

Adhesion Enhancement of Rubbery and Ductile Polyolefin Coatings on Glass Fibers for Epoxy Composites and Effects on Failure Mechanism

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SYNOPSIS

Dilute polyolefin solutions, respectively based on EPDM and UHMWPE, were reacted with functionalized silanes to prepare coatings for glass fibers. These were found to provide adequate bonding characteristics for both glass and epoxy resin (bisphenol type). Unidirectional composites containing fiber matrix interlayers, using fibers coated with the aforementioned functionalized polyolefins, were found to exhibit much larger $\tan\delta$ values over the temperature range of 60 to +60°C and greater ductility in flexural tests, albeit at the expense of a reduction in failure stresses. The UHMWPE coatings produced a multiple step fracture mechanism, which was deemed to provide a more efficient crack stopping mechanism than equivalent EPDM coated fibers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Several methods have been suggested for enhancing the toughness of composites. These include the use of intermittent interlaminar layers and continuous or discontinuous fiber coatings. This work is concerned with the latter method, placing particular emphasis on the effects of vast differences in the modulus of the interlayer between fiber and matrix.

Since fracture normally initiates at the fiber matrix interface, an interlayer can be used to modify the stress distribution in the immediate neighboring regions and to provide an energy absorption mechanism through large scale elastic or plastic deformations. The theoretical predictions for the stress distribution around the fibers when the modulus of the interlayer is changed in steps ranging from 1 MPa, corresponding to that of a rubbery material, to 10 GPa, that is, a modulus value intermediate between those exhibited by reinforcing fibers and ordinary polymer matrices, are reported elsewhere.¹

In this article is discussed the methodology used to deposit continuous coatings on glass fibers, from

solutions of ethylene-propylene elastomers (EPDM) and ultra high mol wt polyethylene (UHMWPE), exhibiting varying levels of adhesion with both glass fibers and epoxy resins. This represents an alternative approach to the one previously used to bond UHMWPE to glass fibers and Nylon 6.² The energy absorption characteristics of the resulting composites are illustrated by means of dynamic mechanical tests and flexural strength measurements.

An early attempt to use a rubbery coating on large diameter fibers was reported by Lavengood and Michino³ and later elaborated upon by Tryson and Kardos.⁴ These authors used a plasticized epoxy resin interlayer between glass fibers and the highly crosslinked epoxy matrix and were able to achieve a 67% increase in transverse strength and a 1000% improvement in torsional fatigue life.

Hancox and Wells⁵ later reported an 100% increase in the work of fracture for carbon fiber/epoxy composites using silicone rubber coatings on the fibers.

Shelton and Marks⁶ used high resolution X-rays to study the effects of a ductile interlayer on the failure properties of composites. In Schwartz and Hartness' work,⁷ ductile interlayers were produced by coating the fibers with a polyamide modified

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epoxy resin and also with a rubber modified epoxy formulation. Similarly McGarry and Mandel⁸ coated carbon fibers with epoxy resin modified with a carboxy terminated nitrile oligomer (CBTN) to demonstrate the toughness enhancement achievable with both unidirectional and cross-ply laminates under impact loads. These conclusions were subsequently supported by Gerard on components fabricated by filament winding.⁹

In order to obtain coatings of uniform thickness, Crasto and Subramanian^{10,11} used an electrodeposition method in which carbon fibers acted as the electrodes of an electrolytic cell containing solutions of ionic polymers, such as butadiene-maleic anhydride and ethylene-acrylic acid copolymers. In these studies, the improved impact properties of the resulting epoxy-based composites were attributed to the ability of the interlayers to deform plastically to prevent the crack propagating through the brittle carbon fibers.

Bell et al.,^{12,13} on the other hand, were able to polymerize, by an electrolytic process, random copolymers of methyl acrylate and acrylonitrile directly on to the surface of carbon fibers. Subsequent investigations^{14,15} revealed significant improvements in mode I fracture energy (G_{IC}), but a large reduction in mode II crack initiation energy (G_{IIC}) using the same electropolymerized polymers as interlayers between carbon fibers and an epoxy resin matrix.

In selecting suitable coating materials for glass fibers in the present work, the emphasis was placed on the potential advantages of using polyolefins due to their low water absorption characteristics and high ductility at subambient temperatures. The low water characteristics are expected to afford a degree of protection for the fibers against moisture enhanced stress corrosion phenomena,¹⁶ while the combined effect of low water absorption and high ductility is expected to be reflected in the performance of composites with respect to damage tolerance under impact loads, particularly at low temperatures.

The choice of EPDM and UHMWPE as the base polymers to coat glass fibers from solutions was made on account of their vast difference in modulus, that is, approximately 1 MPa and 1 GPa, respectively, and for their film forming capability. Unlike conventional grades of HDPE, which precipitate as fine powder upon evaporation of the solvent, UHMWPE produces continuous films via the formation of a thermoreversible gel.² The choice of coating polymers was also made to provide two different energy absorption mechanisms, that is, one by rubbery deformations (EPDM) and another by yielding deformations (UHMWPE).

EXPERIMENTAL

Grafting of Coating Polymers and Evaluation of Bonding Properties

EPDM Based Coatings

Four different grades of EPDM (ethylene propylene diene terpolymer) elastomers were initially evaluated in terms of their receptivity to silane grafting reactions, assisted by peroxide initiators using a Brabender mixer. Screening tests for their adhesion to glass were carried out by squeezing a small amount of grafted polymer between a microscope glass slide and a release film at 150°C and placing the laminates in an oven at the same temperature for 30 min under a 2 kg weight. After cooling to room temperature, the extent of bonding to glass was assessed qualitatively by scraping the polymer coating with a razor blade. Subsequently the most promising systems were grafted in a 5% xylene solution at 100°C and the tests were repeated to verify the validity of the screening tests.

Finally the most promising systems were evaluated by producing single lap shear specimens [Fig. 1(a)] by coating the ends of microscope slides with the polymer solution in successive steps, allowing the solvent to evaporate between each coating application. The single lap shear specimens were then placed in an oven under a 2 kg weight at 180°C for 30 min. Thin metal spacers coated with petroleum jelly were used to control the thickness of the bonding layer. The bond strength was then determined by pulling the specimens in a tensometer at room temperature using a grip separation speed of 5 mm/min.

To increase the intensity of stresses at the interfaces, as opposed to the bulk of the polymer interlayer, a number of specimens were constructed by using a film of UHMWPE (0.4 mm thick) as a central layer and by treating the glass surface with a dilute silane solution [Fig. 1(b)].

UHMWPE Based Solutions

2% solutions of UHMWPE in xylene were heated at 100°C with various amounts (up to 10% based on the polymer content) of silane Z6032 ($(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)\text{NHCH}_2\text{CH}_2\text{NH}(\text{HCl})\text{CH}_2\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$) and silane A174 (gamma-methacryloxypropyl trimethoxysilane) in the presence of 0.5% benzoyl peroxide (based on the polymer content) for up to 24 h with continuous stirring.

Samples were taken after 4 h and 24 h and were used to prepare single lap shear specimens, which were tested as described previously. 5 mm thick glass

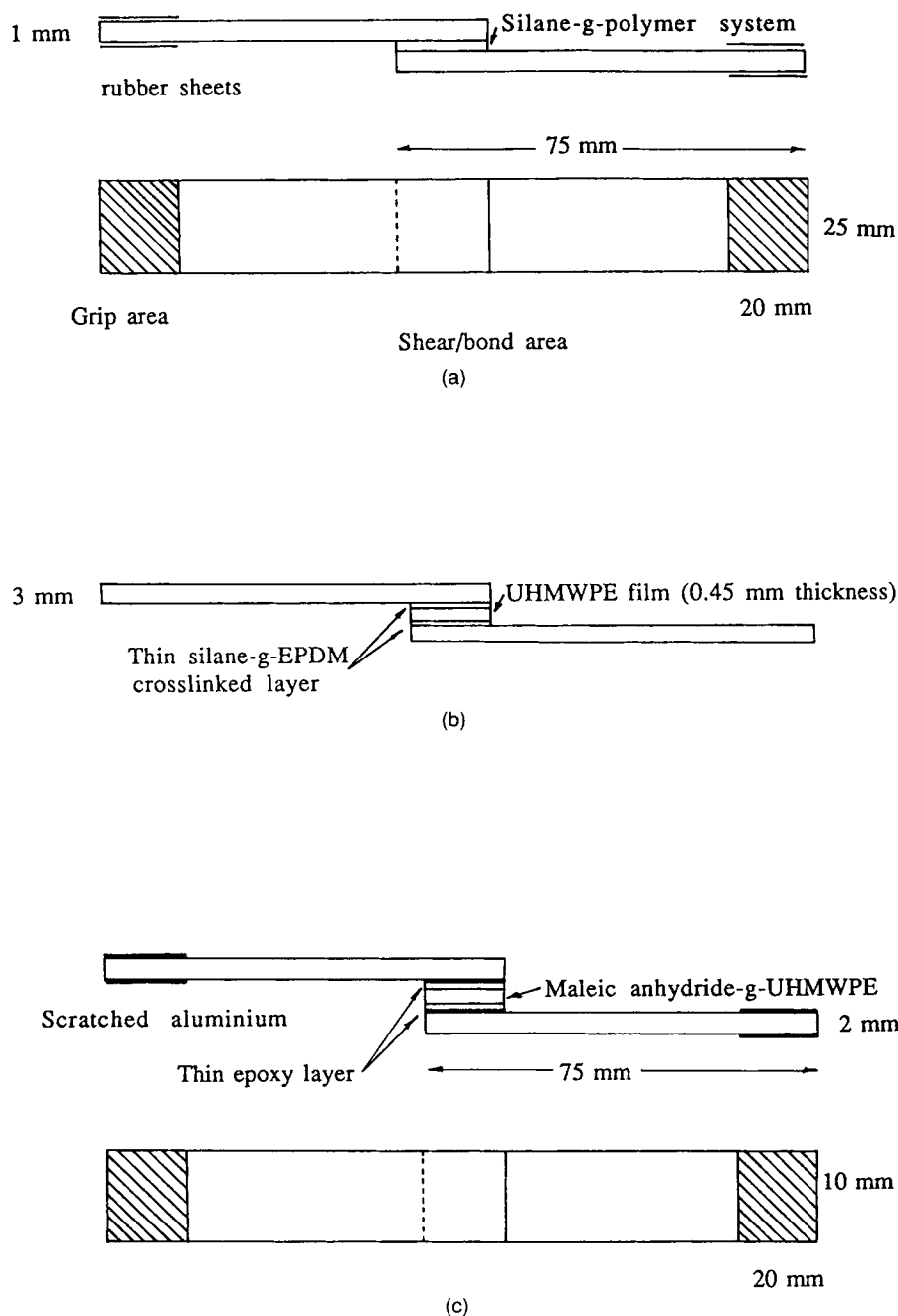


Figure 1 Lap shear test specimens (a) Glass slides with single interlayer, (b) Glass slides with EPDM/UHMWPE sandwich interlayer, and (c) Aluminium strips with epoxy/UHMWPE sandwich interlayer.

slides had to be used to ensure that failures always occurred in the bonded film.

The glass slides were also previously degreased and treated with a 0.5% solution of Z6302 in propanol/water (99/1) containing 0.005% dicumyl peroxide. The specimens were prepared by bonding UHMWPE films to the glass slides at 280°C for 2 h under a 5 kg weight.

Bonding to Epoxy Resin

For the case of ethylene propylene elastomer based coatings, a sulfonated polymer grade (Uniroyal I 1025, containing 1.1% ionic groups) was chosen to ensure that reactions would occur at the interface of the fiber coatings with the matrix. For systems based on UHMWPE, on the other hand, the polymer

was grafted in a 1% xylene solution using 2, 6, and 10% maleic anhydride (based on the polymer content) at 100°C for 3 h using 0.5% benzoyl peroxide (based on the polymer content).

The maleic anhydride grafting reactions were also carried out on the polymer previously grafted with silane.

For both polyolefin coating systems their ability to bond epoxy resins was tested by laminating a thin polymer film between thin uncured epoxy layers coated onto aluminium strips to produce sandwich lap shear specimens [Fig. 1(c)]. The epoxy resin was a bisphenol type (Epikote 828), cured with 80 parts hexahydro phthalic anhydride (HHPA) and 1 part *N*-dimethyl benzyl amine (BDMA) at 80°C for 3 h and postcured for 1 h at 100°C and 1.5 h at 150°C under a 3 kg weight.

In all cases, the extent of grafting on the polyolefin chains was assessed by transmission IR analysis for EPDM systems and FTIR for UHMWPE samples.

The films obtained were extracted in propanol over a period of 5 days to monitor the possible leaching of unreacted low mol wt species.

Control films were also made from physical mixtures of polymer and grafting agent to have a more realistic basis for the interpretation of the data.

Coating of Glass Fibers

Glass fibers were coated with the required polymer by passing the rovings through a xylene bath at 80°C to remove the size and then through xylene solutions of the respective grafted polymers, that is, EPDM and UHMWPE, at 120°C. The rovings were dried by means of hot air jets in an attempt to prevent adjacent fibers from sticking to each other.

Different coating thicknesses were obtained by varying the concentration of the polymer solutions. These were calculated from the weight increase of the fibers, assuming uniform coatings over the entire length of the fibers.

Table I Calculated Void Content of Composites from Density Measurements and Theoretical Density Values

Composite	Measured Density (g/cm ³)	Theoretical Density (g/cm ³)	Void Content (%)
Control	2.0691	2.0769	0.38
	2.0703		0.32
			Mean = 0.35
2.8% UHMWPE	2.0447	2.0691	1.18
	2.0329		1.75
			Mean = 1.5
3.7% UHMWPE	1.9934	2.0458	2.56
	2.0075		1.87
			Mean = 2.2
4.2% UHMWPE	2.0118	2.0474	1.74
	2.0017		2.23
			Mean = 2.0
4.6% UHMWPE No silane	2.0033	2.0459	2.08
	1.9907		2.70
			Mean = 2.4
1.2% EPDM	2.0236	2.0422	0.91
	2.0275		0.72
			Mean = 0.8
3.4% EPDM	2.0025	2.0367	1.68
	1.9939		2.10
			Mean = 1.9
8.2% EPDM	1.9436	2.0045	3.04
	1.9474		2.85
			Mean = 2.95

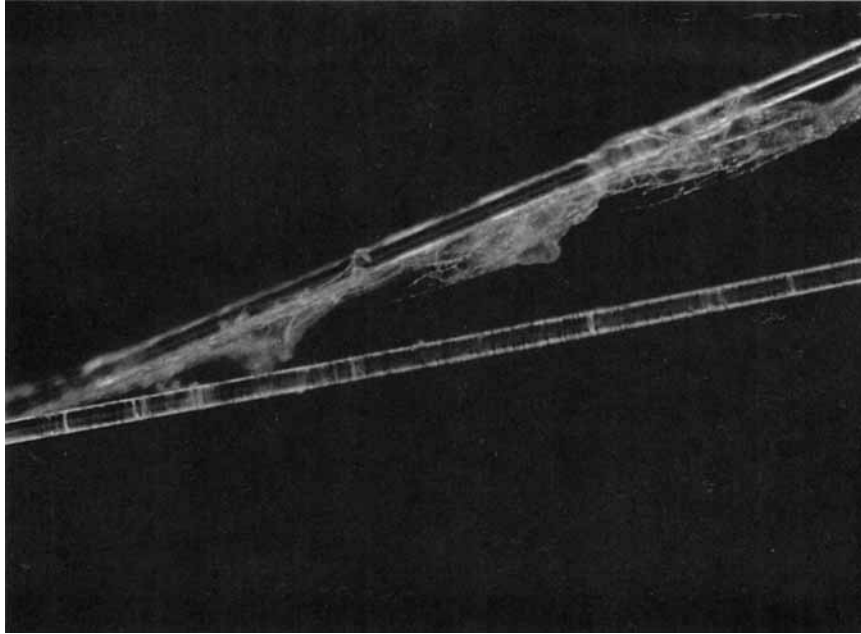


Figure 2 Micrograph of coated fibers.

The rovings used were obtained from Turner and Newall Ltd., consisting of 13 μm diameter fibers coated with an epoxy compatible size, containing a gamma-aminopropyl triethoxysilane.

Preparation of Unidirectional Composites

Glass rovings were wound around a metal frame to the required width (56 mm) and then were placed

lengthwise in the cavity of a "leaky mould" previously coated with a silicone release agent. A pre-weighed quantity of catalyzed epoxy resin, based on the formulation described previously, was spread over the fibers with the aid of a laminating roller. The top side of the mold was placed on top of the impregnated fibers and was gently squeezed onto the impregnated fibers with the aid of G-clamps to

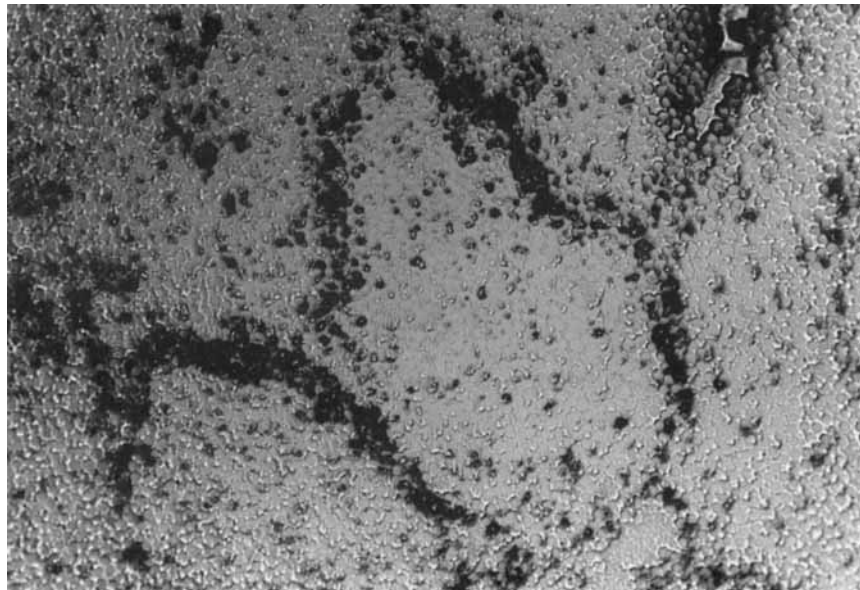


Figure 3 Micrograph of cross-section of composites with EPDM interlayers between fibers and matrix.

remove the entrapped air. Spacers, 2 mm thick, were used to control the thickness of the laminates.

The clamped mold was placed in an oven to cure the resin in two steps, that is, 1 h at 100°C and 1.5 h at 150°C. After removing from the mold, the laminates were postcured for 3 h at 150°C. In each case, the void content was calculated from density measurements, taking into account the effects of the changes in density brought about by the presence of interlayers (Table I).

The glass content was also measured on all laminates by burning the matrix at 600°C to constant weight. This was found to be within the range of 61–63% by weight.

Microscopic examinations were carried out on both coated fibers before use (Fig. 2) and on cross-sections of the laminates to monitor the distribution of the polyolefin coatings within the composites produced. Typical examples are shown in Figures 3 and 4.

Mechanical Properties Measurements

To study the influence of the polyolefin interlayers on the mechanical properties of the composites, dynamic mechanical spectra were first obtained on specimens subjected to 3 point bending deformations (span/width ratio, $S/W = 10 : 1$) along the fibers direction at 1 Hz. The fracture resistance was subsequently evaluated by measuring the flexural strength ($s/w = 15 : 1$) at 5 mm/min.

In all cases, the tests were carried out with loads inducing deformation along the fiber direction.

RESULTS AND DISCUSSION

Efficiency of Grafting Reactions

The infrared spectra for EPDM and UHMWPE grafted in solution with silanes, before and after solvent extraction, are shown in Figures 5 and 6, respectively. In all cases, the characteristic SiOCH_3 vibration bands at 1130, 1160, and 1110 cm^{-1} are clearly evident in all IR spectra, while the multiple peaks between 1077 and 1010 cm^{-1} , due to SiOSi (possibly enhanced by SiOH stretching vibrations), are missing from the spectra after solvent extraction, suggesting that polycondensation reactions were not predominant because these would have produced insoluble crosslinked products.

The IR spectra for UHMWPE and for UHMWPE grafted with maleic anhydride are shown in Figure 7, while the effect of the extraction in methanol, after immersion for 5 days, is shown in Figure 8 and in Table II. The absorbance ratio was taken as the ratio of the peak height of the $\text{C}=\text{O}$ stretching vibration at 1708 cm^{-1} and the height of the CH rocking vibration at 720 cm^{-1} . The data in Table II clearly indicate the reaction yields in solution are low, that is, in the region of 30%. One notes, on the other hand, that the extent of grafting

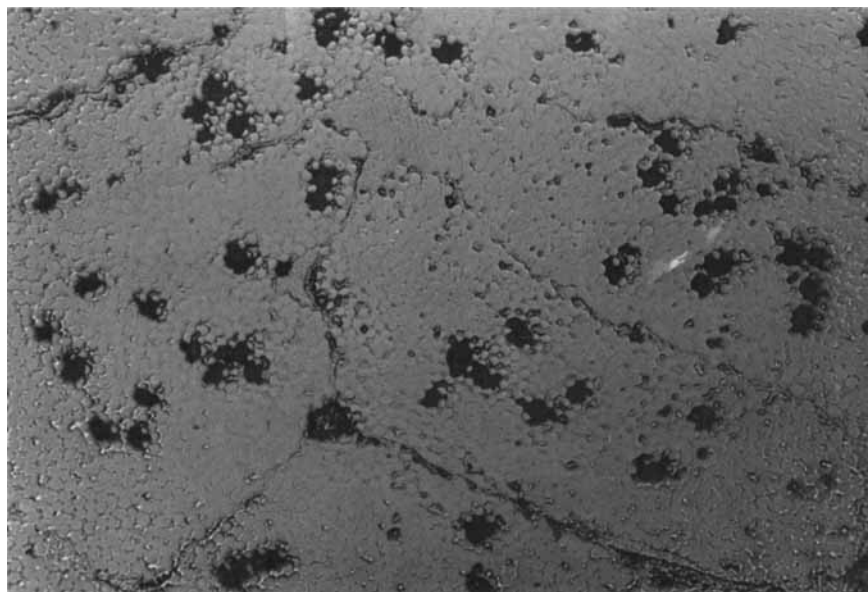


Figure 4 Micrograph of cross-section of composites with UHMWPE interlayers between fibers and matrix.

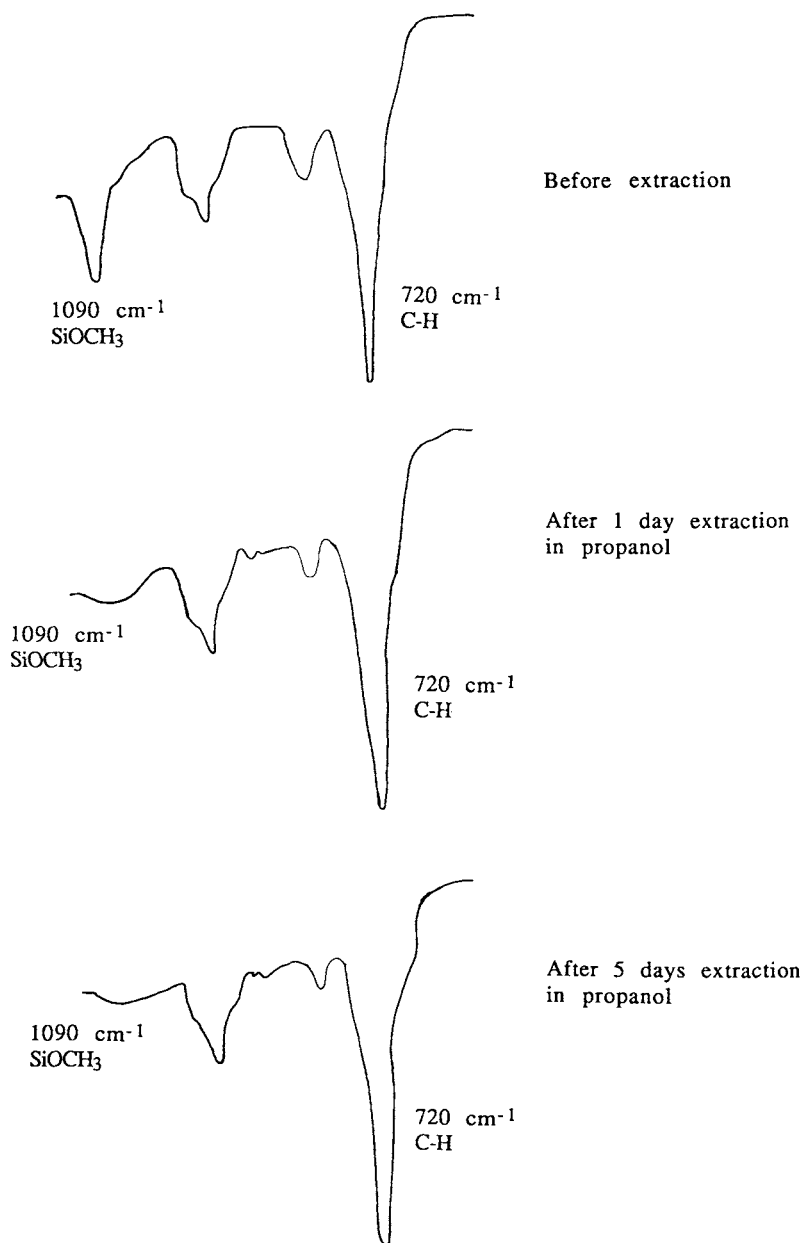


Figure 5 Portion of IR spectra for EPDM grafted with silane A189 after extraction in propanol.

reactions is doubled after heating the dry film at 80°C. The low efficiency of such grafting reactions, when using *p*-xylene as solvent, has been attributed to both radical quenching effects and competition reactions between polymer chains and solvent molecules for the succinyl radicals.^{17,18}

Adhesion of Grafted Polymers to Glass and Epoxy Resin

Qualitative razor scraping tests on coatings showed that the sulfonated ethylene propylene elastomer

gives very poor adhesion to glass when grafted with a methacryloxysilane (A174) and only marginal improvements could be detected when the polymer was coated with the cationic styryl silane (Z6032).

The best results were obtained with the conventional EPDM polymer (5% diene content) grafted with a mercaptosilane (A189) in the presence of small amounts of *N*-cyclohexylbenzothiazyl sulfonamide accelerator.

Single lap shear test results on these systems showed consistently that failure occurred within the bulk of the EPDM interlayers and that the overall

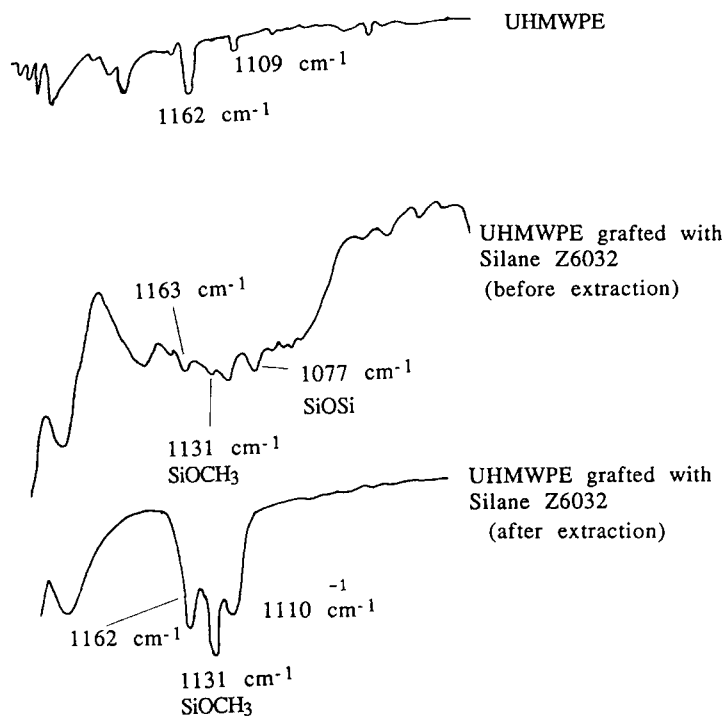


Figure 6 FTIR spectra of UHMWPE grafted with silane Z6032.

bond strength improved when the thickness was reduced, reaching a maximum value of 1.75 MPa.

When the thin EPDM coatings on the surface of the two glass slides were interlayered with a

UHMWPE film, the interlaminar shear strength increased to 4 MPa, with failure always occurring at the polymer/polymer interface. This observation confirms that a high level of adhesion to glass is

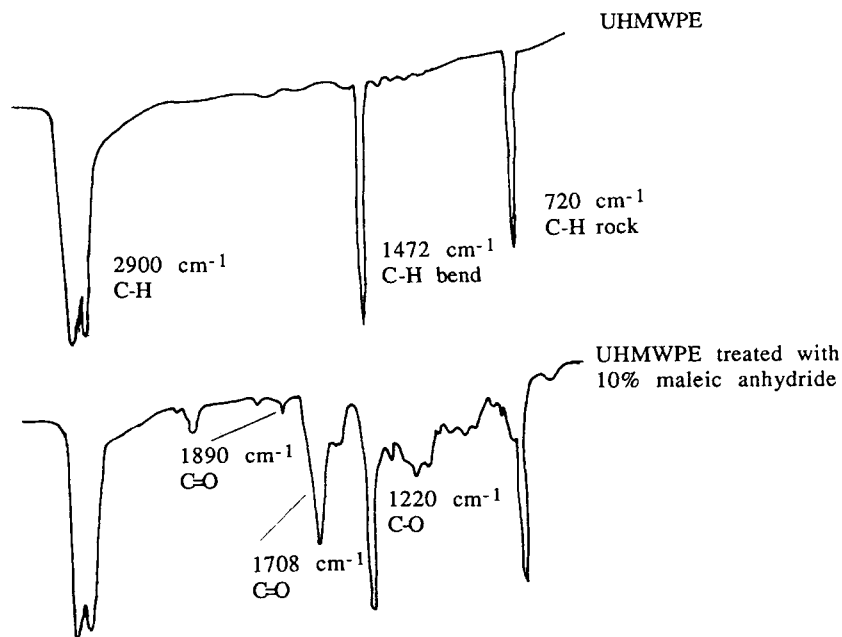


Figure 7 FTIR spectra of UHMWPE grafted with maleic anhydride.

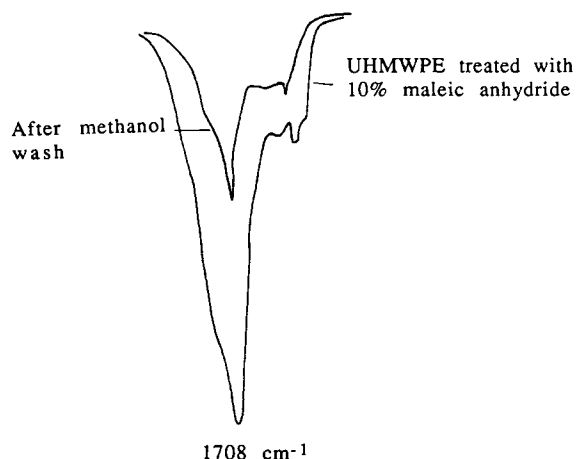


Figure 8 IR absorption band of C=O group before and after extraction in methanol.

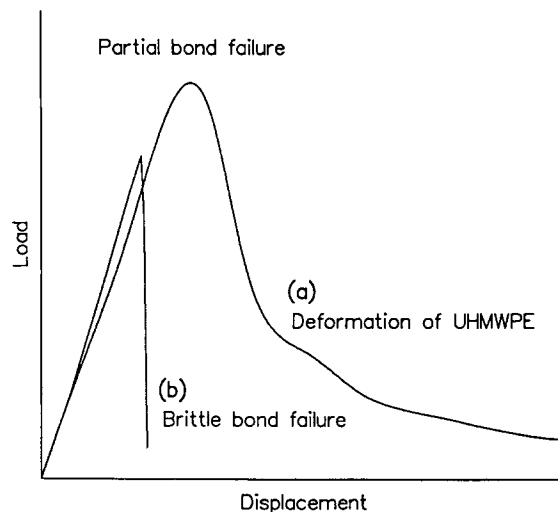
achieved with A189 silane grafted polymers containing diene unsaturation.

For the case of UHMWPE, the highest bond strength (6.96 MPa) was obtained with the methacryloxy silane grafted polymer system. It is interesting to note that such a system yielded a ductile failure, while the polymer grafted with cationic styryl silane produced brittle failures (Fig. 9) and that even higher bond strength values (11.5 MPa) were obtained when the surface of the glass slides was primed with the cationic Z6302 silane solution.

The effects of the various grafting systems on the bonding characteristics of the polyolefin interlayer toward the epoxy resin is shown in Fig. 10. In this diagram, it is noted that while the recorded bond strength values increased with increasing maleic anhydride concentration (based on the polymer

Table II FTIR Analysis of UHMWPE Treated with Maleic Anhydride

Maleic Anhydride Treatment	IR Absorbance Ratios (C=O/CH)	
	Before Methanol Wash	After Methanol Wash
2% maleic anhydride	0.03	0.01
10% maleic anhydride	0.475	0.08
10% maleic anhydride no peroxide	0.11	0.005
10% maleic anhydride film heated at 80°C, 3 h	0.62	0.15



(a) eg. 2% silane A174 treatment

(b) eg. 2% silane Z6032 treatment

Figure 9 Typical load/displacement curves for lap shear tests with silane grafted UHMWPE interlayer.

content), the best results were obtained with the silane grafted system. No further improvements were achieved when the polymer was grafted with both maleic anhydride and silane.

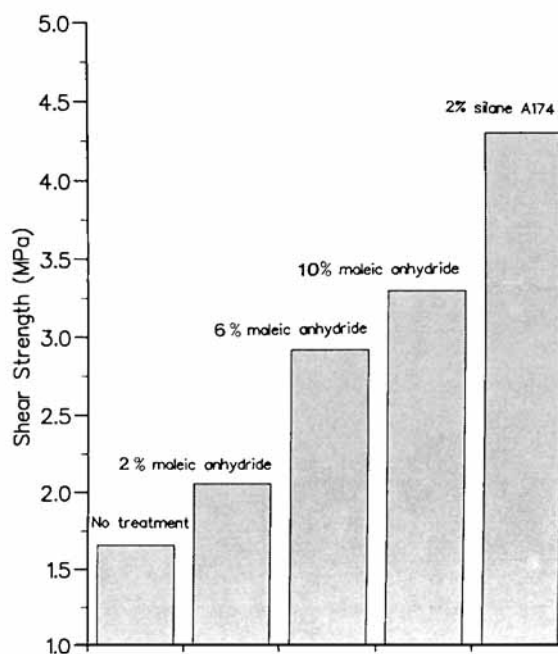


Figure 10 Effects of graft functionalization of UHMWPE on level of adhesion (shear strength) to epoxy resin.

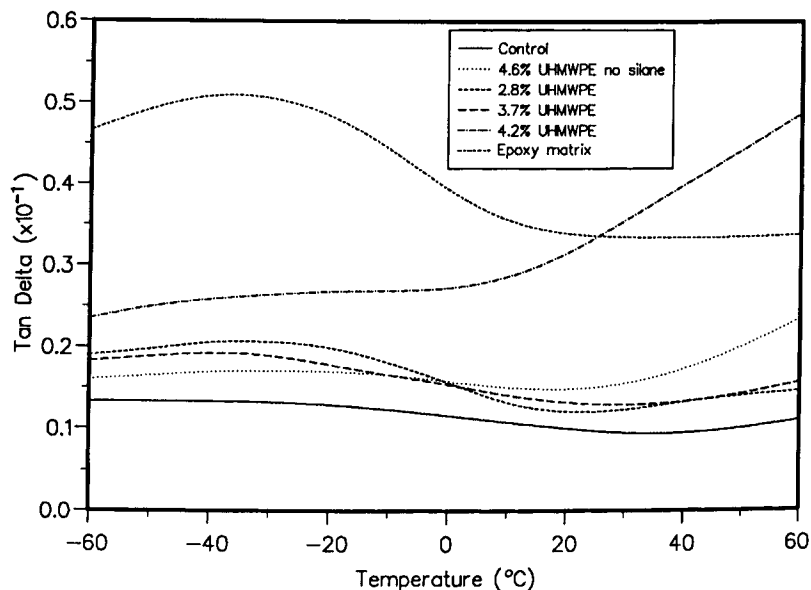


Figure 11 $\text{Tan}\delta$ variation with temperature for UHMWPE interlayered composites.

Mechanical Properties of Fiber Coated Composites

The dynamic mechanical spectra for the various interlayered composites, containing different levels of polyolefin modifications, are presented in Figures 11 and 12 as plots of $\text{tan}\delta$ against temperature in the range -60 to $+60^\circ\text{C}$. A progressive increase in $\text{tan}\delta$ values is observed with increasing the amount of polyolefin deposited on the glass fiber rovings. An inspection of these curves suggests that a critical

level of polyolefin exists for both silane grafted systems, above which the value of $\text{tan}\delta$ increases rapidly. This could be related to the conditions for which the polyolefin phase acquires a predominant influence on the mechanical losses.

The much lower $\text{tan}\delta$ value exhibited by the composite containing fibers coated with 4.2% silane grafted UHMWPE, in comparison to the equivalent composite, in which the fibers are coated with similar amounts (4.6%) of unmodified polymer, can be interpreted in terms of a reduction in interfacial en-

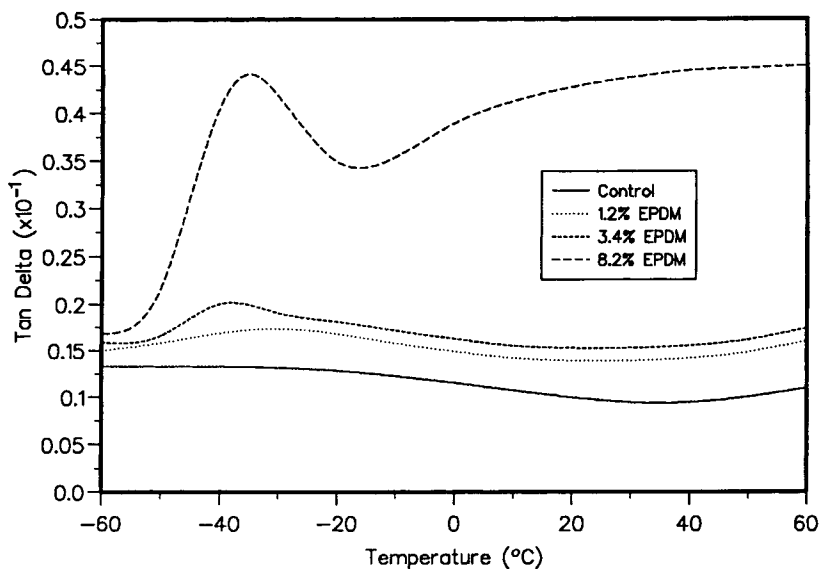


Figure 12 $\text{Tan}\delta$ variation with temperature for EPDM interlayered composites.

ergy, which allows greater penetration into the rovings to coat the individual fibers and, therefore, decreasing the amount of polyolefin left around the outer layers.

These interpretations are supported by the results of the flexural strength measurements, shown as force/deflection traces in Figures 13 and 14. One notes a gradual reduction in peak load with an increasing amount of polyolefin on the fibers, but a larger reduction is experienced when the UHMWPE coatings are deposited from the unmodified polymer solution. It can also be observed that multiple step fractures occur with the fiber matrix interlayered composites, whereas with the control composite specimens, failure occurs in one single step, starting on the outer surface and propagating through the thickness. These multiple step fractures are a manifestation of interlaminar failures rather than crack propagation. Furthermore, when the coating thickness is relatively small, that is, below 3.5%, based on the fibers content, the UHMWPE interlayers produce smaller reductions in loads to fracture and exhibit a larger number of load peaks during fracture propagation. This is indicative of a step-wise delamination process, involving an increasing number of laminae through the specimen thickness.

It has to be pointed out also that the samples showing progressive step-wise delaminations (i.e., those produced with coated fibers) did not fracture in the flexural tests, but were forced through the supports.

This can be deduced from the load/deflection traces in Figures 11 and 12 by the observation that

the load at the maximum deflection shown does not fall to zero.

CONCLUSIONS

The results of this study have shown that:

1. Although the efficiency of grafting silane groups onto the polyolefin chains in xylene solutions is low, the resulting bonding characteristics to glass surfaces are adequate to provide cohesive failure within the polymer layer.
2. Polyolefins grafted in solution with silanes are also capable of providing adequate bonding to epoxy resins, making it unnecessary to perform additional grafting with maleic anhydride.
3. It is difficult to achieve substantial and uniform coatings on glass fibers from continuous impregnation of rovings with solutions of silane grafted EPDM or UHMWPE. Nevertheless, these are capable of imparting substantial ductility to composites containing an epoxy matrix. Fiber matrix interlayers, based on silane grafted UHMWPE, provide a multiple peak-load fracture mechanism in flexural tests, which is considerably less pronounced in equivalent systems, based on fibers coated with silane grafted EPDM.

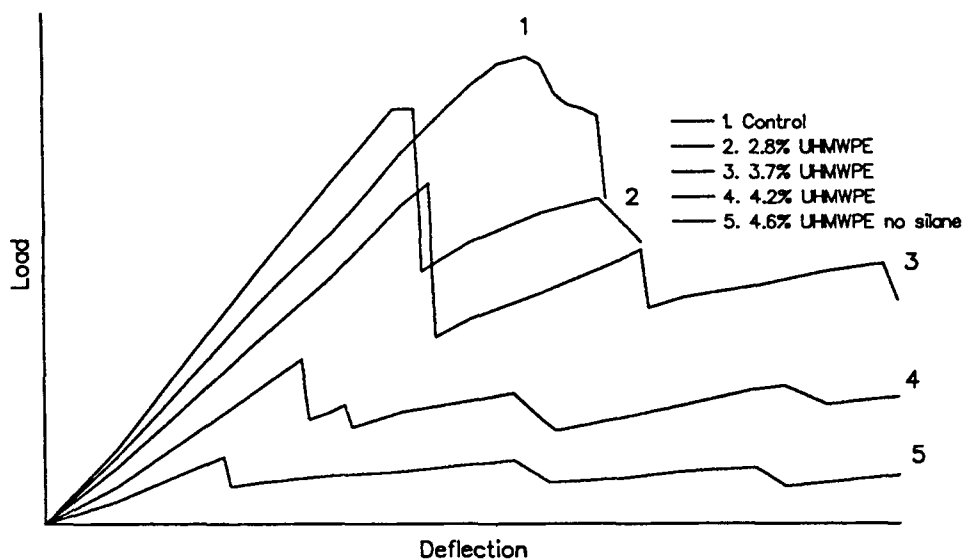


Figure 13 Typical load/deflection curves recorded in flexural strength measurements on UHMWPE interlayered composites.

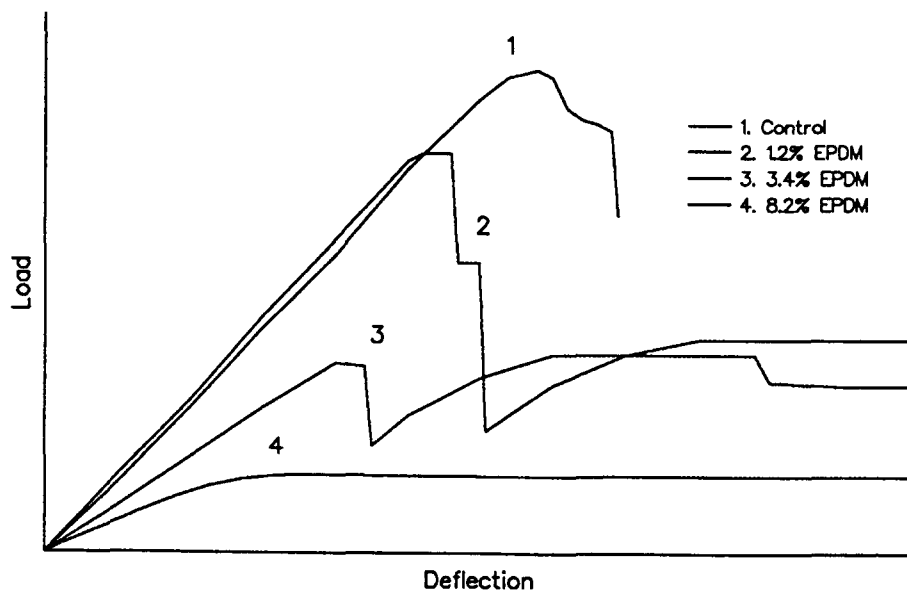


Figure 14 Typical load/deflection curves recorded in flexural strength measurements on EPDM interlayered composites.

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