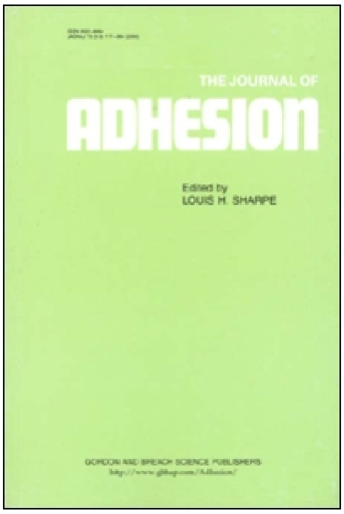


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Effect of Interphase Structure on the Debonding of Polycarbonate from S-2 Glass Fibers

Shrirang V. Ranade[a]; Xiang-Qun Xie[a]; Anthony T. Dibenedetto[a]
[a] Institute of Materials Science, University of Connecticut, Storrs, CT, U.S.A.

To cite this Article Ranade, Shrirang V. , Xie, Xiang-Qun and Dibenedetto, Anthony T.(1997) 'Effect of Interphase Structure on the Debonding of Polycarbonate from S-2 Glass Fibers', The Journal of Adhesion, 64: 1, 7 — 30
To link to this Article: DOI: 10.1080/00218469708010530
URL: http://dx.doi.org/10.1080/00218469708010530

J. Adhesion, 1997, Vol. 64, pp. 7–30
Reprints available directly from the publisher
Photocopying permitted by license only

Effect of Interphase Structure on the Debonding of Polycarbonate from S-2 Glass Fibers*

SHRIRANG V. RANADE, XIANG-QUN XIE
and ANTHONY T. DIBENEDETTO**

Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, U. S. A

(Received 30 September 1996; In final form 23 December 1996)

The effect of interphase structure on the debonding of polycarbonate from S-2 glass fibers has been studied. The shear strength, fracture toughness and hydrolyic stability of the interphases were measured in a single fiber composite of a continuous S-2 glass fiber embedded in a polycarbonate matrix. Polycarbonate oligomers were chemically grafted onto the glass fiber surfaces through use of a silicon tetrachloride intermediary and the properties of the resulting interphases were compared with those of two commercial sizings and ozone-cleaned surfaces. Evaluation was accomplished by measuring the stress transmission across the interphase, τ, by carrying the embedded single fiber fragmentation test to saturation and by using computer simulations and a finite element analysis to calculate the strain energy release rate, G, of the observed fiber-matrix debonding accompanying the first fiber fracture. The oligomer-grafted interphase exhibited improved stress transmissibility and toughness, after 24 hours in boiling water. The tenacity of the tightly bound oligomers was confirmed *via* DRIFT, TGA and GC/MS experiments on Soxhlet-extracted fibers.

The grafting reaction was modeled on a high surface area silica and studied using solid state NMR to determine reasons for the greater stability of the oligomer-treated surfaces. Measurements of chemical shifts and spin-lattice relaxation times indicate that the oligomers are chemically attached to the surfaces, providing for a well bonded, water resistant interphase. Parallel experiments on a monomeric Bisphenol A-primed silica surface provided evidence that chemical bonding was primarily responsible for the greater hydrolytic stability.

Keywords: Single fiber composites; hydrolytic stability; solid state NMR; interfacial debonding; S-2 glass fibers; polycarbonate; adhesion

---

*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997.

**Corresponding author.

INTRODUCTION

Fiber-reinforced polymeric matrix composites are used in a wide variety of applications because of the versatility they lend to the design process. By the judicious combination of the components it is possible to generate a unique set of requisite properties that is unattainable by the individual constituents alone. The overall properties of a composite material are dependent upon the nature of the interface, or interphase, formed between the reinforcing fibers and the surrounding matrix. Composites containing 40 to 60% by volume of 10 μm diameter fibers have 10^5 to 10^6 square meters of interfacial surface area per cubic meter of material. The ability to tailor the properties of these interfaces is, therefore, crucial in attaining the desired properties in the composite. Previous studies [1], for example, have indicated the viability of using continuous fiber reinforced composites in dental applications, especially as splints, retainers, prosthodontic frameworks and orthodontic wires. More cost-effective, esthetic and efficient procedures are envisioned. A critical factor in their utility has been the hydrolytic stability of the material when adhesively bonded to the tooth structure. Commercial sizings for glass fibers in composites used for dental applications have proven to be inadequate because of their hydrolytic instability when exposed to oral environments for long periods of time [2]. Clinical tests have shown that premature failure of the dental appliance often occurs within the composite due to the hydrolytic deterioration of the fiber/matrix interface. The present work was initiated with the primary objective of creating a hydrolytically-stable composite system for dental applications. The approach adopted was to graft, chemically, oligomers having the same structural repeat units as the polymeric matrix at available silanol sites on the glass fiber surfaces [3, 4]. In the present case, a continuous S-2 glass-fiber-reinforced polycarbonate composite used for bridges and orthodontic wires was modified by chemically grafting polycarbonate oligomers onto the glass fiber surfaces as shown in Figure 1 [5, 6].

Diffuse Reflectance Infra Red Spectroscopy (DRIFT) was used to provide qualitative evidence of the presence of strongly bonded polycarbonate oligomers on the surface and an embedded single fiber fragmentation test was utilized to measure the shear strength and fracture toughness of the resulting interphases [6]. When compared

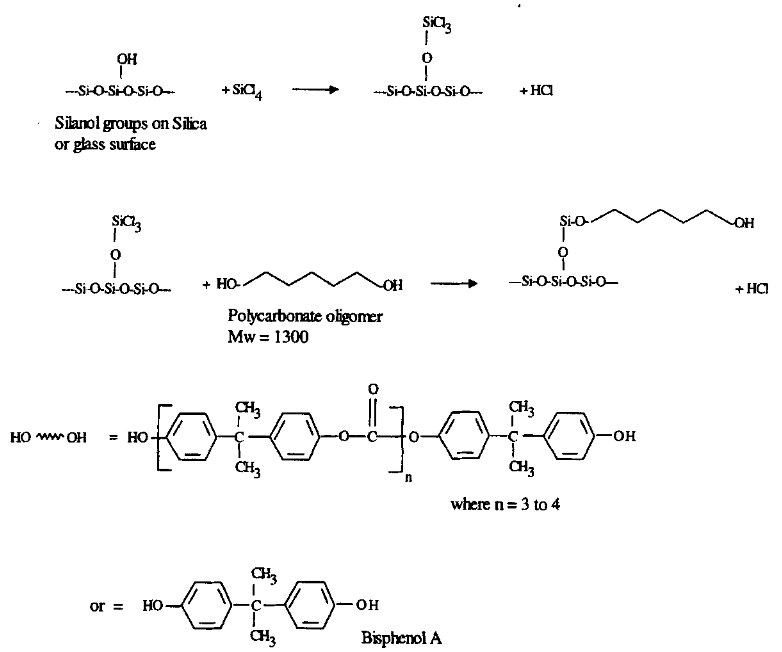


FIGURE 1 Reaction scheme for grafting of polycarbonate oligomers or Bisphenol A at the available silanol sites on the glass fiber or silica surface.

with commercial sizings, the grafted polycarbonatge oligomers provided a far superior hydrolytic stability during exposure to boiling water. Even wet, the interphase retained a substantial fraction of its stress-transmitting character, which is unusual for this class of composite materials. At this point it was not clear whether the oligomers were covalently bonded to the glass surfaces, nor was the mechanism of hydrolytic stabilization well understood.

The present study is an attempt to clarify the nature of the grafting reaction and to characterize the morphology of the oligomeric interphase by utilizing high-resolution solid state NMR. Since the S-2 glass fibers have a relatively low surface area per unit volume, a definitive, high-resolution NMR spectrum is difficult to obtain. However, solid state NMR has been used extensively to characterize the nature of modified silica surfaces [7–11]. Therefore, the fiber-oligomer interface was modeled using a high-surface-area silica. The polycarbonate oligomers were grafted onto a high-surface-area silica and these samples used to obtain spin-lattice relaxation rates of the grafted molecules. The resulting spectra, described in this paper, provided evidence that the interphase consisted of a low-density monolayer of oligomer tethered to the products of the silicon tetrachloride reaction on the glass surface. Apparently, the use of excess $SiCl_4$ scavenges the hydrogen-bonded water and hydroxyl groups on the glass surface forming a residue of $Si—O—SiCl_3$ sites on the surface. The oligomers can then react with the $Si—O—SiCl_3$ sites, thereby shielding the S-glass surface from further interaction with water. However, due to the overlapping of the NMR signals from the relevant carbon atoms in the grafted oligomers, the grafting reaction (*i.e.*, the potential formation of Si—O—C covalent bonds through reaction with the $SiCl_4$ byproducts) could not be confirmed. In order to separate perturbations of the spectrum caused by chemical shifts of grafted carbon atoms, a simpler, structurally-similar molecule, Bisphenol A, was substituted for the polycarbonate oligomer. The "monomeric" Bisphenol A retains the reactive end groups of the oligomer, but does not have the repeat units that are responsible for the overlapping peaks observed in the oligomeric sizing.

In the present work, we summarize the measurements of shear strength and fracture toughness of the interphases in composites of single S-2 glass fibers embedded in a polycarbonate matrix, before and after exposure to boiling water, compare the behavior of the oligomer grafted interphases with those of commercial sizing treatments and ozone-cleaned fibers, report on the results of the solid state NMR studies, and propose a mechanism for the hydrolytic stability of the oligomer-grafted interphases.

EXPERIMENTAL

Lexan® 181 polycarbonate, $M_n = 18{,}600$, was supplied by GE Plastics. Polycarbonate oligomer having a M_n of 959 and a M_w of 1197 was supplied by Enichem America. The S-2 glass fibers (diameter 10 μm) were supplied by Owens-Corning as rovings, from which individual strands were removed and fiber strength measured at three different gage lengths [12]. These values were used to calculate the fiber strength at the critical fragment length *via* a Weibull analysis [19]. The silica, Cab—O—Sil M5, was provided by Cabot (surface area = 200 m^2/g). Oligomer or Bisphenol A grafted fibers were prepared by reaction in solution using $SiCl_4$ (Aldrich Chemicals) as an intermediary. The use of $SiCl_4$ is necessary to prime the surface by removal of any water present and to enable covalent bonding with the silanol moieties on the glass or silica surfaces. The glass and silica surfaces have been shown to have about 4 to 5 OH groups/ nm^2 [13, 14]. The S-2 glass fibers (for grafting, the fibers were first cleaned by UV/Ozone treatment) or silica were dried under vacuum for 24 hours at 250°C and transferred to a three-necked flask under a nitrogen purge, cooled to about 60°C, slurried in chlorobenzene and an aliquot of excess $SiCl_4$ was added. This mixture was allowed to react for a minimum of 4 hours; the excess $SiCl_4$ was then boiled off. A solution of 0.5 percent by weight of polycarbonate oligomer or Bis-phenol A in chlorobenzene was then added and the reaction allowed to proceed at 130°C for 12 hours. The excess solvent was then removed and the physically-adsorbed, unreacted material was extracted using Soxhlet extraction in chlorobenzene at 120°C for 12 hours, followed by drying overnight in a vacuum oven at 130°C. The sized fibers were then stored in a desiccator until used for preparation of embedded single fiber composite specimens. The reaction scheme is represented in Figure 1.

Single fiber composites for the fragmentation test were prepared by sandwiching a single fiber within two polycarbonate dogbones, and then compression molding at 200°C in a heat press with minimal pressure for 10 minutes. Type V polycarbonate dogbones were prepared using procedures specified in ASTM D638. They were cut from sheets that had been previously compression molded from pre-dried polycarbonate and stored in a desiccator. Single strands of commercially-sized fibers were picked randomly from the as-received fiber bundles. Ozone-cleaned fibers were prepared by treating starch-sized S-2 glass fibers in a UVOCS system that produced ozone by using UV radiation of 254 nm to 185 nm wavelengths, for 60 minutes. Fragmentation of the fiber in the single-fiber composite was accomplished by pulling the specimen in tension using a hand-held microtensile tester that utilizes a screw-type mechanism. This unit was mounted onto a high-powered transmission optical microscope and fragment lengths were measured. Samples were tested for hydrolytic stability of the interface by treating in boiling water for 24 hours prior to fragmentation. Samples were also annealed at 200°C for a period of 1 hour prior to fragmentation to determine the effect of annealing on the shear strength and fracture toughness of the interphases.

The shear strength or, more precisely, the shear stress transmissibility of the interphase was evaluated by carrying the fragmentation process to saturation. While it is recognized that there are limitations in obtaining absolute stress transmission properties, the test, nevertheless, serves as a useful means of comparison of fiber-matrix adhesion when used to compare surface treatments or processing conditions in the same fiber-matrix combination [4, 15–17]. In this work, the shear strength of the interphase, τ, was calculated from the average fragment length, $\langle l \rangle$, using the Kelly-Tyson model [18] and a Weibull analysis [19, 20] of the fiber strength as described below.

The strength of the fiber at the critical length was determined using a 2-parameter Weibull law given as:

$$P_f(\sigma) = 1 - \exp\left[-\frac{1}{l_0}\left(\frac{\sigma}{A_f}\right)^{\beta_f}\right]$$

$$\langle\sigma\rangle = A_f\,\Gamma\left(1+\frac{1}{\beta_f}\right)\Bigg/\left(\frac{1}{l_0}\right)^{1/\beta_f}$$

where $\langle\sigma\rangle$ is the fiber strength at length l, l_0 is a reference length equal to 25.4 mm, A_f is a scale parameter and β_f is a shape parameter that characterizes the Weibull strength distribution. The values of A_f and β_f for each population of treated fibers are shown in Table I. A higher value of β_f generally indicates a lower scatter in the strength data, while the A_f is directly related to the mathematical average of the strength. The same values of the statistical parameters were used for the fibers in the as-received and annealed single-fiber composites. This is a reasonable assumption based on the measured average *in-situ* strain at first break for these two populations (Tab. II). The fibers exposed to water, however, probably have been degraded to some extent. The *in-situ* strain to break appears to be lower after exposure to boiling water. In these cases, the average values of A_f have been adjusted appropriately to account for the probable decrease in strength.

TABLE I Embedded single fiber fragmentation test

Fiber Treatment	*Condition*	*Statistical parameters*	*n*	l_c*, mm*	τ*, MPa*
PEEK compatible	Dry	$A_f = 3010$	106	0.585	31.7
	Annealed	$\beta_f = 5.32$	56	0.453	42.9
	Boiled	Insufficient stress transfer to attain saturation in fragmentation test			
Epoxy compatible	Dry	$A_f = 2645$	133	0.484	39.4
	Annealed	$\beta_f = 4.52$	120	0.432	45.3
	Boiled	Insufficient stress transfer to attain saturation in fragmentation test			
UV/Ozone cleaned	Dry	$A_f = 1435$	118	0.528	22.0
	Annealed	$\beta_f = 3.86$	50	0.460	26.2
	Boiled	Insufficient stress transfer to attain saturation in fragmentation test			
PC Oligomer grafted	Dry	$A_f = 1435$	77	0.432	28.4
	Annealed	$\beta_f = 3.86$	69	0.362	35.4
	Boiled	$A_f = 1084; \beta_f = 5.11$	95	0.451	20.2
Bisphenol A grafted	Dry	$A_f = 1435$	71	0.462	26.1
	Annealed	$\beta_f = 3.86$	42	0.352	36.7
	Boiled	$A_f = 857; \beta_f = 6.46$	105	0.357	21.7

n = number of fragment lengths measured in the single fiber test.
l_c = critical fragment length in mm.

TABLE II Observed strains and debond lengths at first fiber break

Sizing	*Strain at* 1^{ST} *Break (%)*			*Debond Length (μM)*		
	Dry	*Boiled*	*Annealed*	*Dry*	*Boiled*	*Annealed*
PEEK	5.39 (0.2)	*	5.09 (0.9)	19.1 (3.5)	*	14.87 (3.5)
Epoxy	6.47 (0.5)	*	5.75 (1.26)	21.8 (1.9)	*	18.45 (2.8)
Bare	5.25 (0.5)	4.50 (1.3)	5.50 (0.6)	15.0 (1.5)	35.1 (6.9)	10.15 (0.9)
PC oligomer	5.68 (0.7)	4.29 (0.8)	5.83 (1.9)	13.5 (0.9)	8.7 (1.3)	8.95 (1.9)
Bisphenol A	6.08 (1.4)	3.63 (0.1)	6.16 (1.6)	10.9 (1.5)	2.7 (0.4)	9.9(4.6)

(values in parentheses indicate Standard deviation).
*no fiber breaks were observed in the epoxy and PEEK sized SFC's for boiling water treated samples.

The interfacial strength is then obtained from:

$$\tau = \frac{\sigma_c d}{2 l_c} = \frac{3\,\sigma_c d}{8\langle l \rangle} \quad \text{where,}$$

τ = stress transmission, σ_c = strength of fiber at critical length, l_c = critical length or fiber, d = diameter of fiber and $\langle l \rangle$ = average fragment length.

Pegoretti and DiBenedetto [21, 22] have measured the strain energy release rate, or fracture toughness, of the crack, G_C, associated with debonding during the first break of fiber in the single fiber composite. Their method of combining experimental observations and finite-element-based simulation of the process is adopted here to calculate G_C [22]. A MARC finite element analysis is used to calculate the change in total elastic strain energy. U, accompanying a simulated debonding at the first fiber break. The strain energy release rate, G, is calculated from the slope of the plot of U versus debond length, x:

$$G = -\frac{\partial U}{\partial A} = \frac{\partial U}{\partial x}\frac{\partial x}{\partial A}$$

where A is the interfacial debonded area given by, $A = 2\pi r_f x$, and r_f is the fiber radius. The fracture toughness, G_C, is then determined by the value of G at the observed value of debond length at the first fiber break, at constant strain. A plot of G *versus* debond length for the polycarbonate/S-glass system at 1.0% strain is reproduced in Figure 2 [22].

Typical fracture patterns observed in single-fiber composite samples are shown in Figure 3. They were obtained using polarized light microscopy. SEM analysis of composite samples prepared by compression molding and after boiling water exposure was carried out on an Amray 1200B SEM. The micrographs are shown in Figure 4.

Diffuse Reflectance FTIR (DRIFT) analysis was carried out on a Nicolet 60SX spectrometer with a Harrick DRIFT attachment to confirm the presence of polycarbonate oligomers or Bisphenol A still grafted onto the glass surface after Soxhlet extraction with chlorobenzene. The spectra were collected at room temperature and at least 512 scans were averaged at a resolution of 4 cm^{-1}.

Gas Chromatography/Mass Spectroscopy (GC/MS) was carried out on a Hewlett Packard GC 5890 series II and MS 5971A coupled to a "Pyrojector" pyrolysis unit made by Scientific Glass Engineering. Treated fibers were pyrolyzed at 650°C and the degradation products were passed into the mass spectrometer for analysis of the molecular fragments.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 on the modified silica samples to determine the percent

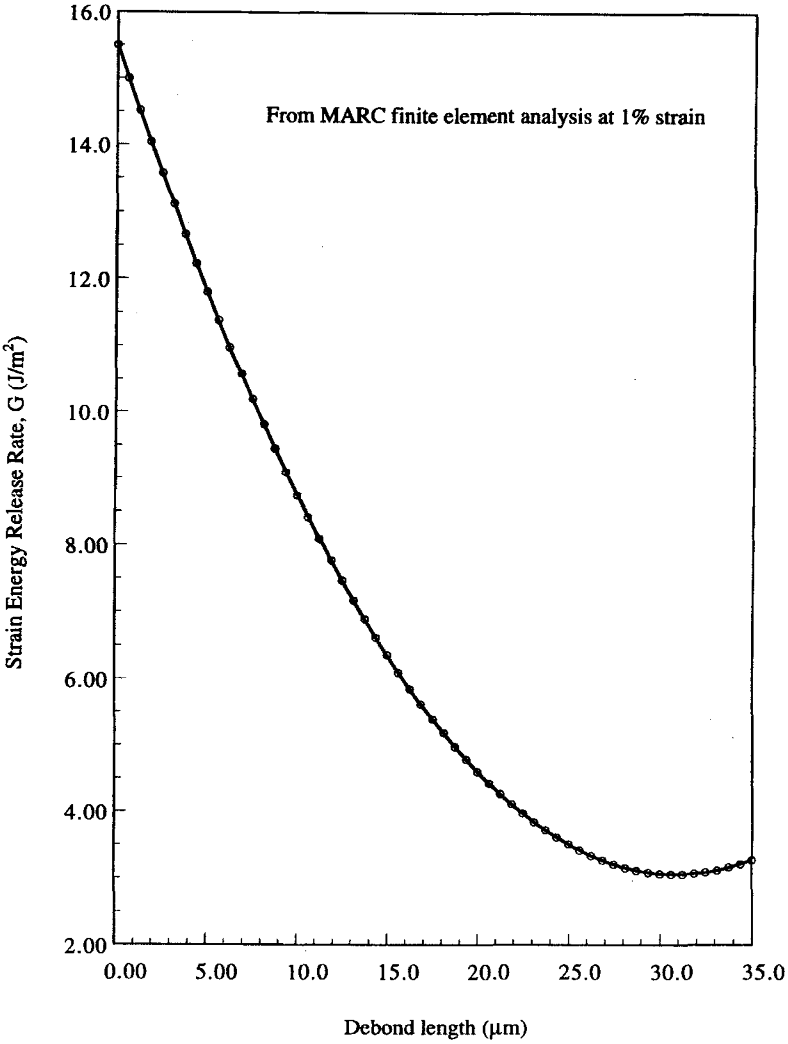


FIGURE 2 Plot of strain energy against debond length, from MARC finite element analysis.

weight loss of grafted material upon heating to 700°C. Scans were done under a nitrogen gas purge from 30 to 700°C at the rate of 20°C per minute.

High-resolution solid state ^{13}C CP/MAS NMR experiments were used to investigate the grafting reactions and the mobility of the organic

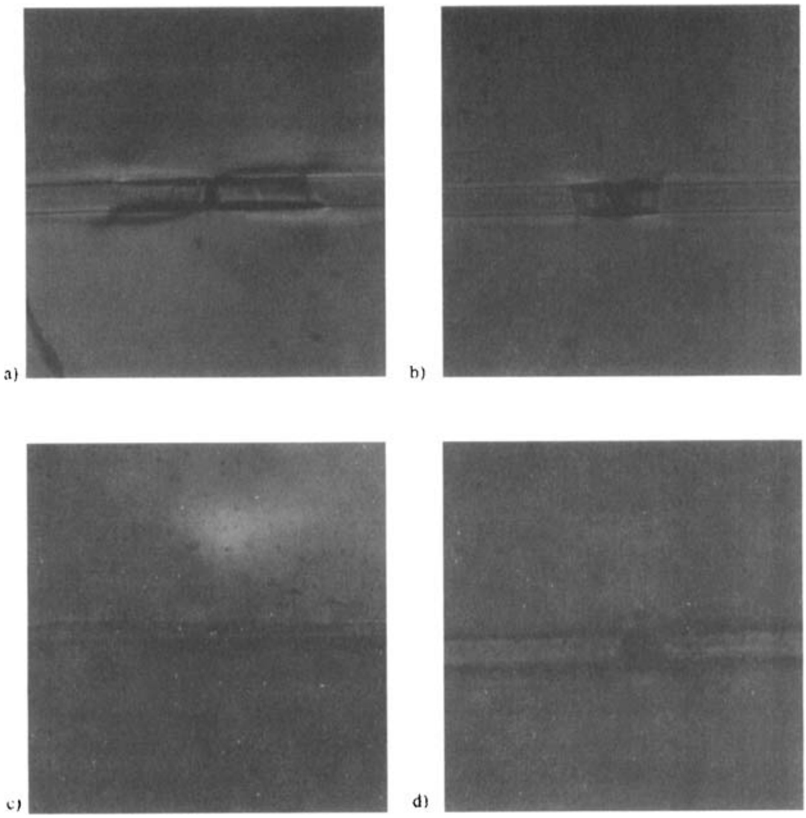


FIGURE 3 Optical micrographs showing typical fracture patterns in single fiber composites. a) PEEK-compatible commercial sizing, dry. b) Polycarbonate oligomer grafted, dry. c) PEEK-compatible commercial sizing, boiled. d) Polycarbonate oligomer grafted, boiled. (See Color Plate I).

molecules at the silica interfaces in the oligomer/silica and Bisphenol A/silica composites. Spin lattice relaxation times in the rotating frame were measured to characterize the dynamics of the grafted and neat molecules. Motions in the 10–100 kHz range can be evaluated, as elaborated in References [7–11]. The spin-lattice relaxation time describes the rate at which the excited nuclear spin system returns to equilibrium

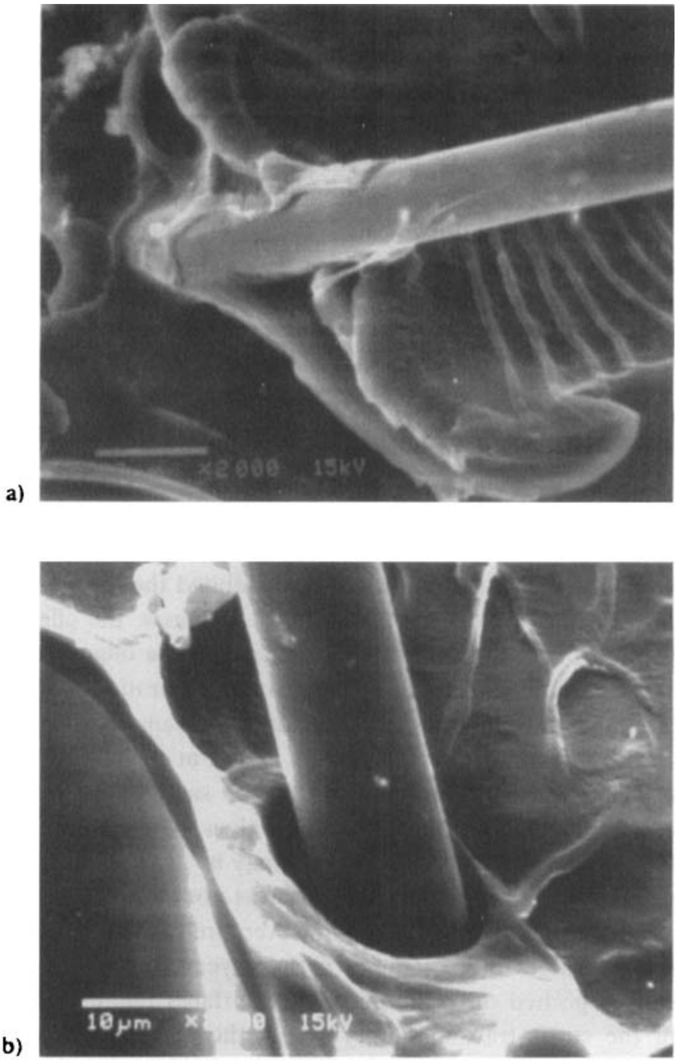


FIGURE 4 SEM micrographs of cold-fractured surfaces of composites boiled in water. a) Polycarbonate oligomer grafted. b) Epoxy-compatible commercial sizing.

with the lattice. Rotating frame proton spin-lattice relaxation time, $T_{1\rho H}$, experiments were used to probe changes in interfacial dynamics as a result of potential grafting. The Bisphenol A was used as a model compound to examine the formation of Si—O—C bonds by grafting.

Spectra were obtained on a Chemagnetics CMX300 NMR spectrometer at 75 MHz using a commercial 7.5 mm MAS probe. Samples (approx. 300 mg) were packed in Zirconia pencil rotors and spectra obtained at a magic angle spinning speed of 5 kHz. Chemical shifts are given with respect to TMS using an external sample of solid glycine (176.03 ppm) as the secondary reference. Spin-lattice relaxation times for protons in the rotating frame, $T_{1\rho H}$, were measured using the Chemagnetics standard pulse sequence. $T_{1\rho H}$ values were calculated by the linear curve fitting of the plot of peak intensity *versus* the proton spin-lock time [23].

RESULTS AND DISCUSSION

Calculated values of the stress transmissibility are shown in Table I. The commercial treatments provided the highest values of τ in the dry state, while the ozone-treated interfaces exhibited the lowest. Annealing improved the stress transmissibility in all cases, the effect being more prominent in samples with the polycarbonate oligomer grafted fibers. This could be the result of better interpenetration and contact of the chains along the interface. The annealed samples also showed the presence of small transverse matrix cracks at the site of the fiber breaks. This effect was more evident in the samples prepared with oligomer-grafted fibers. The calculated values of G_c in the case of annealed samples with transverse cracks may be in error as the change in interfacial debond area in the matrix was not accounted for in the finite element analysis. The trends, however, are consistent with those obtained for values of τ. Samples with polycarbonate oligomers or Bisphenol A grafted onto the glass fiber surfaces retained 70% and 84% of the stress transmissibility across the respective interphases after exposure to boiling water for 24 hours. In the other three cases, however, the wet interphases could not support sufficient shear stress to generate enough fiber fragments to calculate a meaningful value of τ. The PEEK-compatible sizing could not even support enough stress to cause a single break.

The maximum attainable values for τ in these composites is limited by the yield strength of either the polycarbonate matrix or the interphase coating on the fibers. The fact that the grafted interphases, which consist of polycarbonate in contact with a grafted monomolecular layer, support load transfer after boiling, while the other interphases do not, indicates that the strength of the material in the interphase is the limiting factor. While the polycarbonate matrix is hygroscopic and susceptible to hydrolysis, its possible degradation does not seem to be the controlling factor in these cases. Our experiments were conducted in a neutral pH environment and may not be applicable under exposure to boiling water in a non-neutral pH environment.

Typical fracture patterns obtained in a single fiber composite during the fragmentation test are shown in Figure 3. The site of fiber break and the debonded regions are clearly seen. The various debond lengths obtained at the first fiber break are reported in Table II. The oligomer and Bisphenol A grafted fibers have much smaller debonded areas compared with those of the commercially-sized samples, as can be seen in Figures 3a and 3b. Damage to the fibers and interphase is apparent in the samples exposed to the boiling water, and this is clearly seen in Figures 3c and 3d. The interfacial region around the fiber break in bulk composites exposed to boiling water is shown in Figure 4. The matrix and fiber are separated in the commercially-sized fiber, while there appears to be good fiber/matrix adhesion in the composites with grafted fibers.

A strain energy release rate for debonding of the matrix from the fiber is calculated and presented in Table III. Figure 2 is used to calculate values of G, from the debond length, where $G(\varepsilon_b)$ is calculated as: $G(\varepsilon_b) = G(0.01)(\varepsilon_b/0.01)^2$.

TABLE III Strain energy release rates from first fiber break in single fiber composite

Fiber Treatment	*$G_c (J/m^2)$ Dry*	*$G_c (J/m^2)$ Annealed*	*$G_c (J/m^2)$ Boiled*
PEEK-compatible sizing	155 ± 12	168 ± 41	#
Epoxy-compatible sizing	184 ± 13	185 ± 37	*
UV/O_3 cleaned	179 ± 19	263 ± 27	41 ± 10
PC Oligomer grafted	225 ± 45	313 ± 56	175 ± 35
Bisphenol A grafted	303 ± 44	330 ± 59	177 ± 26

Stress transfer insufficient to give even one fiber break.

*6 out of 10 samples did not transfer enough stress to give even one fiber break, of the 4 samples that broke, gave $G = 123$ J/m^2.

The measurements of G show that the oligomer and Bisphenol A grafting resulted in tougher and more water-resistant interphases, while the commercial treatments and UV/ozone-cleaned surfaces produced hydrolytically-unstable interphases under boiling water attack. The PEEK-compatible commercial sizing was displaced by water and could not transfer enough stress while wet to give even a single fiber break. The epoxy-compatible sizing managed to hold up slightly better, in that a few samples showed enough stress transfer to give fiber breaks but it is clear that water also weakened this interphase. The UV/ozone-cleaned surface retained less than 23% of its original dry-state toughness, compared with 78% and 58% of those of the grafted oligomer and Bisphenol A interphases, respectively. The ability to retain interphase shear strength and toughness while still water-saturated after exposure to boiling water is highly unusual for these materials.

Diffuse reflectance FTIR was used to confirm the tenacity of the oligomeric and Bisphenol A interphases after Soxhlet extraction for 12 hours with chlorobenzene. The presence of a silanol peak at $3745\,\mathrm{cm}^{-1}$ in the DRIFT spectrum of the oligomer-grafted silica indicates only partial coverage of the surface by grafted oligomers, while nearly complete disappearance of this peak in the case of the Bisphenol A-grafted surface indicates nearly complete replacement of the silanols by reacted Bisphenol A molecules (Fig. 5). These results are in agreement with the TGA results presented below. Appearance of peaks associated with aromatic groups in polycarbonate oligomer and Bisphenol A at 1500 and 770 to $890\,\mathrm{cm}^{-1}$, and of aliphatic groups at $2968\,\mathrm{cm}^{-1}$, indicate the strong attachment of these molecules to the surface, even after extraction with solvent. The reaction of $SiCl_4$ with glass surface was carried out with a large excess of $SiCl_4$. Thus, it appears reasonable to assume that it reacted with water on the surface to form $Si(OH)_4$ and HCl, and that all of the silanols on the surface were converted to $Si—O—SiCl_3$ at this stage of the reaction sequence. This could not be followed by DRIFT as the chlorine would be immediately quenched by atmospheric moisture and converted to HCl and silanols. In a separate experiment (with the same reaction conditions) both oligomer and Bisphenol A were found to be unreactive in the absence of priming with the $SiCl_4$. This suggests that under the reaction conditions employed, the organic hydroxyls of the graft molecules are capable of condensing only with the $SiCl_3$ moieties created,

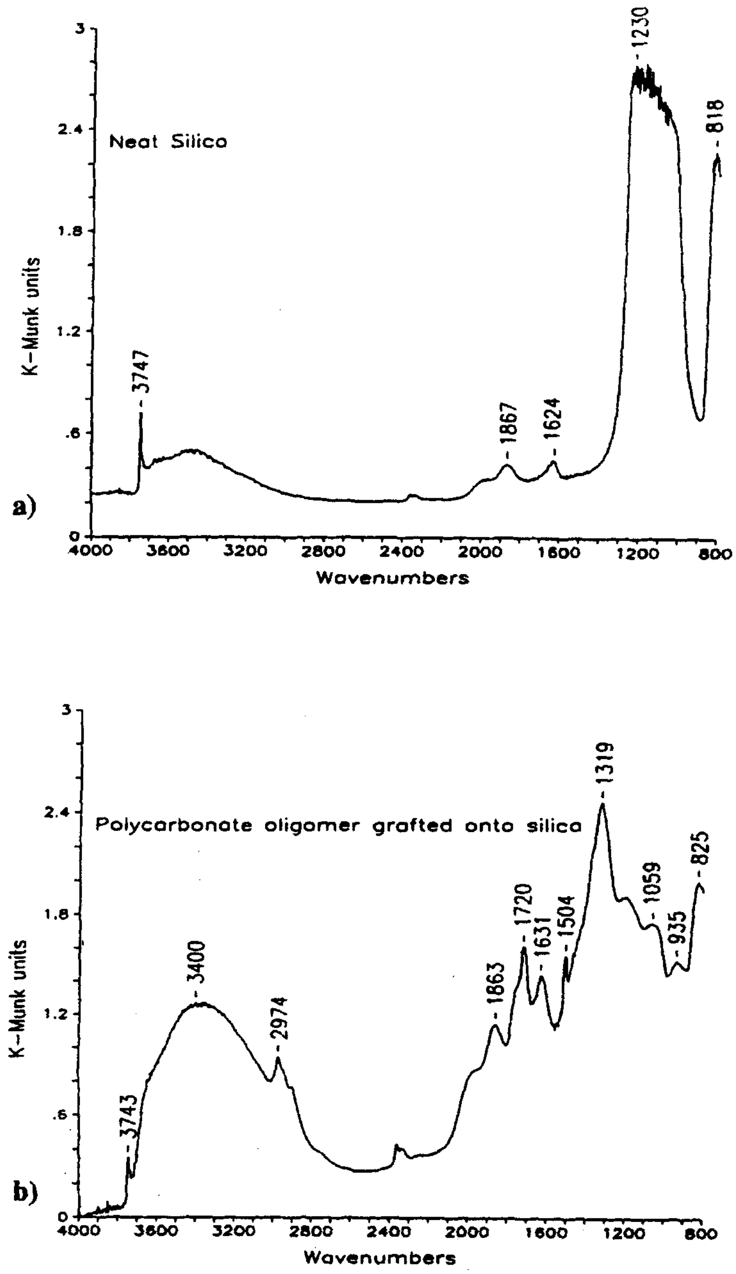


FIGURE 5 Diffuse Reflectance Infra Red Spectra of neat and grafted silica.

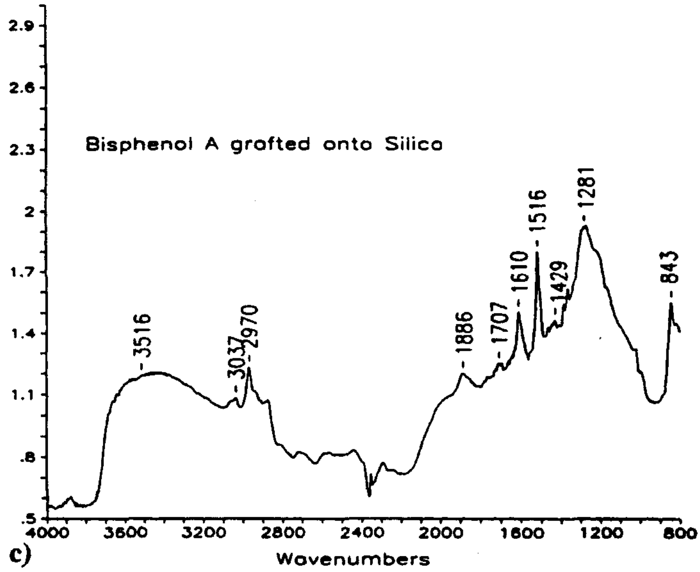


FIGURE 5 (Continued).

but not directly with Si—OH present on the silica surface. In Figure 5b the oligomer-grafted surface shows the presence of silanols while in Figure 5c the Bisphenol A surface shows the absence of silanols. The oligomer seemed capable of condensing with only a fraction of the $SiCl_3$ moieties created, either because of lower reactivity or geometric constraints due to the reacted oligomer molecules shielding the neighboring $SiCl_3$ moieties on the surface. Exposure to atmospheric moisture during the DRIFT experiments, however, would convert unreacted moieties back to silanols. The specific morphology of this interphase layer requires further study. Further evidence for grafting is obtained using GC/MS, which was carried out by pyrolyzing the samples at 650°C. Figures 6a and 6b are the spectra obtained with UV/ozone-cleaned fiber surfaces, before and after grafting, along with those obtained for neat polycarbonate oligomer and Bisphenol A samples. The reactant products break down into phenolic and bisphenolic compounds at 650°C, indicating that the grafted material is tightly bound and has probably reacted chemically or is strongly physisorbed onto the glass surface.

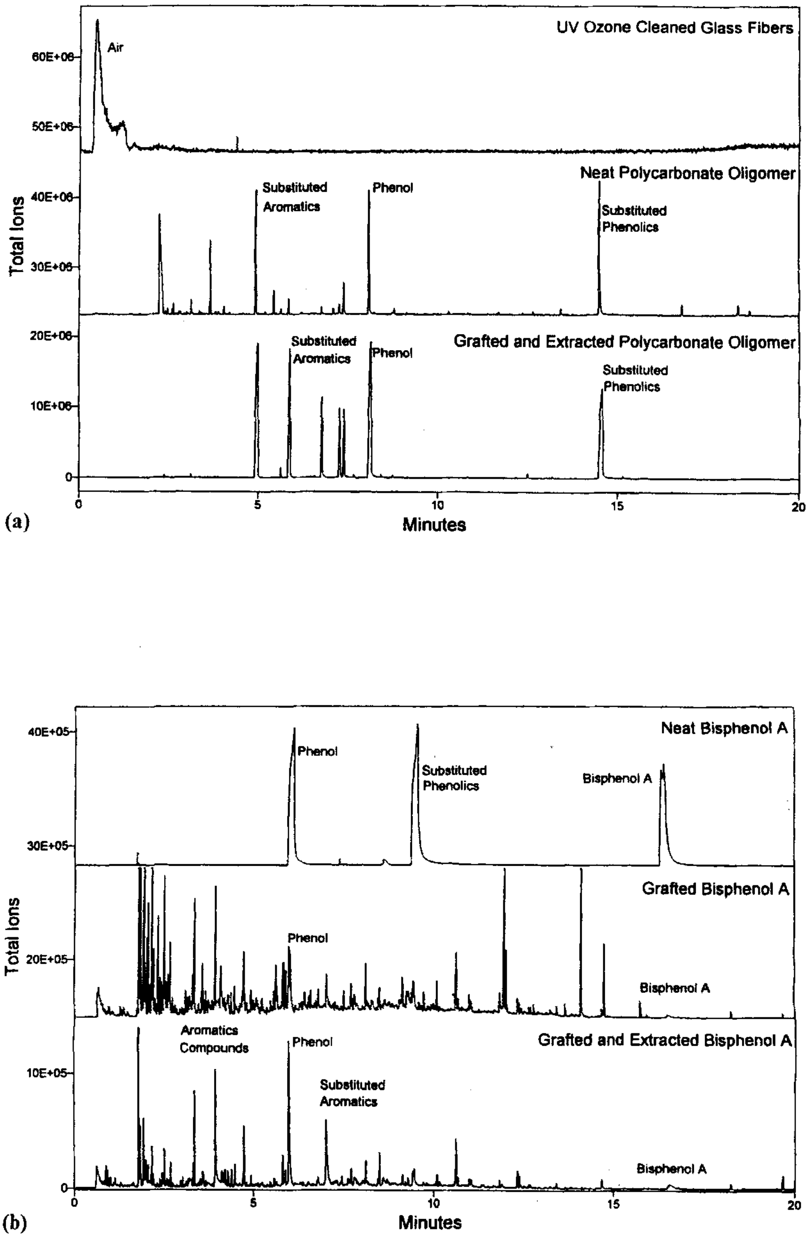
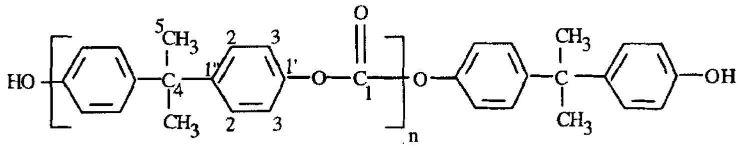


FIGURE 6 Gas chromatograms of a) Neat polycarbonate oligomer, UV/ozone-cleaned and grafted S-2 glass fibers and b) Neat, grafted and extracted Bisphenol A.

High-resolution solid state ^{13}C CP/MAS NMR experiments were used to study further the grafting reaction and to measure the mobility of the grafted molecules at the interfaces. Indirect evidence of the formation of the Si—O—C_4 bond can be obtained from the measurement of the $T_{1\rho H}$ values for the grafted oligomer/silica and Bisphenol A/silica composites (Tab. VI). $T_{1\rho H}$ was measured *via* ^{13}C detection in order to retain the spectral resolution offered by ^{13}C CP/MAS NMR. The increased proton spin-lock $T_{1\rho H}$ indicates the restricted mobility of the grafted oligomer molecule due to the reactive end group of the polycarbonate being tethered to the silica surface by either covalent or secondary bonds. The grafted oligomer and Bisphenol A exhibit at least two domains of behavior indicating a non-homogeneous system having a distribution of relaxation times as shown in Figures 7a and 7b. At the

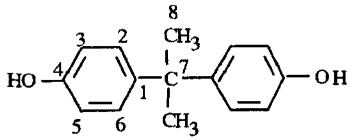
TABLE IV $T_{1\rho H}$ values of the neat and grafted polycarbonate oligomer and bisphenol A at 20°C

Polycarbonate Oligomer (n = 2 to 3, M_w = 1200)



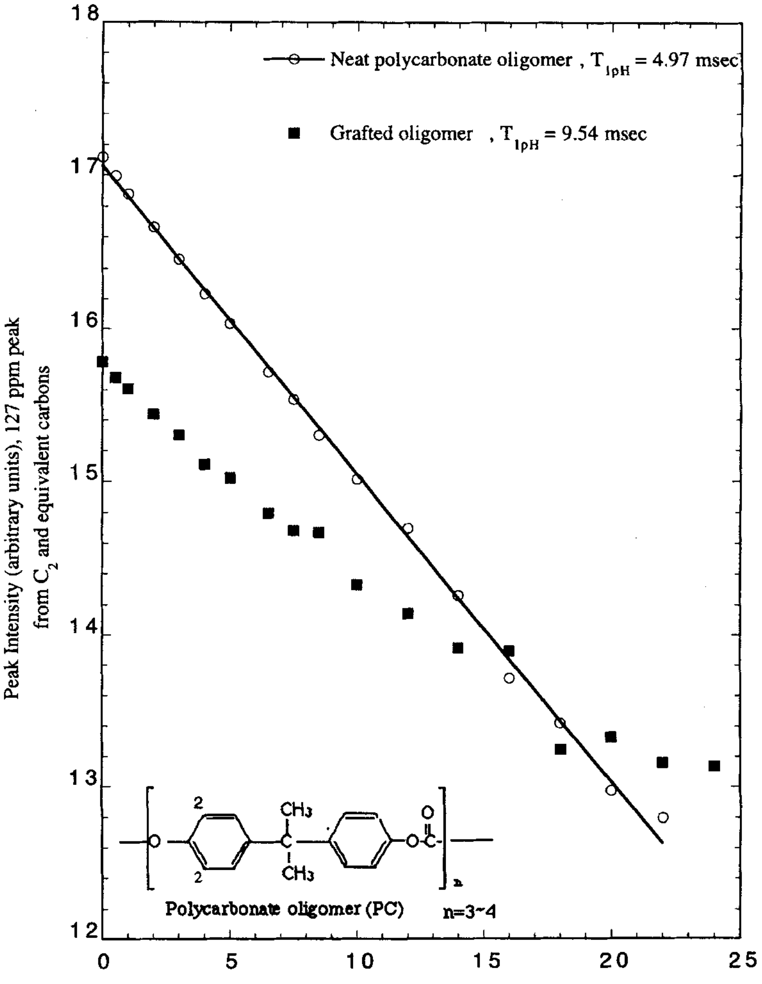
where n = 2 to 3

Bisphenol A



PC Oligomer $T_{1\rho H}$(msec)			*Bisphenol A $T_{1\rho H}$(msec)*		
Site (ppm)	*Neat*	*Grafted*	*Site (ppm)*	*Neat*	*Grafted*
1 (148)	5.07	9.15	**4** (152)	20.48	13.53
			1 (144)	19.95	14.91
2 (127)	4.97	9.54	**2,6** (129, 125)	21.23	7.12
3 (120)	5.06	9.09	**3,5** (116, 114)	20.55	8.68
4 (42)	5.03	9.07	**7** (42)	19.54	10.89
5 (30)	4.65	9.87	**8** (28, 32)	20.71	11.09

short spin-lock times, the slope is steep, indicating a short relaxation time (more mobility) probably associated with parts of the molecule that are further away from the grafted end. At longer spin-lock times, the slope is gentler, indicating a longer relaxation time (less mobility), suggesting that this part of the curve is dominated by the parts of the



(a)

FIGURE 7 Plot of peak intensity against spin-lock time from ^{13}C NMR spectrum for: a) Neat and grafted polycarbonate oligomer. b) Neat and grafted Bisphenol A.

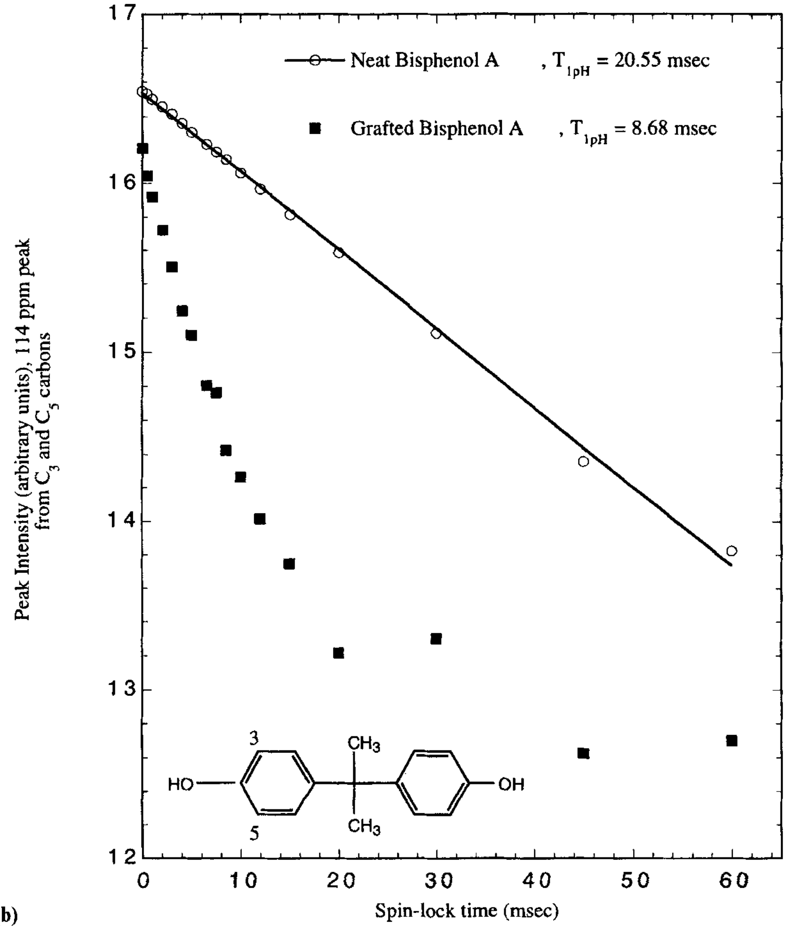


FIGURE 7 (Continued).

molecule that are tethered to the silica surface. The relaxation times of the tethered Bisphenol A molecules are somewhat higher than those of the oligomer-grafted material, which is expected since they are "monomeric" and more densely packed on the surface. The relaxation times of the tethered Bisphenol A molecules are much shorter than those of the neat crystalline solid, however, indicating a lower density packing on the silica surface relative to that in the crystalline state.

Signal overlapping of the phenolic and carbonyl carbons of the polycarbonate oligomer mask the chemical shift changes that may occur because of formation of the Si—O—C_1 linkages, as described by the proposed reaction scheme shown in Figure 1. The Bisphenol A, however, is a useful model compound to look for the possible formation of Si—O—C linkages on the silica surface. Such evidence is clearly obtained in the ^{13}C CP/MAS NMR spectrum of the grafted Bisphenol A in comparison with that of the neat Bisphenol A. As shown in Figure 8, an upfield shift of the C_4 resonance (149.37 ppm) was observed for the grafted Bisphenol A in comparison with that of the neat compound (152.25 ppm). This upfield shift is attributed to the formation of the Si—O—C_4 linkage between silica and Bisphenol A and the electron shielding effect of the Si atom. As a result, the

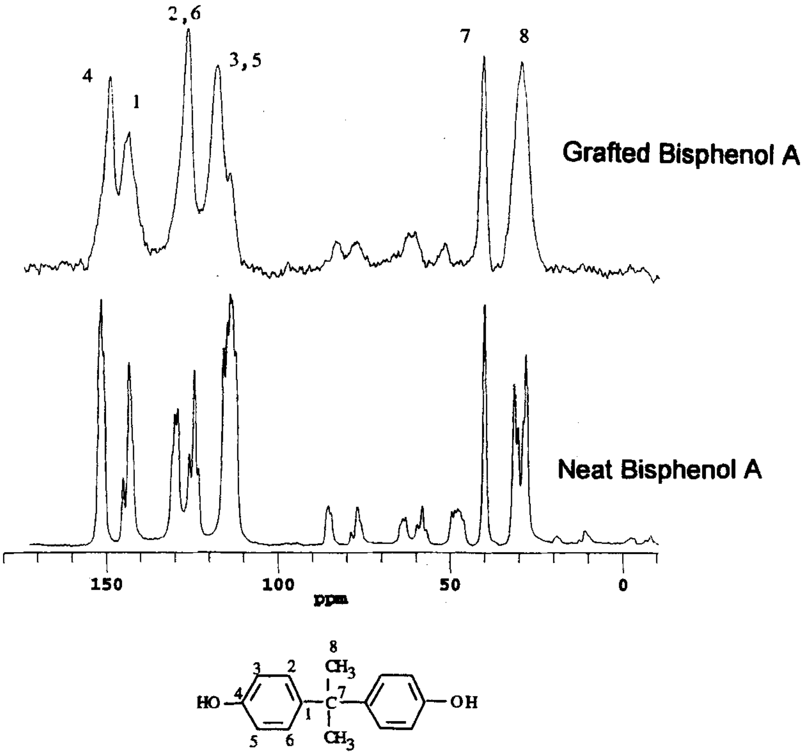


FIGURE 8 . ^{13}C CP/MAS Solid-State NMR spectra of neat and grafted Bisphenol A.

adjacent phenolic carbons C_3 and C_5 were also shifted downfield. The downfield shift of the C_3 and C_5 carbons can be explained by the electron-donating effect of the Si atom now bonded to the O atom instead of the earlier H, thus causing a perturbation in the conjugation of the aromatic π-electron system. The C_2 and C_6 carbons, which appeared as a multiplet at 125.03 ppm and 130.70 ppm in the neat Bisphenol A, now appear as a single peak at 126.65 ppm in the NMR spectrum of the grafted Bisphenol A. In the neat compound, it is postulated that the C_2 and C_6 carbons, though chemically equivalent, appear as two separate peaks due to the differences in their chemical environment caused by crystal packing and the preferred bond conformation about the C_7 carbon, while the grafted material shows one peak as the crystal packing is broken up due to grafting on the randomly-distributed silanol sites on the silica surface. Such NMR-observed results of a Si—O—C bond formation and a mobile oligomer are congruent with the observed hydrolytic stability and good stress transmission properties of the grafted materials as measured by other means discussed above [24].

The weight loss obtained during thermogravimetric analysis (TGA) of treated silica surfaces enables one to approximate the amount of grafted material on the silica surface. If one assumes that the silanol group concentration on the silica surface is 5 OH groups/nm^2 [13, 14] and that each of these takes part in the grafting reaction, then it is possible to arrive at a maximum theoretical weight for monolayer coverage:

$$\frac{200\,\mathrm{m}^2}{\mathrm{g}} \times \frac{5\,\mathrm{PC\ molecules}}{1.0 \times 10^{-18}\,\mathrm{m}^2} \times \frac{1197}{6.023 \times 10^{23}}\,\mathrm{g} = 1.99\,\mathrm{g\ of\ oligomer/g\ silica.}$$

TGA analysis gives a weight loss of 0.075 g of oligomer/g silica, suggesting either that the oligomers have a low level of reactivity on the surface or that there is a shielding of reaction sites in the vicinity of an already-grafted (tethered) molecule. To estimate the range of exclusion that a tethered molecule might create, we postulate that the reaction sites (*i.e.* Si—O—$SiCl_3$ moieties) in an area equivalent to a circle described by the radius of gyration of the tethered polycarbonate oligomer molecule are shielded from reaction with other oligomers. To obtain an area of exclusion large enough to shield approximately 90.6%

of the reactive groups {*i.e.*, 100(1.99–0.075)/1.99}, the effective radius of gyration of the tethered molecule would have to be approximately 1.12 nm. The calculated radius of gyration of a freely-orienting polycarbonate oligomer of $M_n = 959$ is approximately 0.93 nm [26]. This suggests that there is some exclusion effect prevalent in the grafting mechanism for the oligomer.

Similar TGA experiments and calculations for Bisphenol A-grafted silica samples gave a maximum possible weight coverage of 0.3 g Bisphenol A/g of silica, while an experimental weight loss of 0.29 g Bisphenol A/g of silica was observed, suggesting that the Bisphenol A reacted with all available reaction sites, thus forming a monolayer of extended monomeric units in a brush-like morphology. Both hypotheses concerning the molecular conformation in the interphases are consistent with the evidence that a loosely-packed monolayer of covalently-bound molecules has formed hydrolytically-stable chemical bonds across the interface.

CONCLUSIONS

The grafting of polycarbonate oligomers, using a silicon tetrachloride intermediary at the interface between glass fibers and a polycarbonate matrix, results in interphases that exhibit excellent stress transmissibility and hydrolytic stability when compared with those formed by commercial epoxy-and PEEK-compatible sizing agents and ozone-cleaned glass fibers. Spectroscopic and solid state NMR measurements on silica surfaces grafted with polycarbonate oligomer and Bisphenol A monomer, combined with the results of thermogravimetric analysis, indicated that the grafting process scavenged hydrogen-bonded water from the glass surfaces, and formed a chlorinated silicon oxide layer on the surface capable of reacting with the oligomers and the Bisphenol A. It is hypothesized that the grafting resulted in the formation of low-density, randomly-distributed and loosely-packed monolayers of covalently-bound molecules that form hydrolytically-stable chemical bonds across the interface. The grafted monolayer cannot be removed by extraction with a good solvent and its presence is confirmed *via* DRIFT and GC/MS. The stress transmissibility, τ, and the debond fracture energy, G_C, are useful criteria for comparing the strength and interfacial toughness of the interphases in single-fiber composites. The latter property, measured at the first fiber break, is especially useful when saturation cannot be achieved in the fragmentation test. It is interesting to note that the commercial sizings gave higher τ values but lower G values than the grafted fibers in the dry state, suggesting that grafting led to somewhat lower stress transmissibility but a higher toughness of the interphase.

References

[1] Goldberg, A. J. and Burstone, C. J., *Dent Mat* **8**, 197–202 (1992).
[2] Altieri, J. V., *et. al.*, *J. Prosth. Dent* **71**(1), 16–22 (1994).
[3] DiBenedetto, A. T., *et al.*, *Composite Structures* **27**, 73–82 (1994).
[4] Jancar, J. and DiBenedetto, A. T., *J Mat Sci : Mater. in Medicine* **4**, 555–561 (1993).
[5] Ranade, S. V., DiBenedetto, A. T. and Goldberg, A. J., *ACS Polymer Preprints* **37**, 851–852 (1996).
[6] Ranade, S. V. and DiBenedetto, A. T., Tailoring the interface in glass fiber polycarbonate composites", *European Adhesion Conference : EURADH 96* **2**, pp. 717–722 (1996).
[7] Slotfeldt-Ellingsen, D. and Resing, H. A., *J. Phys. Chem.* **84**, 2204 (1980).
[8] Resing, H. A., Slotfeldt-Ellingsen, D., Garroway, A. N., Weber, D. C., Pinnavaia, T. J. and Unger, K., in *Magnetic Resonance in Colloid and Interface Science*, Fraissard, J. P. and Resing, H. A., Eds. (Reidel, Dortrecht, 1980), p. 239.
[9] Maciel, G. E., Sindorf, D. W. and Bartuska, V. J., *J. Chromatogr.* **205**, 438 (1981).
[10] Leyden, D. E., Kendall, D. S. and Waddell, T. G., *Anal. Chim. Acta* **126**, 207 (1981).
[11] Sindorf, D. W. and Maciel, G. E., *J. Am. Chem. Soc.* **105**, 1848 (1983).
[12] Gurvich, M. R., DiBenedetto, A. T. and Ranade, S. V., A New Statistical Distribution For Characterizing The Random Strength of Brittle Materials", *J. Mater. Sci.*, accepted for publication (1996).
[13] Nishioka, G. M. and Schramke, J. M., in *Molecular Characterization of Composite Interfaces*, Ishida, H. and Kumar, G., Eds. (Plenum, New York, 1985), pp. 387–400.
[14] Ellestad, O. and Blindhem, U., *J. Molecular Catalysis* **33**, 275–287 (1985).
[15] Pitkethly, M. J., *et al.*, *Comp. Sci. & Tech.* **48**, 205–214 (1993).
[16] Pisanova, E. V., Zhandarov, S. F. and Dovgyalo, V. A., *Polym. Comp.* **15**(2), 147–155 (1994).
[17] DiBenedetto, A. T., *Comp. Sci. & Tech.* **42**, 103–123 (1991).
[18] Kelly, A. and Tyson, W. R., *J. Mech. Phys. Solids* **13**, 329 (1965).
[19] Van der Zwaag, S., *J. Testing and Eval.* **17**(5), 292–298 (1989).
[20] Gurvich, M. R. and DiBenedetto, A. T., "A Strategy for Measurement and Calculation of Interfacial Strength Using The Single Fiber Fragmentation Test", *J. Mater. Sci.*, accepted for publication (1996).
[21] DiBenedetto, A. T. and Lex, P. J., *Polym. Eng. & Sci.* **29**(8), 543 (1989).
[22] Pegoretti, A., DiBenedetto, A. T. and Accorsi, M. L., *J. Mater. Sci.*, accepted (1996).
[23] Schaefer, J., Stejskal, E. O. and Buchdahl, R., *Macromol.* **10**, 384 (1977).
[24] Schaefer, J., Sefcik, M. D., Stejskal, E. O. and McKay, R. A., *Macromol.* **14**, 275 (1981).
[25] Perez, T., *M. S. Thesis*, University of Connecticut pp. 26–28, (1995).
[26] Brandrup, J. and Immergut, E., Eds., *Polymer Handbook*, Third edition (Wiley, NY, 1982), pp. VII-42.