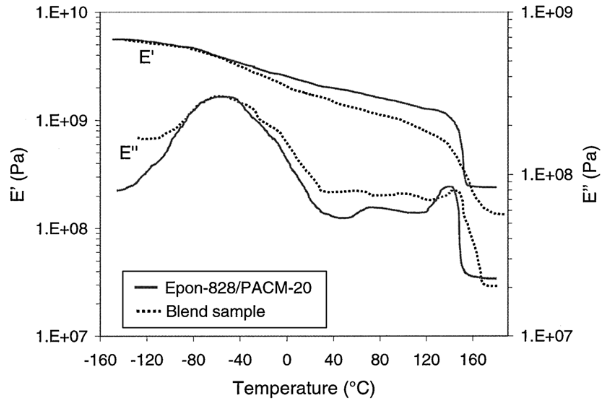


Figure 10 DMA plot for the blend sample and neat Epon-828/Pacm-20 (at stoichiometric ratio of 100/28).

complete amine diffusion into the inclusions during the sample preparation occur as desired.

2.5. Property measurements

Thermophysical analysis of the pure powder particles and the synthesized model interphase materials was done to obtain T_g and flexural modulus (E). A TA-Instruments DSC (model 2920) was used to detect T_g. Samples (typically 10 mg) of polymer were heated from -150°C to 180°C at a constant heating rate of 10°C/min. As the polymer goes from the glassy to the rubbery state, the change in its heat capacity is manifested as the change in the slope of the plot of heating rate versus temperature. For a sample that is a blend of two polymeric phases, the DSC thermogram shows two distinct T_g's.

The storage and loss moduli of the blend sample as a function of temperature were measured using DMA. The DMA samples were prepared from slabs of cured samples. The samples were carefully sanded to approximately $2 \times 15 \times 50$ mm. A Rheometrics Solid Analyzer (model RSA-2) and a 3-point-bend loading configuration were used. The loading frequency and strain values were 1 Hz and 5×10^{-5}, respectively. Samples were heated from -140°C to 180°C at a rate of 5°C/min.

2.5.1. T_g *of model interphase material*

Fig. 9 shows the DSC results in the range of -80 to 20°C for the gel (powder obtained after extraction) and the blend sample (gel + epoxy-amine). The T_g for the pure gel is about -55°C. The blend sample has two T_g's: one at -5°C and the other at 155°C. The higher T_g (155°C) is not shown in Fig. 9 for the sake of clarity. However, this T_g is shown on the DMA plot in Fig. 10. Several results are obtained from this thermogram. One is that the blend sample consists of two phases: a glassy matrix and rubbery inclusions. The T_g of the glassy matrix phase (155°C) in the blend sample is very close to that of stoichiometric Epon-828/PACM-20 (158°C). This indicates that the glassy phase is not plasticized by silane network or any unreacted monomer (i.e. amine). Therefore, it is expected that the matrix phase of the blend sample will have properties similar to those of the neat Epon-828/PACM-20. It can be seen from Fig. 9 that the T_g of the gel particles is increased from -55°C to -5°C. The increase in rigidity is caused by the reaction between amine groups and the epoxide groups of silanes and film former. This result confirms the conclusion drawn from the diffusion analysis: that the concentration of amine in the silane-rich domains reaches equilibrium before the kinetics of cure becomes the rate-limiting factor. The T_g of the samples analyzed using DSC is also summarized in Table III.

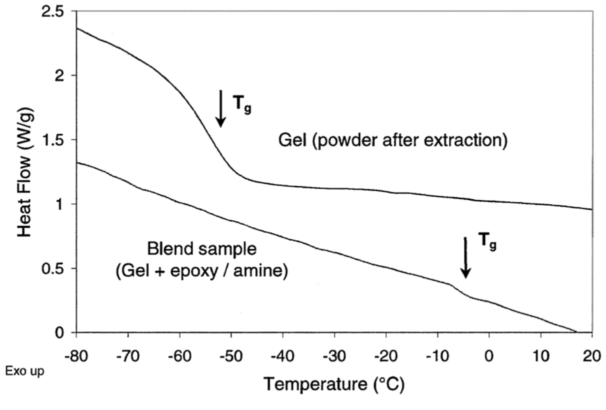


Figure 9 DSC thermogram for gel (powder after extraction) and blend sample (gel + epoxy/amine).

2.5.2. *Thermomechanical behavior of model interphase materials*

The flexural storage (E') and loss (E'') moduli of the blend sample and a neat sample of Epon-828/PACM-20 are plotted as a function of temperature in Fig. 10. In our analysis, T_g is defined as the maximum in loss modulus.

TABLE III Glass transition temperature obtained using DSC technique

Specimen	Temprature (°C)	T_g Assoiciated with
Epon-828/PACM-20 (at stoichiometric ratio)	158	Cured Resin
Gel (dried silane-rich phase after acetone extraction)	−55	Silane-Rich Network
Blend Sample (about 40% mixture of silane-rich powder with Epon-828/PACM-20)	−5	Silane-Rich Phase
at stoichiometric ratio of amine to react epoxide groups of Epon-828 and silane-based network)	155	Glassy Matrix Phase

As shown in Fig. 10, for the Epon-828/PACM-20 system, the storage modulus, which is a measure of the elastic mechanical response of the polymer, decreases at a slow rate from −140°C to around −80°C. At around −80°C, a small relaxation is associated with the β-transition. At the same time, the loss modulus increases from low temperature and makes a broad peak between −100 and −40°C. This broad peak is also due to the β-transition. After the β-transition region, the storage modulus continues to decrease up to 150°C. In this temperature range, the loss modulus stays almost constant. At 150°C, there is a drop of storage modulus by almost one order of magnitude. The loss modulus also shows a peak at this temperature. This transition (α-transition) is associated with the T_g of Epon-828/PACM-20.

For the blend sample, E' first decreases at a slow rate from −140°C to around −70°C. At about −70°C, E' makes a small drop and continues to decrease until it reaches 150°C. A shoulder at about −5°C, associated with the T_g of the rubbery phase, is visible. At about 150°C the sample shows a large drop that is almost an order of magnitude. This transition (α-transition) is associated with the T_g of the glassy matrix phase. The loss modulus forms a broad peak starting from −90°C and ending around 25°C. These broad peaks and the relaxation on the storage modulus over the same temperature range are associated with the β-transition of the epoxy-amine matrix phase. These transitions may also be associated with the T_g of the rubbery gel phase. However, these low T_g's are not distinguishable from the DMA due to the overlapping of the epoxy-amine matrix β-transition. Therefore, DSC, which does not show the β-transition, was employed to investigate these low T_g's, as mentioned in the previous section. Since the T_g of the glassy matrix phase in the blend sample is close to that of Epon-828/PACM-20, as discussed earlier, it can be concluded that the matrix phase in the blend sample has similar properties to neat Epon-828/PACM-20.

3. Discussion

The sample discussed in the previous section is a blend of silane-rich inclusions and epoxy-amine matrix. The results from DSC and DMA clearly show that diffusion of amine and epoxy into the silane-rich inclusions and reaction of functional groups have occurred since the T_g of the silane-rich domains increased from −55°C to −5°C. The silane-rich phase is the model interphase material in whose properties we are interested.

To evaluate the mechanical properties of the model interphase material, a self-consistent micromechanics model, which yields an approximate but simple expression based on analysis of deformation and stress about an inclusion, is applied. The model developed by Takayanagi uses familiar spring and dashpot models, in which each component has the same mechanical properties as those of the blend constituent [38]. It gives an expression for the modulus of the blend E_c in terms of the modulus and volume fraction of the blend components and a single coupling parameter. Based on the Takayanagi model, Kernel [39] obtained an expression that replaces the coupling parameter in Takayanagi's expression with α_1. The term α_1 is a function of the Poisson ratio of the matrix phase V_m. In this model, it is assumed that the blend structure consists of a spherical dispersed particle phase (model interphase material in our case) embedded in a matrix shell, which is in turn embedded in a continuous body having the elastic properties of the blend. Fig. 11 shows an idealized representative blend structure. The expressions for α_1 and for modulus (E_c) are given by Equations 4 and 5, respectively.

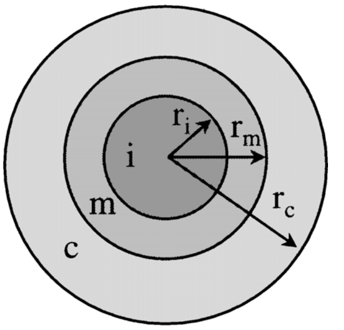


Figure 11 Representation of model blend inclusion for elastic property determination [38].

$$\alpha_1 = 2(4 - 5\upsilon_m)/(7 - 5\upsilon_m) \quad (4)$$

$$E_c = \frac{E_m[V_m E_m + (\alpha_1 + V_i)E_i]}{(1 + \alpha_1 V_i)E_m + \alpha_1 V_m E_i} \quad (5)$$

where V_m and V_i are the volume fraction of the matrix and the model interphase material phase, and E_m and E_i are the shear modulus of the matrix and interphase phases, respectively. The expressions above can be used to predict the modulus of a blend structure comprising materials of different values such as a blend of a rubbery polymer and a glassy one.

The modulus of the model interphase material was calculated using Equations 4 and 5. The measured storage modulus values at room temperature for blend (E_c) and neat epoxy-amine (E_m) samples as well as the material properties used in Equation 5 are listed in Table IV. A simplifying assumption was made that the density of the cured matrix is equal to the silane-rich phase density. Moreover, the results from DSC and DMA show that the epoxy-amine matrix does not contain unreacted excess amine. Based on the assumption of equal density and the fact that the matrix is not plasticized, the volume fraction of the silane-rich phase is calculated to be about 0.5. The value of storage modulus for the

TABLE IV Dynamic flexural storage modulus, E', values at room temperature. The modulus of model interphase material was calculated from blend modulus using McGee and McCullough's "C-Combining Rule" [40]

Phase/Property	E' (GPa)	Volume Fraction	Poisson Ratio υ
Matrix (Epon-828/Pacm-20) (measured)	2.35 (E_m)	0.5 (V_m)	0.35 (υ_m)
Blend (measured)	1.80 (E_c)	-	-
Model Interphase Material, (calculated)	1.35 (E_i)	0.5(V_i)	-

model interphase material (E_i) was then calculated to be 1.35 GPa. According to this result, the storage modulus of the interphase region would be about half that of the matrix.

In addition to the Takayanagi approximation, McGee and McCullough's improved "C-Combining Rule" for compliant inclusions embedded in a rigid matrix was used to calculate the modulus of the model interphase material [40]. C-Combining Rule is a semi-empirical model that provides predictions in good agreement with experimental data over a wide range of concentrations for a variety of polymeric composites. Using the C Combining Rule, the value of E_i was calculated to be 1.27 GPa, which is essentially equal to that calculated using the Takayanagi approximation.

In preparing the silane-rich particles discussed earlier, it was realized that the condensed silane completely precipitated out of the sizing emulsion. This is supported by the absence of silane in the acetone extract. The powdery nature of this silane-rich phase and the fact that this powder is not soluble in common organic solvents suggest that the condensed silane has a cross-link network structure. The cross-link density of the silane-rich inclusions could affect the mechanical properties of the model interphase material. The cross-link density of this network was not determined, but a second set of blend material was prepared to investigate the effect of the silane network structure on model interphase material properties.

A mixture of 47-wt.% glycidoxy propyl trimethoxysilane and the film former-surfactant emulsion was prepared. The same procedure as explained previously was followed to condense the silane in the presence of the emulsion except that the mixture of the hydrolyzed silane and emulsion was dried under vacuum at lower temperature, 25°C, for 2 days. After complete removal of water, the product was a white gel, but there were no powdery particles in the mixture. This indicated phase separation of the mixture into silane- and epoxy-rich phases; however, the silane-rich phase of this mixture is expected to have a low crosslinking density. A stoichiometric amount of amine was added to the mixture to react all epoxide groups. The cure cycle was the same as before. Samples for DSC and DMA were prepared and tested. The DSC thermogram shows two T_gs: one at -70°C and the other at 155°C. The -70°C T_g of the silane-rich phase in this sample is lower than the T_g of the model interphase material discussed earlier (-5°C). This result indicates that this model interphase material possesses a lower degree of crosslinking density compared to the previous one. Furthermore, the T_g of the matrix phase indicates that the matrix does not contain excess unreacted amine. Fig. 12 shows the flexural storage and loss moduli for this sample and the blend sample containing a high cross-link density of silane network. The T_g of the rubbery phase, about -65°C, is clearly visible in both the storage and loss moduli curves. The storage modulus of the sample with low cross-link density of silane at -150°C is less than that of the blend sample previously investigated in this paper. The reason is that the rubbery phase of this sample has a T_g of -65°C; therefore, the storage modulus at -150°C is lower than that of the sample with high cross-link density of silane. However, upon inspection and comparison of the DMA plot in Fig. 12, it is clear that the storage modulus curves for both samples have a similar slope, indicating that the sample with a low crosslink silane-rich phase is also extensively phase separated and not plasticized.

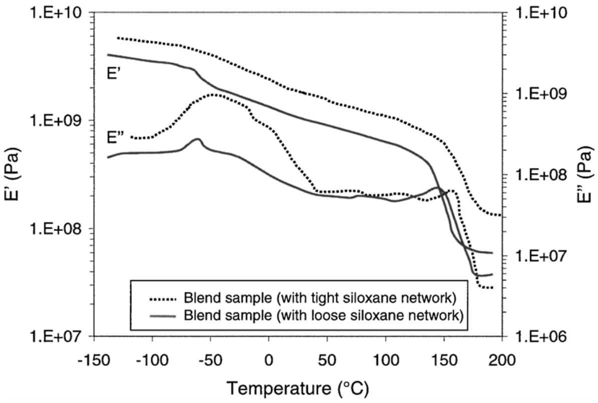


Figure 12 Comparison of DMA plots between the blend samples containing low and high cross-link density of silane network.

The sample that contains a low crosslink density of the silane-rich phase and its corresponding DMA results can be further analyzed. This sample can also be considered as a two-phase blend in which the silane-rich phase is the model interphase material. In doing so, the room temperature storage modulus of the sample (1.05 GPa) and the neat Epon-828/PACM-20 (2.35 GPa) can be used in Equations 9 and 10 to estimate the storage modulus of the model interphase material. A simplifying assumption was made that the density of the matrix and the silane-rich phase are equal. Assuming that there is no excess unreacted amine in the matrix, the volume fraction of each phase was calculated to be about 0.5. Using this data, the modulus value for the silane-rich interphase material was calculated to be 0.3 GPa. The C Combining Rule yielded a value for E_i of 0.5 GPa, providing a range of modules values for the interphase material. This result suggests that the storage modulus of the model interphase material could be about 5–8 times less than that of the matrix.

Comparison of the results from the two sets of model interphase materials shows some interesting points. The storage modulus of material with a high crosslink density of the silane network is 1.35 GPa and that with a low crosslink density of the silane network is 0.3–0.5 GPa. This indicates that the silane network bound to the glass fiber can play an important role in determining the overall properties of the interphase region. This offers a potential route for tailoring the interphase properties for any desired composite performance. In the synthesis of both model interphase compounds, the silane-rich network readily phase-separated out of the epoxy-rich phase. This observation indicates that the thermodynamics of mixing for film former and silane network does not favor miscibility. This could be another important factor affecting network formation at the interphase.

4. Conclusion

An experimental investigation was undertaken in this work to determine the properties of the interphase that could form due to the presence of glass fiber sizings. It is well known that a fraction of sizing may dissolve completely into the matrix and the rest remain bound to the fiber. This bound sizing forms an interpenetrating network with the resin material after curing of the composite specimen. This work focuses on the effects of composition and network structure of the bound sizing on interphase formation and its properties. Considering these factors, model interphase samples were made to replicate the actual interphase materials, and their properties were determined.

For an epoxy-amine compatible sized E-glass fiber, the soluble and bound fractions of sizing and their composition was determined using NMR technique in conjunction with acetone extraction and burnout experiments. About 83% of the sizing may dissolve in the matrix. The soluble portion contains 81% film former. This value is close to that (70%) reported by Thomason [3]. It was found, within the measurement limits, that all silane monomers are condensed into the network that remains bound onto the glass fiber. In fact, the bound sizing is 87% silane by weight.

A new approach is presented for synthesis and characterization of materials that are designed to model the interphase region that forms in the presence of a silane-based sizing. Silane coupling agent was condensed in the presence of film former and surfactant. The silane network was separated and characterized. A 40% mixture of this material with epoxy-amine mixture was prepared. A stoichiometric amount of amine was used to consume all epoxide groups of resin and silane network. The sample is a two-phase blend; one phase is rich in silane network and the other phase is pure epoxy-amine. Full diffusion and reaction of epoxy and amine into the silane-rich network was confirmed. The silane-rich network is the model interphase material whose thermophysical properties were characterized. The T_g of the model interphase was determined to be -5°C and that of the matrix is 155°C. This indicates that the model interphase is rubbery at room temperature, and the matrix is not plasticized by the presence of low molecular weight sizing compounds. The modulus of the interphase was predicted from the DMA measured modulus values of blend samples using a self-consistent micromechanics model that expresses the modulus of the blend (composite) in terms of the modulus and volume fraction of the blend constituents. It was found that the interphase modulus is 1.35 GPa, about half that of the matrix (2.35 GPa). It was also found that the thermophysical properties of the model interphase material could vary with the degree of crosslinking of the silane-rich network. In a similar way, samples of model interphase material using a silane-rich phase with lower cross-link density were prepared. Data from DSC and DMA indicate two transition temperatures: one at -70°C and the other at 150°C. Similar analysis of the DMA data of this sample showed the storage modulus of the model interphase material to be about an order of magnitude lower than that of the neat epoxy-amine resin.

Our results show that the interpenetrating network formed between the silane-rich phase and the subsequently polymerized epoxy-amine network has properties different from those of bulk epoxy-amine. These properties also change with the cross-link density of the silane-rich phase. This implies that factors including the cross-link density of the silane-rich phase, the reactivity of monomers, and the composition of mobile species on interphase properties could be investigated using the approach outlined in this work. Drzal [2], Thomason [3], and Jones [4] showed the effect of the soluble portion of sizing on interphase properties; however, our study focuses on the effects of polymeric structure that remains at the fiber surface.

In the preparation of model interphase materials, the mixture of condensed silane, epoxy film former, and surfactant always phase-separated into an epoxy-rich phase and a silane-rich phase. Our tests showed that the mixture of silane monomer (uncondensed) with epoxy and surfactant forms one homogeneous phase. Phase separation is caused by the condensation reaction of silane. Investigation of the phase separation behavior of silane and other compounds at the interphase region is an important issue in future studies.

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References

1. G. R. PALMESE and R. L. MCCULLOUGH, *J. Adhesion* **44** (1994) 29.
2. E. K. DROWN, H. AL MOUSSAWI and L. T. DRZAL, *J. Adhesion Science and Technology* **5**(10) (1991) 865.
3. J. L. THOMASON, *Composites* **26** (1995) 487.
4. J. BERG and F. R. JONES, *Composites Part A* (1998) 1261.
5. G. R. PALMESE, Ph.D. dissertation, University of Delaware, 1992.
6. T. P. SKOURLIS, Ph.D. dissertation, University of Delaware, 1997.
7. A. GARTON, W. T. K. STEVENSON and S. WANG, *British Polymer Journal* **19** (1987) 459.
8. B. N. TAN, S. H. MCKNIGHT and G. R. PALMESE, in Proceedings of the ACS, Las vegas, NV, September 8–11, 1997, Vol. 77.
9. L. T. DRZAL, in “Tough Composite Materials” (Noyes, Park Ridge, 1985) p. 207.
10. G. R. PALMESE and R. L. McCULLOUGH, *Composites Part A* **30**(1) (1999) 3.
11. T. P. SKOURLIS and R. L. McCULLOUGH, *Composites Sci. Tech.* **49** (1993) 363.
12. B. K. LARSON and L. T. DRZAL, *Composites* **25**(7) (1994) 711.
13. B. K. LARSON, L. T. DRZAL and J. VAN ANTWERP, *Polym. Compos.* **16**(5) (1995) 415.
14. J. L. THOMASON and G. E. SCHOOLENBERG, *Composites* **25**(3) (1994) 197.
15. J. L. THOMASON, *ibid.* **26**(7) (1995) 467.
16. *Idem., ibid.* **26**(7) (1995) 477.

17. L. T. DRZAL, M. J. RICH and M. F. KOENIG, *J. Adhesion* **18**(49) (1985).
18. R. J. STOKES and D. F. EVANS, in "Fundamentals of Interfacial Engineering" (Wiley-VCH, Inc., 1997) p. 380.
19. E. MADER, K. GRUNDKE, H.-J. JACOBASCH and G. WACHINGER, *Composites* **25**(7) (1994) 739.
20. F. HOECKER and J. KARGER-KOCSIS, *Composites* **25**(7) (1994) 729.
21. M. STUART and V. ALTSTADT, in 21st International SAMPE Technical Conference, 1989, p. 264.
22. S. SUBRAMANIAN, J. J. LESKO, K. L. REIFSNIDER and K. L. STINCHCOMB, *J. of Composite Materials* **30**(3) (1996) 309.
23. D. R. HARTMAN, US Patent, 4,842,923, Jun 27, 1989.
24. S. R. CULLER, H. ISHIDA and J. L. KOENIG, *J. Coll. Int. Sci.* **109**(1) (1986) 1.
25. K. P. HOH, H. ISHIDA and J. L. KOENIG, *Polym. Composites* **9**(2) (1988) 151.
26. H. ISHIDA and J. L. KOENIG, *J. Coll. Int. Sci.* **64**(3) (1978) 555.
27. *Idem.*, *ibid.* **64**(3) (1978) 565.
28. *Idem.*, *J. Polym. Sci.: Polym. Phys.* **17** (1979) 615.
29. *Idem.*, *ibid.* **18** (1980) 233.
30. *Idem.*, *ibid.* **18** (1980) 193.
31. V. I. KOSTIKOV, in "Fiber Science and Technology," Soviet Advanced Composites Technology Series (Chapman and Hall, 1995).
32. G. R. PALMESE and R. L. McCULLOUGH, *J. Applied Polymer Science* **46** (1992) 1863.
33. E. P. PLUEDDEMANN, in "Silanes and Other Coupling Agents," edited by K. L. Mittal (VSP, 1992) p. 3.
34. P. G. PAPE and E. P. PLUEDDEMANN, in "Silanes and Other Coupling Agents," edited by K. L. Mittal (VSP, 1992) p. 105.
35. K. L. MITTAL, in "Silanes and Other Coupling Agents," (VSP, 1992).
36. M. TANOGLU, Ph.D. dissertation, University of Delaware, 2000.
37. J. K. KIM and Y.-W. MAI, in "Engineered Interfaces in Fiber Reinforced Composites" (Elsevier, The Netherlands, 1998).
38. R. A. DICKIE, in "Polymer Blends," Vol. 1, edited by D. R. Paul (Academic Press Inc., 1978).
39. E. H. KERNER, *The Proceedings of the Physical Society* **69B** (1956) 808.
40. R. L. McCULLOUGH and S. H. MCGEE, *Polymer Composites* **2** (1981) 149.

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