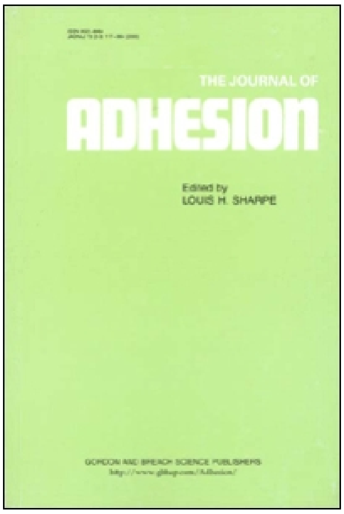

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The Influence of Interfacial Structure on the Flexural Strength of E-glass Reinforced Polyester

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Simultaneous mechanical and molecular characterization of a composite system has been attempted with respect to the interface. The mechanical properties of an E-glass cloth/γ-methacryloxypropyltrimethoxysilane (γ-MPS)/bisphenol-A-fumarate polyester resin composite system were studied as a function of the amount of γ-MPS coupling agent present on the glass fiber surface. Fourier transform infrared diffuse reflectance spectroscopy was used to determine the amount and structure of γ-MPS on the glass. This structure consists of two clearly distinguishable regions: physisorbed layers of γ-MPS which can be dissolved by organic solvents, and chemisorbed layers which are insoluble. The physisorbed layers of γ-MPS reduced the strength of the polyester composite. A polymer blend consisting of siloxane oligomer of γ-MPS and bisphenol-A polyester was also investigated as a model of the silane interphase. Results from this model study are in agreement with the polyester composite data.

INTRODUCTION

Coupling agents are an important component of modern reinforced plastics and composites. Surface treatment of glass fibers with silane coupling agents to improve the mechanical performance of the composite is an accepted practice. Though coupling agents have been extensively studied, there is still considerable controversy about the mechanism by which they improve the mechanical properties of glass fiber composites. Many theories have been proposed to explain this mechanism, and each theory approaches the problem from a slightly different perspective, utilizing concepts from various disciplines. Therefore, these theories are not all mutually exclusive, and several are compatible. The preferential adsorption and the interpenetrating network theory are among many theories of reinforcement.[1-4]

Transfer of stress from the polymer matrix to the glass fibers is certainly the most critical aspect in composites. However, maximum stress transfer (*i.e.*, no slippage at the interface) may not necessarily give the best mechanical performance. Tryson and Kardos[5] have indicated that, for improving certain mechanical properties, a ductile interphase may be necessary. This ductile interphase would relieve interfacial stresses. The preferential adsorption mechanism[6-8] suggests that the coupling agent preferentially adsorbs certain resin components necessary for complete curing in the area immediately surrounding the reinforcement surface. This adsorption process creates an incompletely cured resin layer immediately adjacent to the glass fiber surface.

The interpenetrating network theory offers a possible explanation of the improvement by coupling agents of the properties of thermoplastic composites.[9,10] Silane oligomers on the glass fiber surface may act as a partial solvent for the thermoplastic resin at molding temperatures. However, when the composite cools, the silane and resin phase separate into an interpenetrating network structure. It is also possible that the silane and the resin form an interpenetrating network structure without phase separation. The silane oligomers may crosslink themselves through SiOH and R groups at molding temperatures. Interpenetrating polymer networks containing polysiloxane as one of the phases have been reported by several researchers.[11]

It is well known that coupling agents adsorb on glass fiber surfaces as multilayers. Furthermore, several authors have indicated that these layers of coupling agent do not form one homogeneous phase, but form two or three regions of different structure.[12-16] Regardless of whether these silane layers form one homogeneous phase or not, when the treated glass fibers are mixed with resin and cured to form a composite, a region known as the silane interphase is formed. The word interphase is used to describe a silane rich region of finite thickness between the glass fibers and the matrix resin. The coupling agent theories mentioned above explicitly recognize the formation of a coupling agent interphase during cure. These theories also recognize that the composite interphase region can have a significant effect on the overall mechanical properties of the composite.

It is believed that the silane interphase can be divided into two regions: the chemisorbed and physisorbed. Physisorbed silane can be washed from the glass fiber surface by organic solvents, while the chemisorbed cannot. It is thought that the physisorbed layers of silane dissolve into the resin during cure, forming a complex region or interphase of a resin/silane oligomer mixture immediately around the fiber surface.[27] This region would have mechanical properties different from the bulk resin, and therefore, would affect the mechanical performance of the composite.

The goal of this research is to study the effects of silane multilayers on composite properties, and to distinguish the effects of the physisorbed and chemisorbed layers. Presumably, altering the structure of the silane on the glass fiber surface alters the structure of the silane interphase in the cured composite. A model mechanical system designed to simulate the silane interphase is also investigated. The model is admittedly crude, but represents a first attempt at quantification of interphase structure.

The mechanical properties of an E-glass cloth/γ-MPS coupling agent/bisphenol-A-fumarate polyester resin composite system are studied as a function of the amount of γ-MPS coupling agent present on the glass fiber surface. The amount of γ-MPS on the fibers is varied by changing the concentration of the γ-MPS treating solution. Fourier transform infrared diffuse reflectance spectroscopy is used to determine the amount and structure of γ-MPS on the surface of the E-glass cloth. A three point flexural test is used as a measure of the mechanical properties for the E-glass composite. This flexural test is widely used in industry for glass fiber composites. The structure of the silane on the glass surface was altered by washing the glass cloth with THF which is a good solvent for γ-MPS. That the physisorbed portion is indeed removed by the THF washing is confirmed by the infrared analysis. The model system consists of a blend of siloxane oligomer and bisphenol-A polyester. This blend is thought to be a reasonable model of the composite interphase. The mechanical properties of this model system were measured by the same three point flexural test used for the E-glass cloth/polyester composites.

EXPERIMENTAL

The E-glass cloth used in this study was supplied by Dr. James Jen of

Owens Corning Fiberglas. The fibers from the cloth have a nominal diameter of four microns. The E-glass cloth received a 112 surface finish (heat cleaned) at the factory, and was used as received. The coupling agent, γ-methacryloxypropyltrimethoxysilane (γ-MPS) used in surface treatment was purchased from Petrarch Systems Inc., and the γ-MPS used in the model study was supplied by J. G. Marsden of Union Carbide. Both were used as received. The resin, a room temperature curing bisphenol-A thermoset polyester (Atlac 382–05A), was supplied by Dr. M. K. Antoon of ICI Americas Inc. A methyl ethyl ketone peroxide (Quickset Extra) used to cure the resin was supplied by Dr. Ron Pastorino of Witco Chemical Corp.

The E-glass cloth was treated with γ-MPS by the following procedure. The γ-MPS was hydrolyzed in deionized, distilled water which had been adjusted to pH 3.5 with acetic acid. The hydrolysis times varied between one and three hours according to the solution concentration (0.1–2.0 wt%). The cloth was immersed in the solution for five minutes, after which the cloth was allowed to drip dry. The cloth then received an 80°C heat treatment for two hours to cure the silane on the glass.

The E-glass cloth was made into polyester composites *via* a hand-layup procedure. Ten layers of glass cloth were wetted with initiated resin and pressed to a constant thickness. The bisphenol-A polyester resin was initiated with 0.5 wt% cobalt naphthenate (6% active solution), 0.2 wt% dimethylaniline, and 0.5 wt% methyl ethyl ketone peroxide (9% active oxygen). All composites were allowed to cure at room temperature for eight hours before being given a post cure treatment of 100°C for two hours. The glass content of the finished composites was measured by resin burnoff at 500°C.

The E-glass cloth/polyester composites were cut and tested in flexure in accordance with ASTM standard D790–71, method 1. The cloth composites were conditioned prior to testing by two different methods. Normal or dry conditioning was done in accordance with ASTM standard D618–61, procedure A. This method consists of placing the samples in a controlled humidity environment at a temperature of 23°C for 40 hours immediately before testing. Hydrothermal or wet conditioning was done by immersing the test pieces in distilled water at 80°C for 48 hours prior to testing. The span length for the three point bend attachment was 6.35 cm, and the Instron testing machine was operated at a crosshead speed of 0.5 cm/min. All samples except for the untreated ones failed in a similar mode. A minimum of 7–10 samples each normalized for glass content were averaged to obtain each data point reported for the flexural test.

Bulk siloxane oligomer was obtained by hydrolyzing the γ-MPS at 20 wt% concentration in pH 3.5 deionized, distilled water and setting the solution aside. After several days the hydrolyzed silane condenses to a siloxane oligomer which phase separates from the aqueous solution. This viscous siloxane oil was collected and dried in a vacuum oven at 80°C for three hours. For the model blend study, the siloxane oligomer was well blended with the resin in various proportions, and then cured in exactly the same fashion as the composite. Postcuring was done at 100°C for two hours. Samples of this cross-linked blend were tested in flexure according to the same specifications that were used for the glass fiber composites.

The infrared analysis was made using a Fourier transform infrared spectrometer (Digilab FTS-20E) with a diffuse reflectance accessory (Digilab DRA 100). This spectrometer system is equipped with a dry nitrogen purge and MCT (mercury cadmium telluride) detector. Typically, between 200–400 scans were co-added at a resolution of 2 cm^{-1} throughout the spectral range of 3800–700 cm^{-1}. All of the diffuse reflectance spectra are shown in Kubelka Munk format ($[1-R]^2/2R$ where R is the reflectance spectrum). No sample preparation was done on the cloth for the diffuse studies. All reflectance spectra (R) were obtained by ratioing the sample single beam diffuse spectra against a potassium bromide single beam background spectrum. Digital subtractions of spectra were made on the basis of least-squares curvefitting analysis.[17–19]

RESULTS AND DISCUSSION

As mentioned previously, diffuse reflectance infrared spectroscopy was used to quantify the relative amount of silane coupling agent on a sample of glass cloth. Diffuse reflectance methods have long been used in UV-visible spectroscopy, but only within the last five years have diffuse techniques been practical for the mid-infrared region. Diffuse reflectance, as opposed to specular reflectance, permits the surfaces of particulate and rough samples to be studied. The principal advantages of diffuse reflectance methods in the infrared are that (a) it is a surface spectroscopic technique which is quantitative, and (b) it allows opaque and/or strongly absorbing solids and other problem samples to be studies with relative ease. A more complete discussion of the theory and application of diffuse reflectance infrared spectroscopy can be found elsewhere.[20–24]

Diffuse reflectance rather than transmission methods were used in this study for several reasons, the first and foremost being the increased sensitivity of diffuse reflectance to the coupling agent on the glass fiber surface. This sensitivity made the observation of very small amounts of coupling agent possible. These measurements would have been difficult with ordinary transmission techniques. Secondly, it is not necessary to alter the sample in any way to obtain a spectrum. For transmission studies the sample must be ground to a small particle size, dispersed in potassium bromide, and pressed into a pellet. This KBr support medium will adsorb water during the grinding process. Thus, diffuse reflectance permits the entire glass coupling agent spectrum to be studied without interference from water peaks around 1640 cm^{-1} and 3400 cm^{-1}.

Figure 1 displays the Fourier transform infrared diffuse reflectance

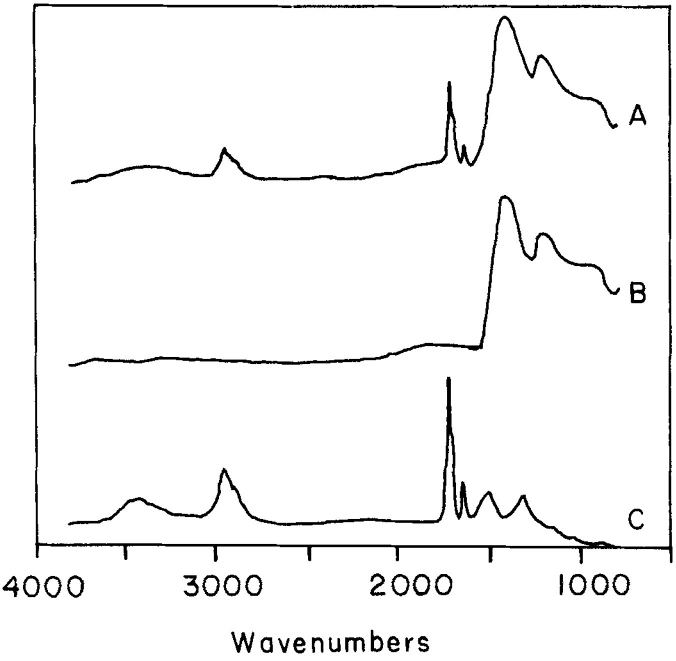

FIGURE 1 Spectrum A: DRIFT spectrum of γ-MPS on E-glass.
Spectrum B: DRIFT spectrum of pristine E-glass.
Spectrum C: DRIFT difference spectrum A – B = C.

spectra of E-glass cloth treated with γ-MPS, pristine E-glass cloth, and their difference. The band at 1720 cm^{-1} in Figures 1A and 1C is the carbonyl peak of the γ-MPS coupling agent. The bands at 2800–3000 cm^{-1} are carbon-hydrogen stretching vibrations of the γ-MPS. The barely visible peak at 1640 cm^{-1} is the C=C double bond stretching mode. The large, broad absorbance from 1600–1000 cm^{-1} in Figures 1A and 1B is due to SiOSi and MO (where M is B, Al, Mg, Ca, Na) stretching vibrations of the glass substrate. The carbonyl peak will be used for relative calculations of the amount of γ-MPS on the glass cloth surface.

Normally, in diffuse reflectance spectroscopy, the sample, if not already in powder form, is ground to a fine powder of controlled particle size and mixed with powdered KBr also of controlled particle size. The single beam spectrum of this sample is then ratioed against a background spectrum of pure powdered KBr. For the E-glass cloth under study this procedure is not necessary because the coupling agent concentration on the fibers is sufficiently low. The cloth is used as treated rather than ground to a powder for the following reasons. Grinding exposes fresh glass surface to the beam, reducing the γ-MPS peaks relative to the glass bands. Grinding may alter the chemical state of the coupling agent. The fibers are of sufficiently small diameter to give a good reflectance spectrum. A constant effective particle size is assured.

The flexural strength of the polyester composite as a function of the amount of methacryl silane coupling agent present is shown as the solid data points in Figures 2 and 3. As already mentioned, the amount of coupling agent on the glass fibers was varied by changing the concentration of the aqueous silane treating solution. This solution concentration forms the abscissa axis in Figure 2. The DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) analysis revealed the amount of silane deposited on the glass, and the relative intensity from this analysis forms the abscissa axis in Figure 3. The unique aspect of these results is the combination of spectroscopic characterization with mechanical analysis. Thus, the amount of coupling agent on the glass fiber surface can be correlated with the mechanical properties of the cured composite made from those glass fibers. Previous studies have varied the amount of coupling agent present on the glass fiber surface also, but they did not characterize the amount present by spectroscopy.[25,26] Other researchers have quantitatively studied the uptake of silane by glass fibers as a function of treating solution concentration.[27,28] The present results for both spectroscopic and mechanical

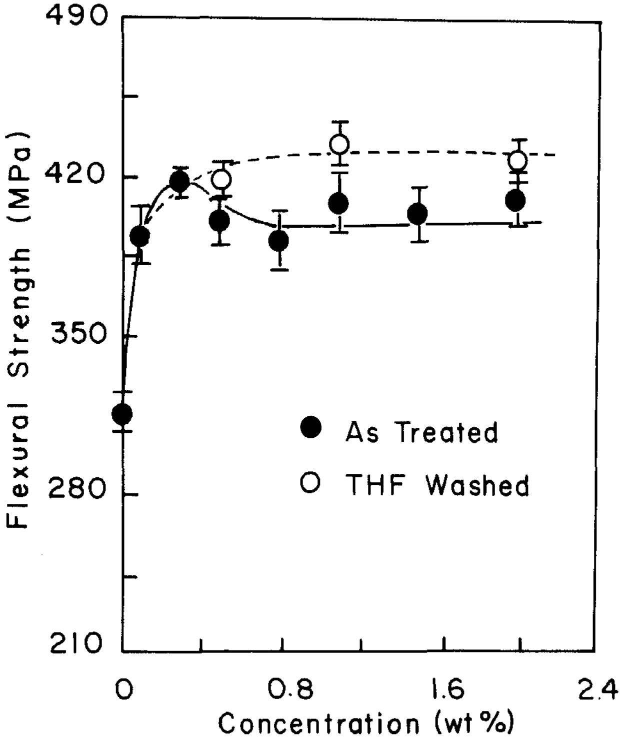

FIGURE 2 Dry strength of composites using silane treated and silane treated/THF washed glass cloth as a function of silane treatment concentration.

measurements used the same glass cloth samples (*i.e.*, eleven plies of cloth were treated with silane solution of a certain concentration, one ply was chosen at random for the diffuse reflectance work, and the other ten plies were used to make the polyester composite).

The results shown in Figure 2 and Table 1 are in general agreement with data obtained for an E-glass/γ-MPS/polyester system by Johannson *et al.*[28] There is a large increase in strength between the composite system without silane and the system with the lowest amount of silane in Figures 2 and 3. The system with the least amount of silane corresponds to a silane treating solution concentration of 0.1 wt%. Lower concentrations were not used. Nevertheless, Johannson *et al.*[28] have shown that concentrations as low as 0.01 wt% produce mechanical property improvements over the untreated composite.

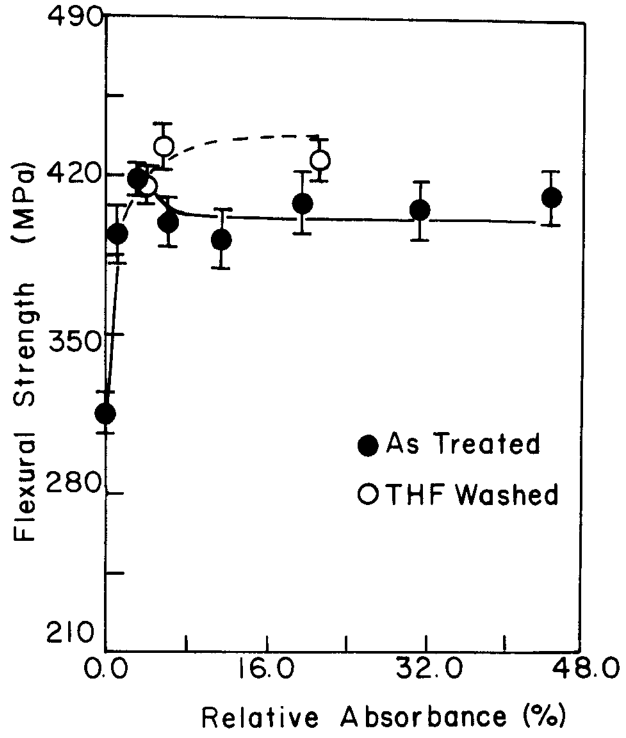

FIGURE 3 Dry strength of composites using silane treated and silane treated/THF washed glass cloth as a function of the relative amount of silane on the glass cloth.

TABLE I

Results of Flexural Test as a Function of the Amount of Silane on the Glass Fibers

% Relative Absorbance C = O of MPS	Young's Modulus ($MPa \times 10^{-3}$) DRY	WET	Ultimate Strength (MPa) DRY	WET
0.0	17.2 ± 0.16	14.8 ± 0.64	312 ± 8.9	183 ± 3.9
1.01 ± 0.38	21.2 ± 0.21	19.5 ± 0.15	388 ± 12.6	362 ± 12.5
3.14 ± 0.45	21.2 ± 0.25	20.5 ± 0.75	412 ± 5.5	396 ± 11.9
6.64 ± 1.05	20.5 ± 0.27	21.9 ± 0.77	395 ± 10.6	418 ± 8.6
11.6 ± 1.43	20.0 ± 0.27	20.8 ± 0.24	387 ± 12.6	405 ± 15.4
19.3 ± 2.07	20.5 ± 0.67	20.5 ± 0.21	403 ± 13.9	421 ± 9.1
32.9 ± 5.62	21.8 ± 0.25	21.2 ± 0.35	399 ± 13.4	419 ± 16.0
45.6 ± 6.14	20.1 ± 0.20	20.0 ± 0.20	405 ± 13.2	387 ± 8.2

The limits on the above data represent 90% confidence intervals.

It is important to realize that the concentration of the silane treating solution alone does not determine the amount of γ-MPS coupling agent adsorbed on the glass fiber surface. The method of treatment (aqueous or organic solvent solution), and the method of application (laboratory, industrial) both affect how much γ-MPS is actually adsorbed. Thus, a treating solution concentration of 0.5 wt%, for example, may give different amounts of silane on the fibers depending on how it was deposited. While concentration alone does not determine the amount adsorbed it does have other effects. Concentration determines the structure of the silane in solution,[29,30] and hence probably affects the structure on the glass surface.

Another aspect of the results in Figure 2 that has also been observed by other researchers is the slight maximum in strength and modulus which occurs at low silane concentrations. The reduction of mechanical strength at higher concentrations of silane is believed to result from diffusion of coupling agent into the resin layer immediately surrounding the glass fibers. This diffusion process creates a resin-silane blend near the fiber surface, which presumably has inferior mechanical properties compared to the pure resin. Only the physisorbed layers of silane would be able to migrate into the resin, since the chemisorbed layers of silane are bound by primary chemical bonds.

The open data points in Figures 2 and 3 show the dry strength of the THF washed samples. These data indicate that the physisorbed layers do indeed reduce the mechanical strength of the composite. In Figure 3 the flexural strength is plotted as a function of relative IR absorbance of the γ-MPS instead of treating solution concentration as in Figure 2. The samples washed with THF are shifted down relative to the other points in Figure 3. This is true because the THF is removing the physisorbed layers of silane. The infrared analysis revealed that between 30–60% of the silane was lost after washing with THF. Figures 4 and 5 show wet strength retention as a function of silane concentration. This graph was generated by dividing the wet strength by the dry strength, and plotting the results as a function of the silane treating solution concentration or the amount of silane present as measured by DRIFTS. As expected, the wet strength retention of the composite system without silane is very poor ($<60\%$), while the retention of all the systems with silane is very good ($>90\%$). Quite surprisingly, the concentration range 0.5–1.5 wt% produces wet strength retention values greater than 100%. Although the hydrothermal conditioning was not severe (48 hrs./H_2O/80°C), it is generally expected

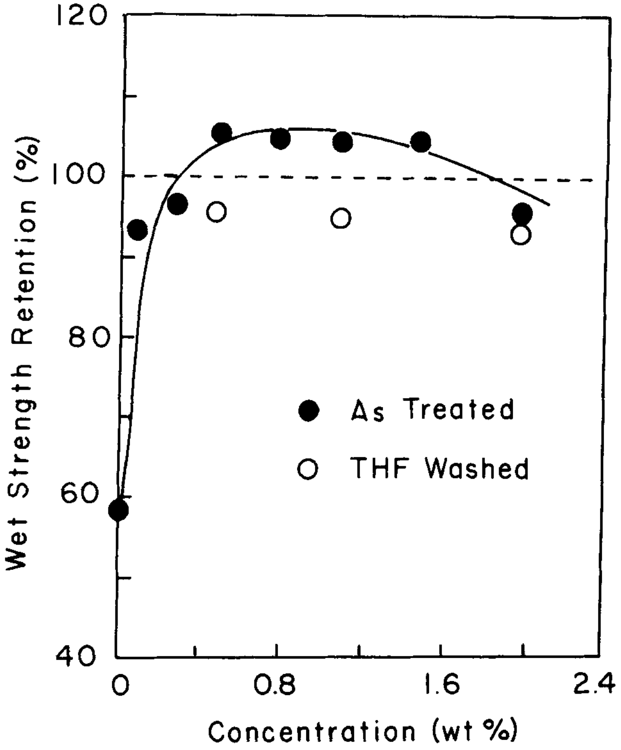

FIGURE 4 Wet strength retention of composites using silane treated and silane treated/THF washed glass cloth as a function of silane treatment. Wet strength retention values are obtained by dividing the wet strength by the dry strength.

that wet properties will be inferior to dry properties. The results from the THF washing experiments (open data points in Figure 4) exhibit the expected 90% wet strength retention. This indicates that the physisorbed silane layers are responsible for the >100% wet strength retention. It is possible that the physisorbed layers increase the wet strength relative to the dry strength by a plasticization mechanism. Ishida *et al.*[31] hydrolysis kinetics data indicate that major hydrolysis of Si-O-Si to Si-OH would not occur before 48 hours at 80°C. Therefore, the expected primary effect of strength reduction after hydrothermal aging due to hydrolysis of the Si-O-Si groups of γ-MPS may not occur. Instead, a secondary effect resulting from the physisorbed layers determines the hydrothermal performance.

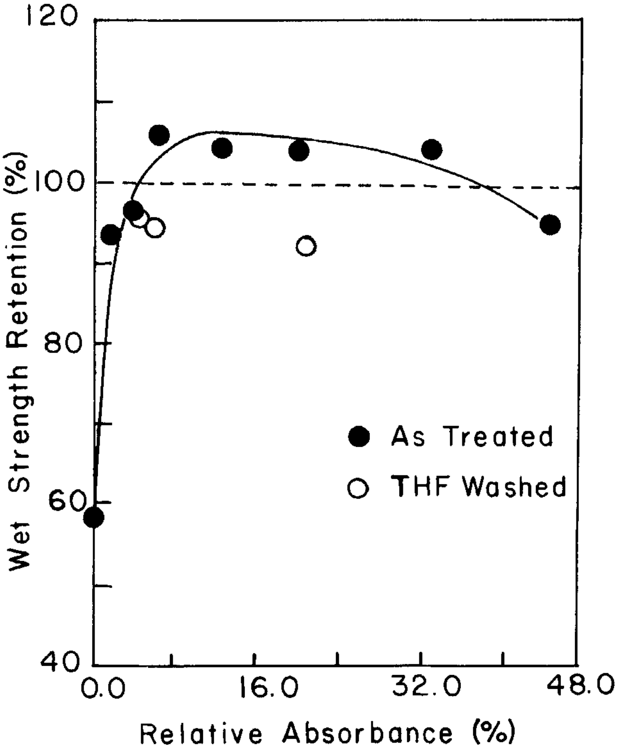

FIGURE 5 Wet strength retention of composites using silane treated and silane treated/THF washed glass cloth as a function of the amount of silane on the glass cloth.

To determine the mechanical response of the proposed polyester/physisorbed γ-MPS interphase, a model study was performed. Systems of bulk polyester blended and cured with different proportions of siloxane oligomer were tested in flexure. The results are shown in Figures 6–8. In Figure 6 the stress at failure decreases more rapidly than would be predicted by the "rule of mixtures." Though good mechanical samples could not be obtained from blends with greater than 40 wt% siloxane, the pure siloxane gave testable samples. It is obvious that the initial steep decrease in strength with increasing siloxane concentrations must change to a more gradual slope above approximately 50 wt% siloxane. The behavior of Young's modulus as shown by Figure 7 offers an interesting contrast to the failure stress

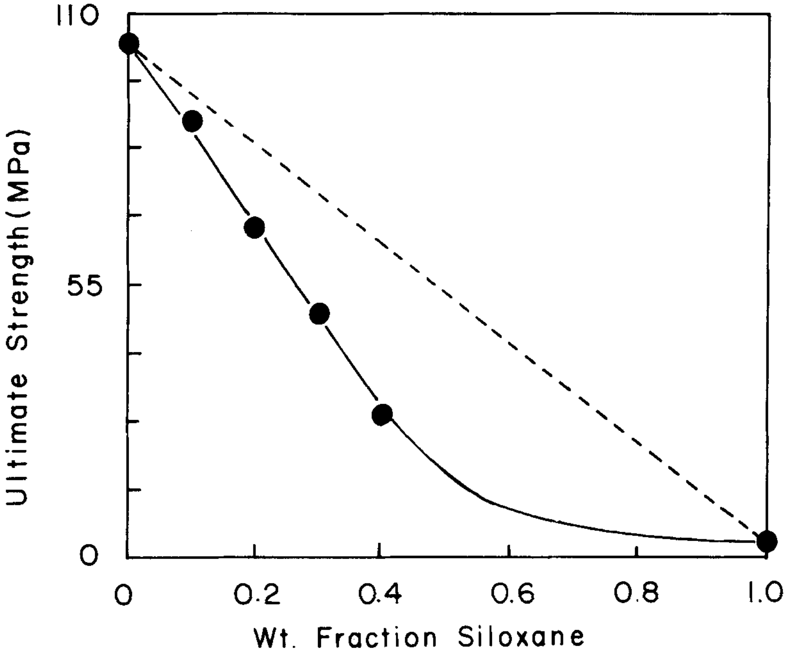

FIGURE 6 Stress at failure for model blend of polyester and siloxane oligomer as a function of siloxane content.

behavior. Initially there is a slight increase in the modulus as siloxane is added to the resin. The maximum modulus occurs at about 50 wt% siloxane. Thus, while the stress at failure initially decreases more rapidly with increasing siloxane content than predicted by the rule of mixtures, the Young's modulus decreases less rapidly. This phenomenon is similar to the antiplasticization effect observed with plasticized PVC.

The desired nature of the interphase for maximum mechanical strength of the composite is not well understood. Some researchers state that a brittle interphase is desirable.[32] Others have indicated that a ductile interphase is necessary.[5] This model study gives an indication of the type of behavior which is possible. If the necessary interphase properties for maximum mechanical performance can be determined, then a knowledge of possible interphase modifications would be useful. The failure envelope shown in Figure 8 summarizes the ultimate stress and strain values for this model study. This diagram makes clear that

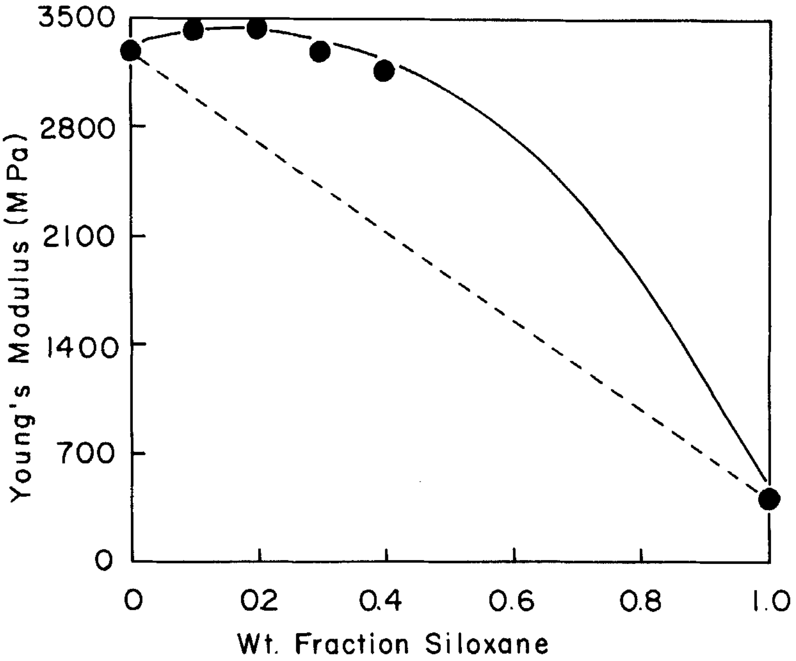

FIGURE 7 Young's modulus for model blend of a polyester and siloxane oligomer as a function of siloxane content.

the stress–strain behavior is very regular until the siloxane content exceeds 40 wt%. It is believed that above 40% the siloxane becomes the continuous phase, and the mechanical strength drops off sharply. It should be noted that the inferior mechanical properties of the physisorbed silane/polyester blend near the glass surface is solely determined by the particular combination of the materials. Thus, it is possible that for some other silane/resin systems, strengthening could be observed.

The hypothesized effect on the silane interphase of the THF washing experiments is shown schematically in Figure 9. As stated previously, the physisorbed silane which is normally present is believed to dissolve and diffuse into the resin matrix during cure (Figure 9A). This diffusion process forms a weak thermoset blend near the interface. If the physisorbed layers are removed by washing the glass fibers with THF, then no weak blend is formed near the interface (Figure 9B). This would improve the final composite mechanical properties.

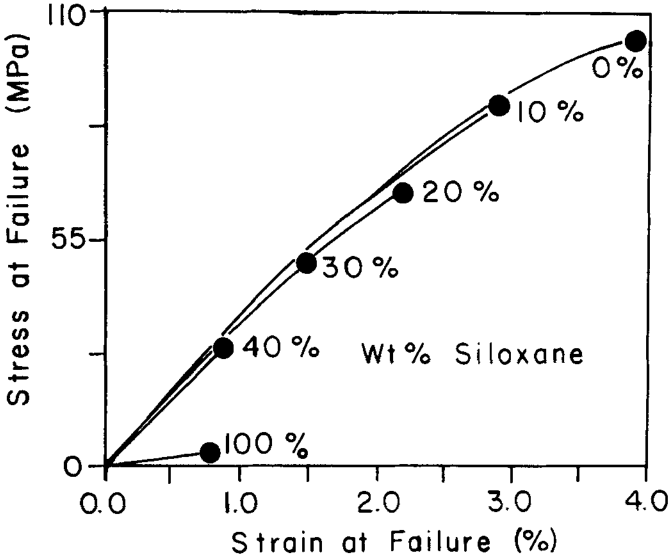

FIGURE 8 Stress at failure for model blend of polyester and siloxane oligomer as a function of strain at failure.

CONCLUSIONS

The mechanical response of polyester composites depends on the amount of γ-MPS present and the structure of the γ-MPS. This structure can be classified into two regions: physisorbed layers of γ-MPS which can be dissolved by organic solvents, and chemisorbed layers which are insoluble. The physisorbed layers of γ-MPS reduce the strength of a polyester composite. Presumably this strength reduction is caused by migration of the physisorbed layers into the resin forming a blend of γ-MPS and polyester near the fiber surface. A model study of this γ-MPS/polyester blend confirms that strength does decrease as the wt% of γ-MPS is increased.

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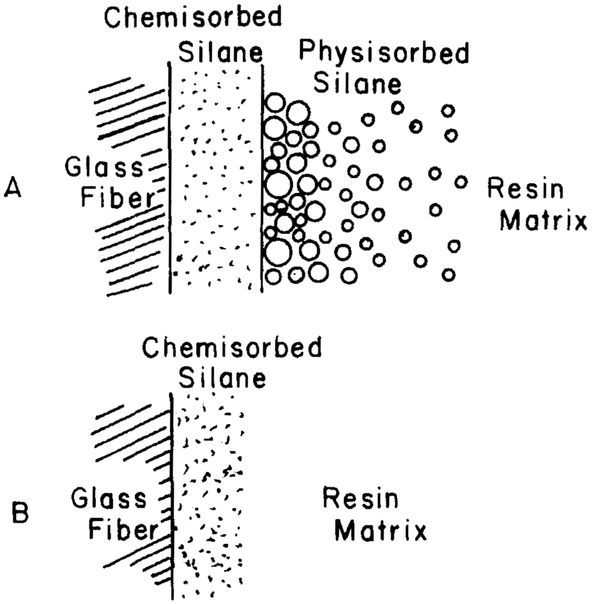

FIGURE 9 Schematic diagram of the effect of THF washing on the final composite interphase.
Diagram A: As treated
Diagram B: THF washed.

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