Macromol. Symp. ***194****, 135–140 (2003)*

Novel Surface Treatments for Glass Fillers

*David A. Boyles**[1], *Jon J. Kellar*[2], *William M. Cross*[2]

South Dakota School of Mines and Technology

[1] Department of Chemistry and Chemical Engineering

[2] Department of Materials and Metallurgical Engineering, 501 E. St. Joseph, Rapid City, South Dakota, 57701, USA

Summary: Glass fillers were suface modified by direct formation of a silicon-carbon non-hydrolyzable linkage between glass and coupling agent. The grafted silane monolayer was evaluated by infrared spectroscopy. Samples were subjected to hydrolytic conditions to compare their surface treatment stability with traditional surface treatment hydrolytic stability. Composite specimens were fabricated and their mechanical properties were compared with traditional aminopropylsilane coupling agent treatment.

Introduction

Research has failed to reveal a smooth continuity between inorganic and organic phases of polymer matrix composites even in the presence of coupling agents (1,2,3). The disparity between the conceptual model as depicted by Plueddemann (4) and the inhomogeneous multilayers of adsorbed silane served for reconsideration of the fundamental strategy underlying composite coupling methods utilizing γ-aminopropyltrimethoxysilane (γ-APS) and similar coupling agents. By changing the fundamental strategy from one of unorganized multilayers to a more precise graft, it was proposed to form a more hydrolytically stable polymer matrix composite.

Methodology

Two strategies were adopted for surface modification of glass powders: the Speier route and the Grignard route (**Figure 1**) (5,6,7,8). Grafting was performed on E-glass beads, 4 microns in diameter. The Speier route was used for compounding into epoxy polymers via condensation polymerization while the Grignard route constituted a more facile route affording modified E-glass which could be reacted with monomers such as vinyl esters via free-radical polymerization. Fourier transform infrared (FT-IR) spectroscopy using diffuse reflectance (DRIFT) spectroscopy indicated that the desired functionality was present.

CCC 1022-1360/00/$ 17,50+.50/0

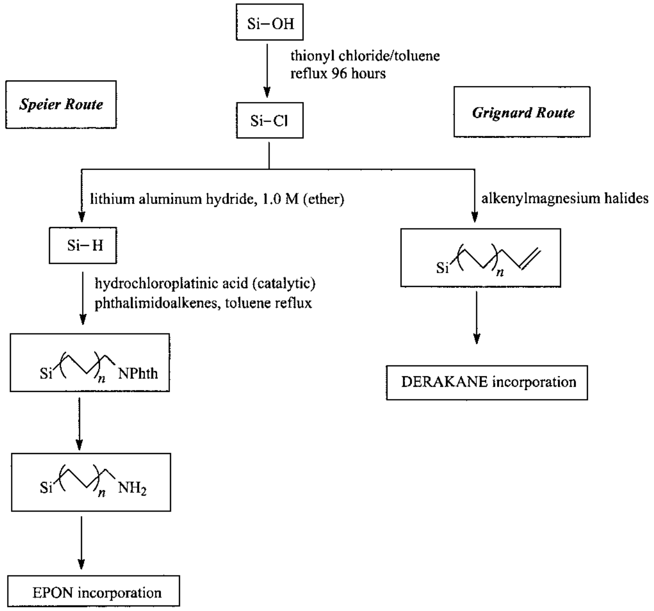

Figure 1. Synthetic strategies.

Hydrolytic stability of the grafted material on E-glass beads was tested by stirring the grafted beads in a 0.75 mmol solution of trifluoroacteic acid (TFAA) for 1 day. The amount of the grafted material remaining after 1 day in TFAA was determined by FT-IR and compared to the same beads with adsorbed APS that had been treated in the same manner. **Table 1** summarizes the average amount of band height decrease for the grafted E-glass and for APS treated E-glass upon respective TFAA hydrolysis. The grafted material was clearly superior to APS in terms of the amount of material removed from the surface by TFAA treatment. No significant visible differences among beads could be distinguished using scanning electron microscopy (SEM), however.

Table 1. Summary of FT-IR Hydrolytic Stability Data

Material Tested	Percent remaining after 1 day in TFAA
Grafted Vinylbenzyl (Grignard route)	66-75
Grafted Undecenyl (Grignard route)	50-66
Grafted Undecenylamine (Speier route)	50-66
Grafted Allyl (Grignard route)	50-66
Grafted Allylamine (Speier route)	75-80
Adsorbed APS (1 wt% solution)	35-50

Following grafting to E-glass beads, composite materials were made. Due to initial materials problems with vinyl-ester resin, only epoxy matrix systems were tested. The epoxy resin used was Epon 828 (Resins-Versatics) cured with 27 phr methylene dianiline (MDA) curing agent. When utilized, E-glass beads (50% by weight) were compounded with the epoxy. Curing was accomplished by heating the mixture to 80 °C for 2 hours followed by additional heating at 150 °C for 2 hours. Curing was performed in a vacuum oven operating at approximately 0.3-0.4 atmospheres. Tensile test specimens were made of each sample type, then used for tensile testing. All tensile test specimens were made at the same time from the same compounding. **Figure 2** shows typical stress-strain curves for the various composites and for pure epoxy cured in the same manner as the composites.

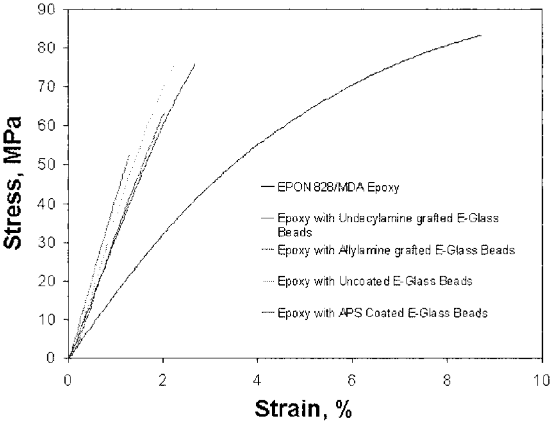

Figure 2. Typical stress-strain curves.

Table 2 shows these trends more clearly. Young's modulus increased by about a factor of 2 from about 1.7 GPa to about 3.5 GPa. The different surface treatments did not exhibit a significant difference in Young's modulus. However, the different surface treatments did exhibit a difference in tensile strength. The undecylamine and allylamine grafted E-glass beads in epoxy were found to have an approximately 15-25% lower tensile strength than untreated and APS treated E-glass beads in epoxy. This is attributed to curing differences between the samples as the undecylamine and allylamine treated samples were still tacky after completion of the curing cycle.

Table 2. Summary of Mechanical Testing Data

Material	Young's Modulus (GPa)	Tensile Strength (MPa)
Epon 828 with MDA	1.68 ± 0.07	81.5 ± 3.0
Epoxy with undecenylamine grafted E-Glass beads	3.70 ± 0.40	54.3 ± 20
Epoxy with allylamine grafted E-Glass beads	3.61 ± 0.27	62.6 ± 1.6
Epoxy with untreated E-Glass beads	3.44 ± 0.39	73.7 ± 5.3
Epoxy with APS treated E-Glass beads	3.16 ± 0.13	80.5 ± 7.5

Figure 3 shows an SEM micrograph of the fracture surface for a composite made with untreated E-glass beads. Several beads pulled from the fracture surface were evident and the beads do not appear wetted by the polymer. **Figure 4** and **Figure 5** show similar SEM micrographs for APS treated and undecenylamine grafted E-glass beads. In both of these figures, the beads were well wetted by the polymer and few cavitations were observed. **Figure 6** shows a higher magnification view of an allylamine grafted E-glass bead indicating wetting of the bead by epoxy.

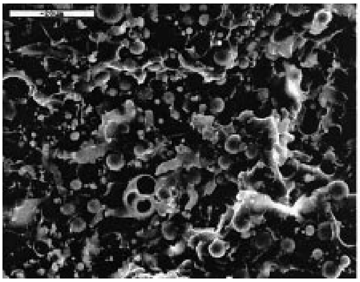

Figure 3 SEM micrograph of the fracture surface of epoxy filled with untreated E-glass beads.

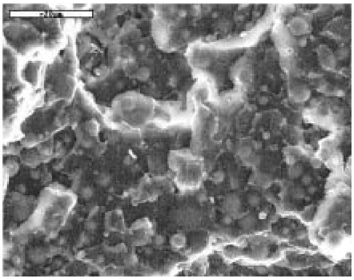

Figure 4. SEM micrograph of the fracture surface of epoxy filled with APS treated E-glass beads.

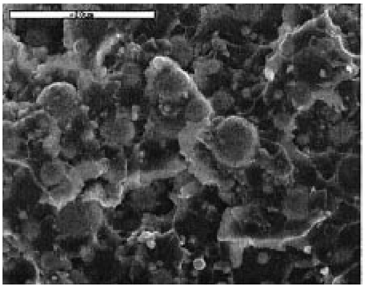

Figure 5. SEM micrograph of the surface of epoxy filled with undecenylamine grafted E-glass beads.

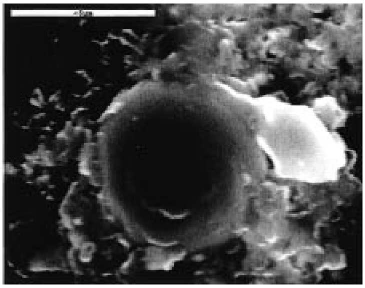

Figure 6. SEM micrograph of fracture the fractured surface of epoxy filled with allylamine grafted E-glass beads.

Hydrolytic stability testing was performed by boiling tensile test specimens for 8 hours in water with subsequent tensile testing. **Table 3** shows results for Young's modulus obtained from tensile testing of hydrolytically exposed samples, while **Table 4** shows resulting tensile strengths. All treatments displayed significant loss of stiffness. Undecenylamine grafted E-glass and adsorbed APS treated E-glass filled composites exhibited least loss of stiffness, and the change from the non-hydrolytically treated composite was about the same in both cases. The loss in stiffness is not attributable to changes in the matrix as the pure matrix properties exhibited essentially the same Young's modulus whether or not it had been hydrolytically exposed.

Table 3. Young's Modulus of Composites After Hydrolytic Exposure

	Young's Modulus (GPa)		
Filler Treatment	No Exposure	Hydrolytic Exposure	% Change
None	3.4	2.2	-35.3
Adsorbed APS	3.1	2.5	-19.4
Grafted Allylamine	3.7	2.3	-37.8
Grafted Undecenylamine	3.4	2.8	-17.6

The tensile strength data exhibited a different trend. As indicated in **Table 4**, the degree of change was essentially constant for no filler treatment, APS adsorption and allylamine grafting. These three data are somewhat greater than the change observed for undecenylamine grafted E-glass bead filler.

Table 4. Tensile Strength of Composites After Hydrolytic Exposure

	Tensile Strength (MPa)		
Filler Treatment	No Exposure	Hydrolytic Exposure	% Change
None	73.7	36.8	-50.1
Adsorbed APS	80.5	45.0	-44.1
Grafted Allylamine	62.5	34.0	-45.6
Grafted Undecenylamine	54.0	32.0	-31.5

The good retention of tensile strength after hydrolytic exposure for the grafted amines as compared to the APS treatment and no surface treatment is most probably due to the good adhesion of the beads after grafting as shown in **Figures 5** and **6** for undecylamine grafted E-glass in the epoxy (**Figure 5**) and allylamine (**Figure 6**).

Conclusion

E-glass beads with grafted material were prepared which demonstrated enhanced resistance to loss of grafted organic material upon acid hydrolysis compared with E-glass beads having APS treatment. Scanning electron microscopic imaging indicated that both APS treatment and undecenylamine grafting altered the surface chemistry of the E-glass beads to facilitate wetting, and both APS and the grafted materials appeared to allow adhesion to the polymer system. Mechanical properties of epoxy resin composites prepared with the grafted material indicated hydrolytic differences between the allyl- and undecenyl-amine grafting which may be due to differences in chain length, since the longer chain of the undecenylamine graft is able to cover more of the surface in areas where no grafting occurs, than does the relatively short allylamine graft. Thus, more water may be occluded from the surface by the undecenylamine graft with the effect of improving the hydrolytic stability of the surface.

[1] Nishio, E., Ikuta, N., Okabayashi, H., Hannah, R., **Applied Spectroscopy**, 1990, **44**, 614.
[2] Schrader, M.E. in Composite Materials, Vol. 6: Interfaces in Polymer Matrix Composites, Ed. E.P. Plueddemann, Academic Press, New York, NY, 1974, pp. 110-130.
[3] Ishida, H. in Proc. Symp. Polym. Composites, Seattle, Washington, March 1983, pp. 25-50
[4] Plueddemann, E.P., Silane Coupling Agents, 2nd ed. Plenum Press, New York, NY, 1991.
[5] Pesek, J., Sandoval, J., and Minggong, S., **Journal of Chromatography**, 1993, **630**, 95.
[6] Sandoval, J. and Pesek, J., **Anal. Chem.**, 1991, **63**, 2634.
[7] Sandoval, J. and Pesek, J., 1991, US Pat. 5,017,540
[8] Sandoval, J., and Joseph J. Pesek, **Anal. Chem.**, 1989, **61**, 2067.