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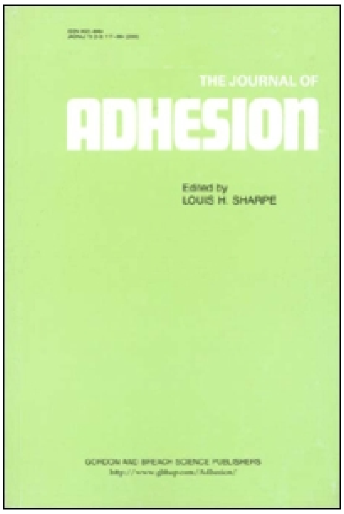

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A Modified Silane Treatment for Superior Hydrolytic Stability of Glass Reinforced Composites

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A silicon tetrachloride-modified silane treatment of E-glass particles and fibers improved the hydrolytic stability of the glass reinforced composites by creating a water-resistant silane copolymer interphase of approximately 30 Angstroms thickness. SEM observation of E-glass particulate reinforced dimethacrylate-based resin composites showed that strong interfacial adhesion was maintained even under 72 hours of exposure to boiling water, while interfacial adhesion in the conventionally-treated materials was destroyed under the same conditions. Interfacial fracture energy was measured using an embedded single fiber fragmentation test. In the initial dry state, no interfacial debonding was observed in either the modified or conventionally-treated microcomposites, indicating strong interfacial adhesion in both cases. However, after exposure to boiling water for 24 hours, debonding occurred in both cases, with interfacial fracture energies of 281 J/m^2 and 54 J/m^2 for the modified and conventionally-treated interfaces, respectively. The improvement in hydrolytic stability of the interface is believed to be caused by a higher degree of crosslinking in the silane layer and the replacement of at least some of the hydroxyl groups on the glass surface by covalent O—Si—O bonds.

Keywords: Glass surface treatment; silane; interface adhesion and hydrolytic stability; embedded single fiber fragmentation test; TGA; DRIFT; SEM

INTRODUCTION

Environmental temperature changes and humidity are often responsible for the degradation of glass reinforced polymeric composites.

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A common degradation mechanism is the loss of adhesion between the reinforcing glass particle or fiber and the polymer matrix [1,2]. As a result of the large differences in physical properties between the fillers and matrices, environmental changes create interfacial stresses which tend to separate the constituents at their interface. There have been continuous efforts to improve the interfacial adhesion in glass reinforced materials by using surface sizes or adhesion promoters, such as silane coupling agents [3]. Their effectiveness depends on the nature and pretreatment of the substrate, the type of silane used, the thickness of silane layer and the process by which it is applied. In a relatively dry state, most silane coupling agents are effective for promoting interfacial adhesion and enhancing the mechanical properties of glass reinforced composites. Under wet conditions, however, the effectiveness of all silanes tends to decrease substantially, thus bringing into question the long-term durability of the composite materials [4–6].

Several mechanisms have been proposed to explain the function of the silane at the interface [7]. Two mechanisms, supported by a considerable amount of experimental data, are the formation of both primary covalent bonds and secondary hydrogen bonds at the interface. The covalent bonds are expected to be more stable than hydrogen bonds, since their breakdown depends on the hydrolysis of siloxane bonds. The strength of hydrogen bonding, on the other hand, can be weakened by diffusion of moisture to the interface. As water diffuses to an interface containing no more that a few atomic layers of water between the constituents, the buildup of atomic layers creates a weakened water layer incapable of transmitting sufficient stress. Another factor of primary importance is the hydrolytic stability of the crosslinked siloxane coating, generally on the order of 50 to 100 nanometers in thickness, formed on the glass surface during a typical commercial treatment. A schematic description of the process can be found elsewhere [8]. The competing reaction of self-condensation of silanol groups will lead to the formation of a variety of crosslinked siloxane oligomers which cause steric hindrance to complete bonding with the glass surface. Since the hydroxyl groups on the glass surface are immobilized, the self-condensation reactions are often favored. Although catalysts can be used to accelerate the condensation reactions, they may not be able to change the selectivity of the reactions because they are the same type of reactions. Usually, a higher temperature is used to make the inter-condensation proceed. Tripp and Hair reported that the percentage of the methylsilanols reacting with the surface Si_sOH is in the order

$$(CH_3)_3SiOH > (CH_3)_2Si(OH)_2 > CH_3Si(OH)_3$$

They explained this in terms of the differing basicities of the SiOH groups and the difference in kinetics between self-condensation and reaction with Si_sOH groups [9]. Thus, the commonly used tri-silanols do not bond to the surface easily. Instead, they are not stable and tend to form oligomer through self-condensation. Methods for improving the performance of silane coupling agents were reviewed by Plueddemann and Pape [7]. It has been reported that using crosslinking agents to increase the crosslinking of the siloxane structure in the interface region could increase bond strength and moisture resistance.

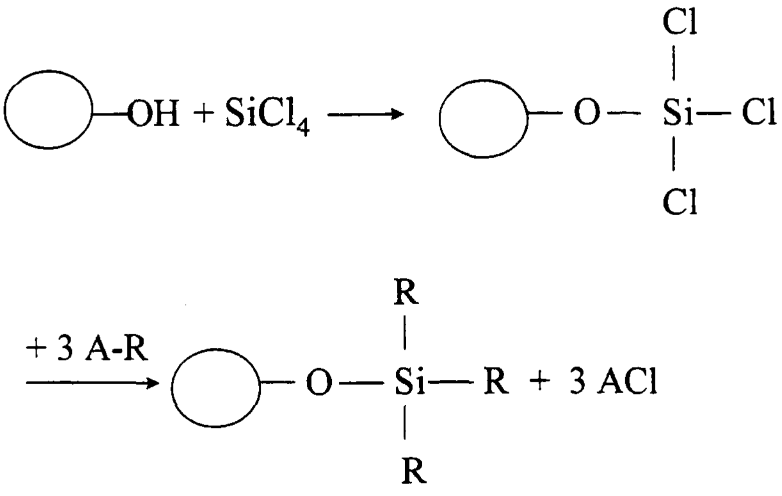
In this study, the conventional process of silylation from solution was modified by using $SiCl_4$ as a copolymerizing agent along with the silane coupling agent 3-methacryloxypropyltrimethoxysilane (MPS). The $SiCl_4$ was assume to act as both a surface grafting and crosslinking agent to promote the chemical bonding on the surface and increase the crosslinking density in the coated silane layer. Thermogravimetric analysis (TGA) and Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFT) were used to characterize the silane coating on the surface. The retention stability of the coated silane layer was tested by Soxhlet solvent extraction and ultrasound washing. The adhesion at the glass-matrix interface was examined by Scanning Electron Microscopy (SEM). The hydrolytic stability of interface adhesion was studied by boiling the composites in water. Interfacial strength was measured using the embedded single fiber fragmentation test [10, 11] and interfacial fracture energy evaluated with the model proposed by Wagner *et al.* [12].

MATERIALS AND METHODS

Glass beads (Potters Industries Inc.) with mean diameter of 4 microns were used as fillers. Dimethacrylate monomers BisGMA and triethylene glycol dimethacrylate (TEGDMA) (Aldrich) were mixed in 1:1

weight ratio and used as the matrix phase for the evaluation of the effectiveness of filler treatment. These two monomers are the main components of commercial dental restorative materials [13]. Five tenths weight percent of camphaquinone and dimethylaminoethyl methacrylate were added, respectively, into the mixture of monomers as photoinitiators. The curing process is a free radical polymerization, the details of which can be found elsewhere [14]. All the above components were mixed together and then loaded into a mold with dimension of 30 × 10 × 3 mm. Each side of the specimen was photo-cured for 5 minutes to ensure that equilibrium conversion of the double bonds had been reached. The silane coupling agent 3-methacryloxypropyltrimethoxysilane (MPS) was selected since its methacrylate groups can react with monomers during the curing process [4]. $SiCl_4$ was used as the bonding promoter and crosslinker, since it had been shown to be highly effective in promoting direct grafting to glass surfaces [15].

As previously shown [15], some of the chlorine atoms of the $SiCl_4$ can react first with the hydrogen-bonded water and the hydroxyl groups on a glass surface to produce a reactive, chlorinated surface. The chlorine atoms on the surface provide reactive sites for further grafting when a second reactive agent is introduced into the system. This process is shown schematically in Scheme 1. This sequential



SCHEME 1 Glass surface grafting *via* $SiCl_4$.

process, however, cannot be employed in a solution silylation process since the water in the silane solution will preferentially react with the chlorine atoms, thereby eliminating the opportunity for the silane component to react with the covalently bonded constituent. Therefore, we developed a non-sequential process as described below.

First, MPS was hydrolyzed for 15 minutes in acetone solution containing 2% (wt) of water. The initial MPS concentration was about 0.5% by weight. The pH value of the solution was adjusted to about 4 by adding acetic acid. The amount of MPS used for the filler treatment was three times the amount needed for minimum uniform coverage, calculated as follows [16]:

$$X = 3\frac{AW}{\omega} \tag{1}$$

where X = the amount of MPS (g); A = the specific area of the filler (m^2/g); W = the amount of fillers to be treated (g); ω = wetting surface of MPS (m^2/g).

For the materials used, A was estimated to be $0.6\,m^2/g$, based on the mean diameter and density of the particles, and ω was given to be $315\ m^2/g$ for MPS [8].

Second, untreated glass beads were washed with fresh acetone three time to remove possible surface adsorbed contaminants, and then dried prior to the surface treatment. A slurry of the pre-cleaned glass beads in the silane solution was stirred for 20 minutes to allow adsorption of the MPS on the glass surfaces. The solvent was then evaporated and the glass beads were dried at 90°C under vacuum for half an hour. At this stage, the MPS was probably physically adsorbed on the glass surface through hydrogen bonding.

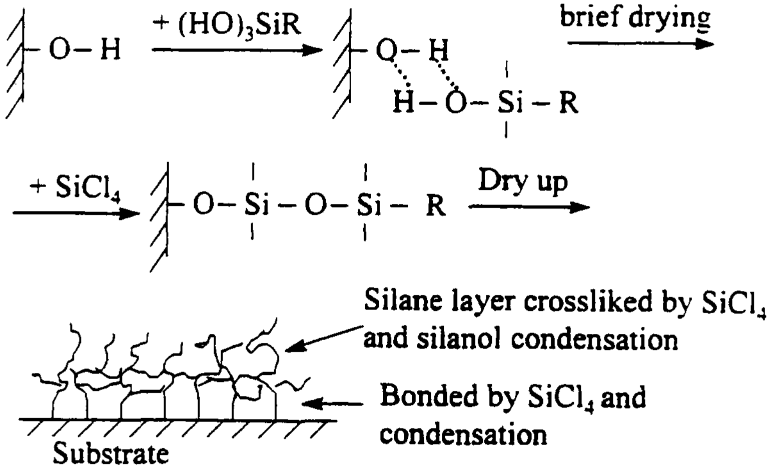
Third, the $SiCl_4$ was then added to the dried glass beads in a sealed flask. The mixture was stirred for 5 minutes before evaporating completely the unreacted (surplus) $SiCl_4$. This step was designed to form covalent bonding on the glass surface and crosslinking in the siloxane layer through simultaneous reactions of the $SiCl_4$ with both the hydroxyl groups of the glass surface and silanol groups of the physically adsorbed MPS. If one chlorine atom of a $SiCl_4$ molecule reacts with a hydroxyl group on the glass surface and another chlorine atom of the same $SiCl_4$ molecule reacts with a silanol group of the

MPS, a covalent bond is formed between the glass surface and the MPS. If all the four chlorine atoms of a $SiCl_4$ molecule react with the MPS molecules, the crosslinking density of the siloxane layer is increased. It is believed that neither of the above reactions would occur exclusively to the other, though it has not been determined which one was favored. At this point, the resulting silane coating layer is thought to be crosslinked and covalently bonded to the glass surface.

Finally, the treated glass beads were dried overnight, under vacuum at 90°C, during which period the bonding and crosslinking reactions were moved further toward completion. The complete process is shown schematically in Scheme 2.

A conventional silane treatment process was also conducted as a control experiment. In this process, all the above steps were the same except that the third step was skipped.

TGA was used to determine the amount of siloxane coating on the surface and DRIFT to examine the existence of carbon – carbon double bonds before and after Soxhlet extraction in toluene and ultrasound washing in acetone, respectively. The level of retention of interfacial adhesion in E-glass beads-BisGMA/TEGDMA composites, prepared using the above-mentioned treatment, before and after exposure to boiling water, was observed with SEM and compared with that in



SCHEME 2 Modified silane treatment process which incorporates $SiCl_4$.

composites prepared with E-glass beads treated using a conventional solution deposition process.

Single filaments of E-glass fibers were embedded in the polymer matrix in order to measure the interfacial fracture energies before and after exposure to boiling water. The glass fibers were UV-ozone cleaned for one hour and then treated using the above-mentioned and conventional silylation processes, respectively. The treated fibers were embedded in the monomer mixture and photo-cured in a mold to form dogbone specimens. The monomer mixture was 1:1 weight ratio of BisGMA and tetraethylene glycol dimethacrylate. The elongation-to-break of the matrix was 4%, so that under tension the filament would fracture first (at approximately 2%). Upon first fracture of the fiber, the sample was held at constant strain and the debonding and/or matrix cracking at the fractured fiber end were observed under a microscope and their dimensions measured. The interface fracture energy was estimated using the method proposed by Wagner *et al.* [12]. The mechanical properties of the fiber and matrix used in the calculation were measured separately.

RESULTS AND DISCUSSION

For both the conventional and the modified process treatment, the TGA indicated 0.4% weight loss of the glass beads at around 400°C, corresponding to the decomposition of the bonded siloxane coatings, as shown in Figure 1. Many researchers reported that more than monolayer coverage is necessary to get optimum interfacial adhesion and mechanical properties [4,16]. The glass beads used in this study have a mean diameter of 4 microns, as reported by the manufacturer. However, the specific surface area was found to be 1.5 m^2g, using the BET adsorption technique. This was about 2.5 times the estimated value based on the mean diameter. Surface roughness and a broad distribution of smaller particles account for the difference. Based on the measured surface area, the average thickness of the silane layer was approximately 30 Angstroms which is about the minimum uniform coverage based on Eq. (1). The optimum thickness for these materials has not been determined in this study.

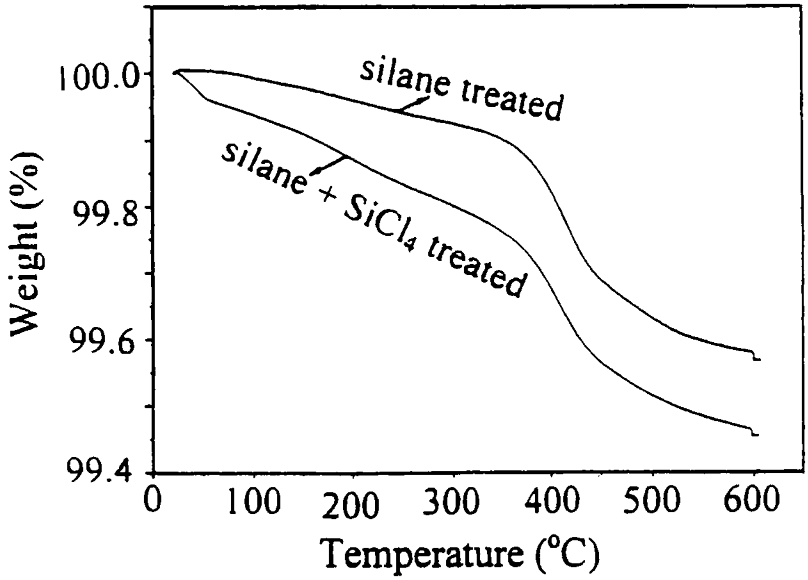


FIGURE 1 Weight loss of the treated glass beads, by TGA in N_2 environment.

To determine the tenacity of the coated layer, Soxhlet extraction was carried out with toluene as the solvent. After 24 hours of extraction, the glass beads were dried overnight under vacuum at 110°C and the retention of the coating measured using TGA. Figure 2 shows that the glass beads treated by the MPS – $SiCl_4$ process still had about 0.3% weight loss, while the conventionally-treated glass beads had virtually no weight loss. The tenacity of the former silane layer suggested that it was either covalently or strongly hydrogen bonded, and/or it was much more densely crosslinked than the latter. Ultrasound washing of the treated glass beads was also carried out. The glass beads were washed in four successive 15-minute cycles with fresh acetone as solvent. The TGA of the glass beads, after washing and drying, showed similar results, as shown in Figure 3.

The TGA results only confirmed the presence of combustible species on the glass surfaces, not whether chemical groups capable of reacting with the dimethacrylate monomers were still present. DRIFT was employed to determine if the carbon–carbon double bonds of MPS were still available. Mixtures of 5%(wt) glass beads in KBr powder

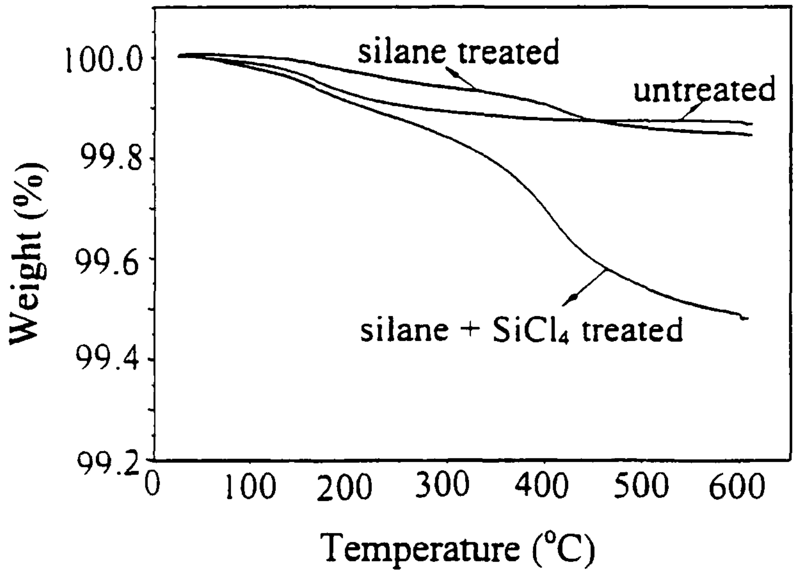


FIGURE 2 Weight loss of the treated glass beads after 24-hour Soxhlet extraction in toluene, compared with untreated glass beads, by TGA in N_2 environment.

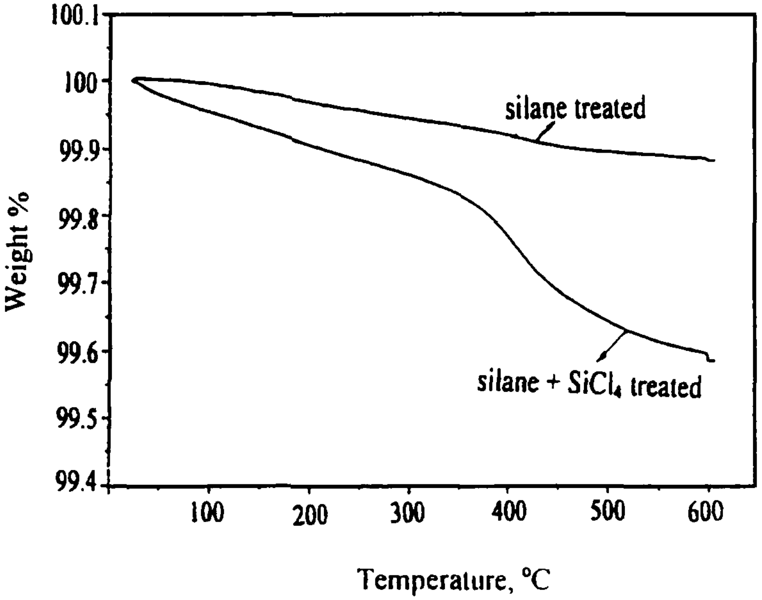


FIGURE 3 Weight loss of the treated glass beads after 4 times of successive ultrasound washing in acetone, by TGA in N_2 environment.

were prepared. The spectrum of pure KBr was used as the background and the spectrum of untreated glass beads was subtracted from that of the treated glass beads. Figures 4 and 5 show the absorbance spectra of the two treated glass bead systems before and after toluene extraction. Both show strong absorbance at 1635 cm^{-1} and 1720 cm^{-1} before the glass beads were extracted with toluene. These two peaks correspond to the carbon–carbon double bond and carbonyl stretching modes. After extraction in toluene for 24 hours, the absorbance of vinyl groups was still obvious for the MPS – $SiCl_4$ treated glass beads. But it was barely detectable for the glass beads treated in the conventional manner.

Figure 6 shows SEM microphotographs of fracture surfaces of fresh composite samples. For untreated glass beads, the glass surfaces were

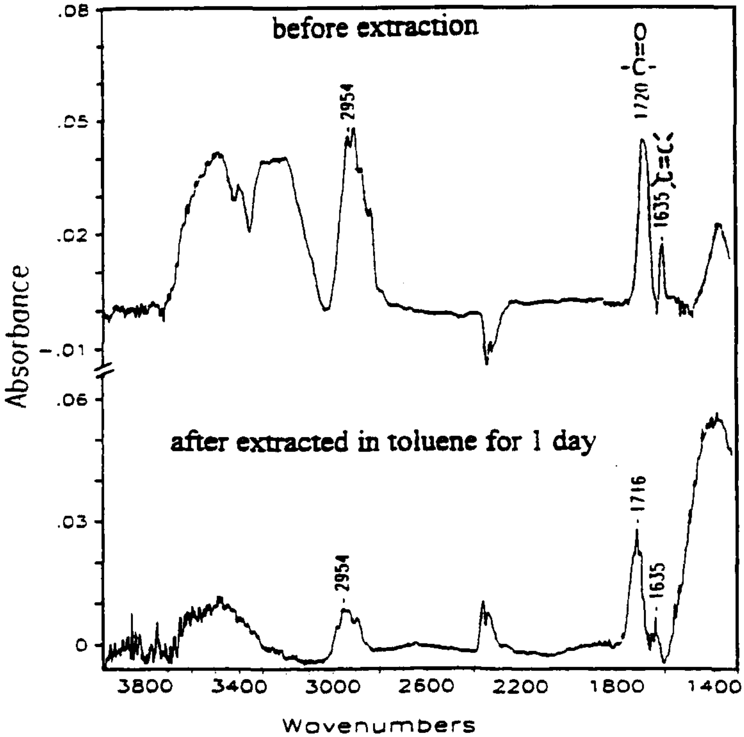


FIGURE 4 DRIFT results of the MPS – $SiCl_4$ treated glass beads before and after 24-hour Soxhlet extraction in toluene.

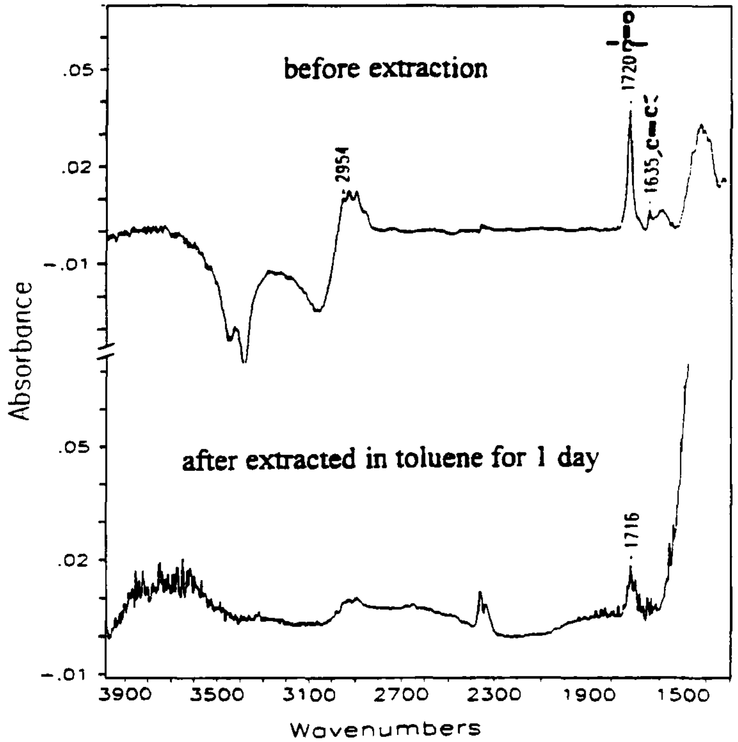


FIGURE 5 DRIFT results of the conventional silane treated glass beads before and after 24-hour Soxhlet extraction in toluene.

smooth and clean, indicating poor adhesion. The adhesion was improved substantially by both treatment methods, though it appeared that the modified method resulted in better adhesion. Figure 7 shows the effect of water boiling on the interface adhesion. After boiling for 24 hours, the MPS – $SiCl_4$ treated sample still had very good adhesion, while the conventionally-treated sample showed obvious deterioration of the interfacial adhesion. When further boiled for 72 hours, the interfacial adhesion deteriorated considerably for conventionally-treated sample, showing almost no evidence of adhesion. While the MPS – $SiCl_4$ treated sample had obvious deterioration, it still retained some degree of adhesion. It is clear that the MPS – $SiCl_4$ treatment will provide a more durable material under long-term exposure to moisture

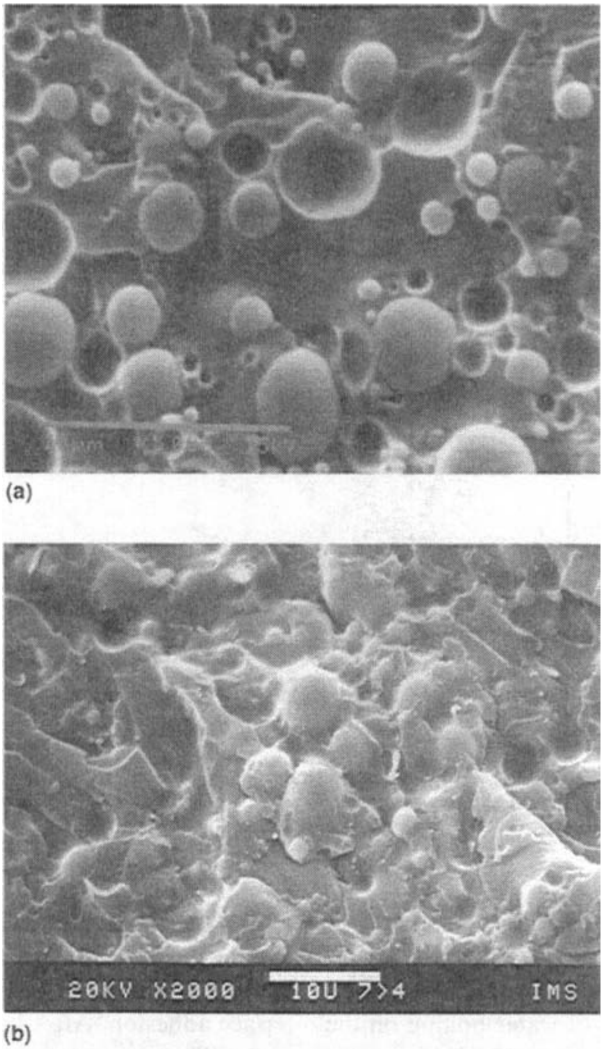


FIGURE 6 SEM microphotographs of fractured surface of fresh samples, (a) untreated; (b) silane treated; (c) MPS-$SiCl_4$ treated.

under less severe conditions. Long term durability measurements are presently underway.

The debonding lengths and interfacial fracture energies, measured using the embedded single fiber fragmentation test, are listed in Table I. A short debonding length was recorded upon fracture of the fresh,

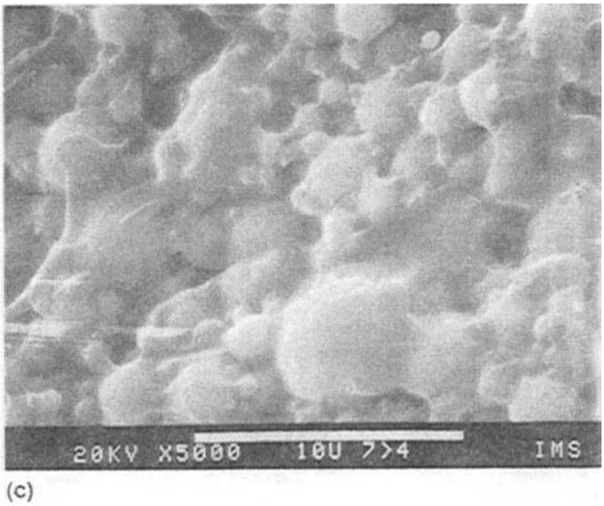


FIGURE 6 (Continued).

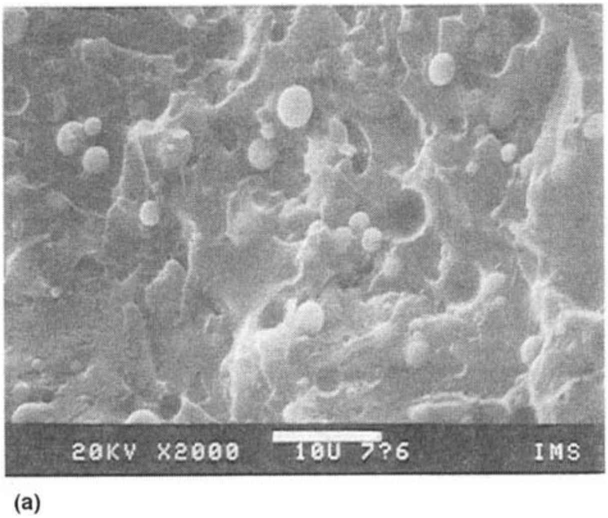


FIGURE 7 SEM microphotographs of fractured surface of water-boiled samples, (a) silane treated, boiled 24 hours; (b) MPS – $SiCl_4$ treated, boiled for 24 hours; (c) and (d) correspond to (a) and (b), respectively, but boiled for 72 hours.

dry samples of UV-ozone cleaned glass fibers, Figure 8(a), and the corresponding interfacial fracture energy was estimated as 311 J/m^2. There was no interfacial debonding observed for either of the silane-

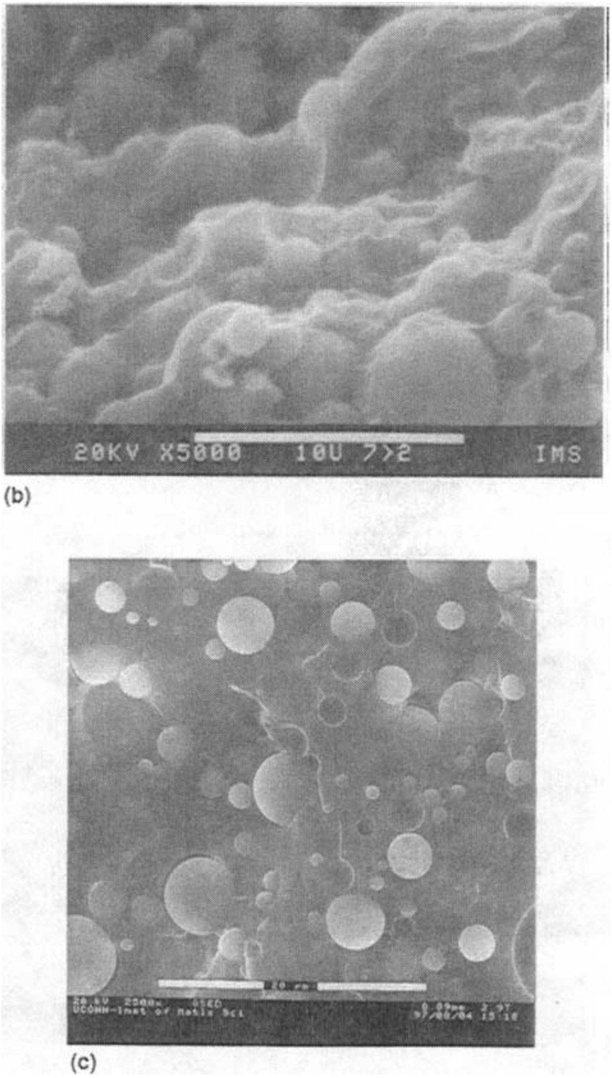


FIGURE 7 (Continued).

treated samples, Figure 8(b, c). Thus, in the dry state the siloxane interfaces were stronger than the matrices, resulting in matrix cracking at the broken fiber end rather than interfacial debonding. Much larger

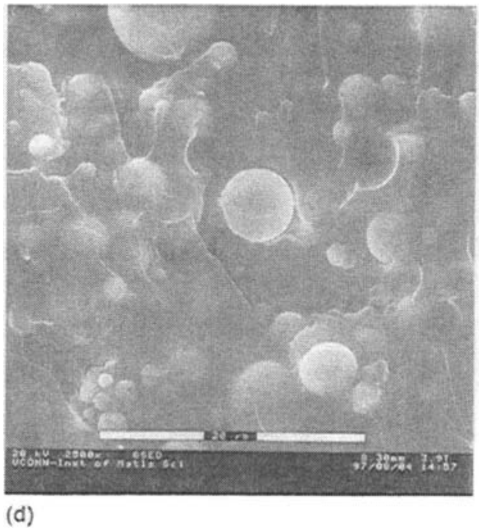


FIGURE 7 (Continued).

TABLE I Debonding length and interface fracture energy measured by embedded single fiber fragmentation test

Surface treatment	*UV-O_3*	*Silane*	*MPS-$SiCl_4$*
		Debonding length, μm	
fresh samples, dry state	11.6	none	none
boiled samples, wet state	179.5	114.4	15
		Fracture energy, J/m^2	
fresh samples, dry state	311	–	–
boiled samples, wet state	47	54	281

debonding lengths were observed after 24 hours of water boiling, as shown in Figure 8(d–f). The UV-cleaned and conventionally-treated glass fiber microcomposites had much larger debonding lengths and, therefore, weaker interfaces. Their estimated interfacial fracture energies were 47 J/m^2 and 54 J/m^2, respectively. The microcomposites containing the MPS–$SiCl_4$ treated glass fibers, had a much smaller debonding length, 15 μm compared with 179.5 μm and 114.4 μm, and a much higher interfacial fracture energy of 281 J/m^2 when tested at the same conditions as the other two samples. The superior hydrolytic

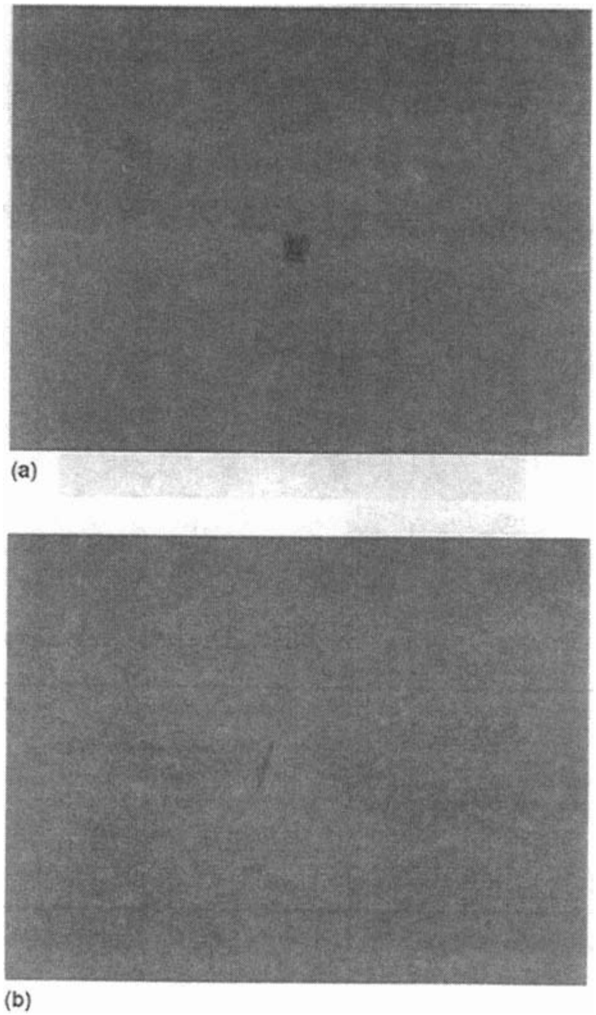


FIGURE 8 Photographs of first fiber break in embedded single fiber fragmentation test; (a), (b) and (c) are fresh samples of UV$-O_3$, silane and MPS$-SiCl_4$ treated fibers, respectively, tested dry; (d), (e) and (f) are samples corresponding to (a), (b) and (c), respectively, but boiled 24 hours and tested wet. [See Color Plate I].

stability of the interphase achieved by the modified silylation method is attributed to chemical bonding at both the glass-silane and silane matrix interfaces and a higher degree of crosslinking of the siloxane

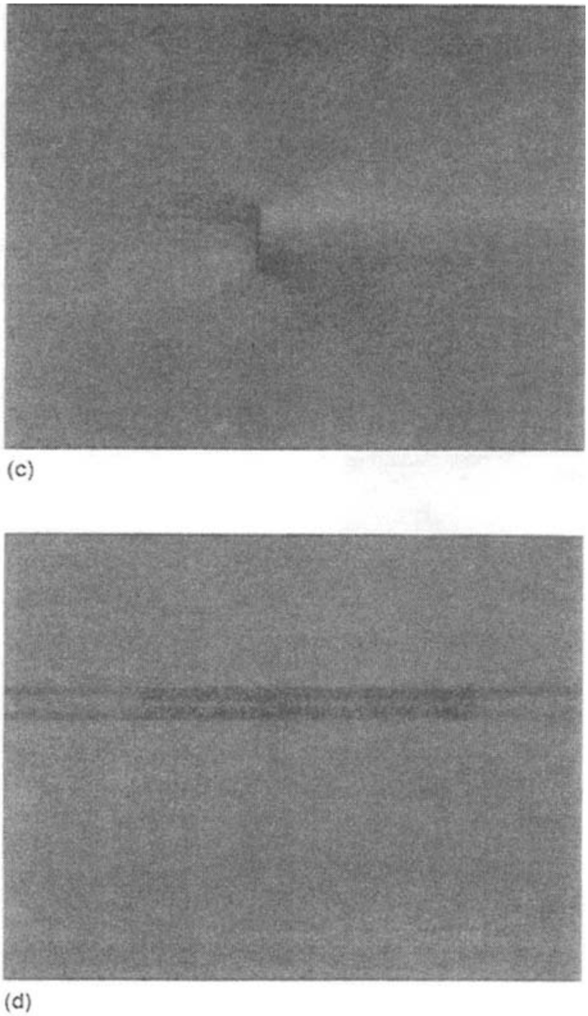


FIGURE 8 (Continued).

layer, as implied indirectly by the DRIFT, TGA and solvent extraction data. This interpretation is consistent with the evidence that a higher degree of crosslinking is conducive to the chemical and mechanical stability of siloxane coatings [17].

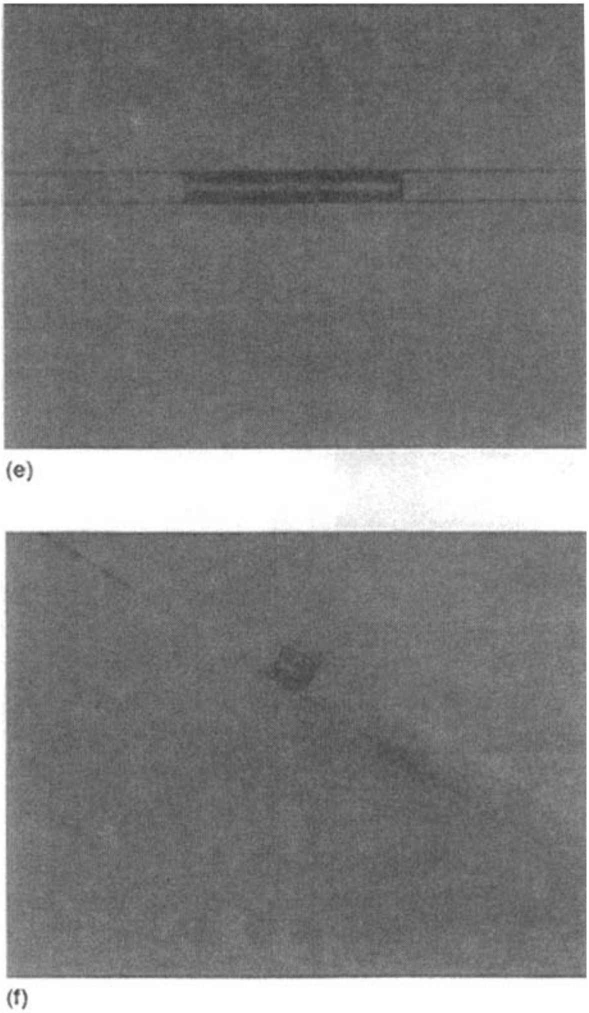


FIGURE 8 (Continued).

CONCLUSIONS

A conventional silylation process has been modified by incorporating $SiCl_4$ into the process. Glass beads were chosen as the fillers and MPS as the silane coupling agent. The siloxane layer obtained with the modified process could not be removed by toluene extraction or ultrasound washing in acetone, as shown by TGA. The results of DRIFT analysis confirmed that carbon–carbon double bonds were available on the surface for futher reaction with monomers of matrix, suggesting that the siloxane layer could be chemically bonded to the matrix. The MPS–$SiCl_4$ treatment led to better interface adhesion and higher hydrolytic stability as demonstrated in the SEM microphotographs of the fractured surfaces before and after water boiling. Measurement of interfacial fracture energies, using embedded single fiber microcomposite specimens, confirmed that the MPS–$SiCl_4$ treated fibers possessed tougher interphases after 24-hour exposure to boiling water than were obtained with either untreated or conventionally-treated fibers. The improvement of interfacial adhesion and hydrolytic stability were attributed to stronger chemical bonding between the glass reinforcement, the siloxane layer and the matrix resin, and to a higher degree of crosslinking in the siloxane interphase.

References

[1] DiLandro, L., DiBenedetto, A. T. and Groeger, J., *Polym. Compos.* **9**, 209 (1988).
[2] Madhukar, M. S. and Drzal, L. T., *J. Compos. Mat.* **25**, 932 (1991).
[3] Plueddemann, E. P., *Silane Coupling Agents* (Plenum Press, New York, 1990), 2nd Ed.
[4] Mohsen, N. M. and Craig, R. G., *J. Oral Rehabilit.* **22**, 213 (1995).
[5] Kaul, A., Sung, N. H., Chin, I. and Sung, C. S. P., *Polym. Eng. Sci.* **24**, 493 (1984).
[6] Sodefholm, K.-J. M. and Roberts, M. J., *J. Dent. Res.* **69**, 1812 (1990).
[7] Pape, P. G. and Plueddemann, E. P., in *Silanes and Other Coupling Agents*, Mittal, K. L., Ed. (VSP, The Netherlands, 1992), p. 105.
[8] Arkles, B., *Metal-Organics Including Silanes and Silicones* (Gelest, Inc., 1995), pp. 36–48.
[9] Tripp, C. P. and Hair, M. L., *Langmuir* **11**, 149 (1995).
[10] Pegoretti, A., Accorsi, M. L. and DiBenedetto, A. T., *J. Mat. Sci.* **31**, 6145 (1996).
[11] Graf, R. T., Koenig, J. L. and Ishida, H., *Anal. Chem.* **56**, 773 (1984).
[12] Wagner, H. D., Nairn, J. A. and Detassis, M., *Appl. Compos. Mat.* **2**, 107 (1995).
[13] Clarke, R. L., *Biomat.* **10**, 549 (1989).
[14] Linden, L., *Proc. Indian Acad. Sci.* **105**, 405 (1993).
[15] Ranade, S. V., Xie, X. Q. and DiBenedetto, A. T., *J. Adhesion* **64**, 7 (1997).
[16] Mohsen, N. M. and Craig, R. G., *J. Oral Rehabilit.* **22**, 183 (1995).
[17] Plueddemann, E. P. and Pape, P. G., *42nd Reinforced Plast./Composites Conf.* (SPI, 1987), paper 21-E.