Graft Copolymerization of Glass Fiber and Its Application

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Synopsis

Modified glass fibers, containing unsaturated hydrocarbon surface groups, were prepared by a hydrothermal treatment, with allylglycidylether in excess as reagent. Graft polymerization of the treated glass fiber with styrene and methylmethacrylate was carried out in sealed tubes, under nitrogen, using benzoyl peroxide (BPO) and cumene hydroperoxide (CHPO) as initiators. When BPO was used as the initiator, the grafting efficiency was extremely low, but the graft copolymerization behavior was similar to that of usual organic polymers. With CHPO, both grafting ratio and grafting efficiency were very high. Various properties of composite materials containing grafted glass cloth were studied. Flexural strength, flexural modulus, and interlaminar shear strength increased proportionally to the increase of the grafting ratio; the same values were decreased only in a small extent after the boiling test.

INTRODUCTION

It is well known that mechanical, electrical, and water-resisting properties of composite materials containing glass fiber are lowered when the cohesion between glass fiber and the matrix is incomplete. Various coupling agents such as alkoxysilanes have been developed and put to practical use for the improvement of these properties. However, no satisfactory results have yet been obtained in forced deterioration tests (such as the boiling test), even with such coupling agents.[1-7]

Recently, various studies on modified glass fiber, obtained by grafting monomers onto glass fiber by means of an ionic polymerization process, were reported.[8-14] With these grafted glass fibers, it may be possible to correct the defects of the composite materials and also to improve their mechanical properties, especially their interlaminar shear strength, their impact strength, etc. In this study, glass fibers containing unsaturated groups were produced by reacting them through a hydrothermal treatment with an excess of allylglycidylether. The graft copolymerization of this modified glass fiber with styrene or methyl methacrylate was carried out in sealed tubes in presence of nitrogen. Their graft copolymerization behavior as well as the properties exhibited by the composite materials made of the grafted glass fiber were investigated.

EXPERIMENTAL

Glass Fibers and Reagents

E glass fibers (SiO_2 54.5%, Al_2O_3 14.5%, CaO 17.0%, B_2O_3 8.5%, MgO 4.0%, TiO_2 1.0%) were subjected to hydrothermal treatments under various conditions. Styrene, methyl (ethyl, n-butyl) methacrylate, glycidyl methacrylate, methacrylic acid and allylglycidylether, and benzene were first distilled. Benzoyl peroxide (BPO) was used after recrystallization. Cumene hydroperoxide (CHPO) (special grade reagent) was used without further purification.

Preparation of Glass-Fiber-Containing Unsaturated Groups and Grafting Procedure

Glass fibers were subjected to hydrothermal treatment in the 30–100°C temperature range for 1–15 h. After vacuum drying at 60°C, for 24 h, and elimination of oxygen by flushing with dry nitrogen, an excess of allylglycidyl-ether (AGE) [containing $BF_3O(Et)_2$ 0.01 mol % to AGE][15] was added, and the reaction was carried out, at 0°C, for 24 h. After treatment, the glass fibers were washed thoroughly with benzene to remove unreacted allylglycidylether.

The glass fibers containing unsaturated hydrocarbon groups were immersed in benzene solutions of monomers and initiators of various concentrations. Graft copolymerization was carried out, at 40–80°C, under nitrogen in sealed tubes. After the prescribed reaction time, the reaction was quenched by addition of methanol. The treated fibers were washed with an acetone methanol mixture. The ungrafted polymers were extracted with acetone, in a Soxhlet extractor, for 15–30 h (extraction to a constant weight). After drying, grafting ratios and the grafting efficiency were determined according to the following formulas:

$$\text{grafting ratio} = \frac{\text{wt grafted polymer}}{\text{wt original sample}} \times 100$$

$$\text{grafting efficiency} = \frac{\text{wt grafted polymer}}{(\text{wt grafted polymer}) + (\text{wt ungrafted polymer})} \times 100$$

Properties of the Treated Glass Fibers

(a) Tensile strength, the ultimate elongation, and Young's modulus of the grafted glass fiber were measured with a KS-type fiber tester (Koa Shoukai Ltd.) according to the earlier method.[16]

(b) The contact angle of the grafted glass fiber was determined by means of the dropping method.[16]

(c) Silanol groups on the surface of glass fiber were determined by the method of Boehm and Schneider.[17] The unsaturated group content was estimated by the method of Weber et al.[18]

(d) The composites were prepared in the following way:

The epoxy resin (Epcot 828) was cured with metaphenylenediamine. The grafted glass cloths were carefully aligned in a mold, and 2-g samples of each were used to prepare composite bars (30 mm × 2.5 mm × 1.05 mm) with a volume fraction of the grafted glass cloths equal to 0.52. The mold was heated at 150°C
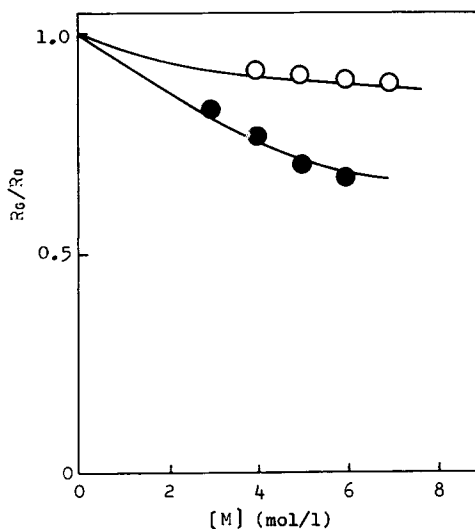
Fig. 1. Influence of monomer concentration on the rate of the graft polymerization (R_G) and on the rate of homopolymerization (R_0). [BPO] = 0.04 mol/L; [GF] = 20 g/L; T = 80°C; (O) St; (●) MMA.

for 1 h. Flexural strength and modulus were measured by the three points bending method, at a 20:1 span-to-depth ratio. Interlaminar shear strength was measured by the short beam test modified for flat bars and using a 4:1 span-to-depth ratio.

(e) Fracture surfaces of selected samples were examined by scanning electron microscopy (Mini-SEM-MSM, Akashi Seisakusho Ltd.).
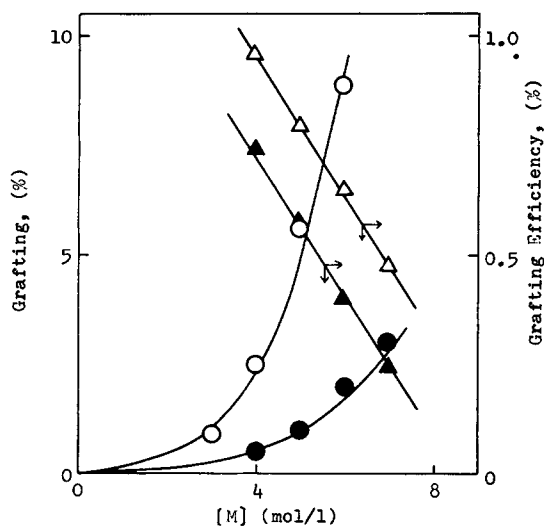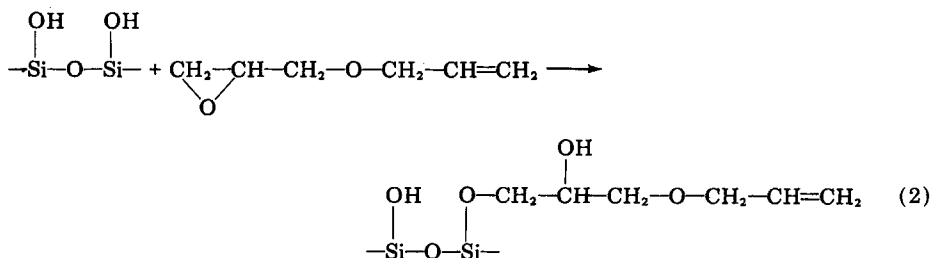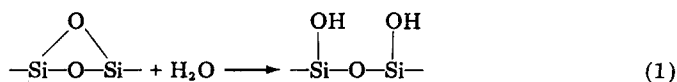

Fig. 2. Influence of monomer concentration on grafting ratios and on grafting efficiency. [BPO] = 0.04 mol/L; [GF] = 20 g/L; t = 60 min; T = 80°C. Grafting ratio: (O) St; (●) MMA. Grafting efficiency: (△) St; (▲) MMA.

RESULTS AND DISCUSSION

Preparation of Glass Fiber Modified by Unsaturated Group

The amount of silanol groups, formed by hydrothermal treatment[19] of the glass fiber under various conditions, was measured. The results are summarized in Table I. Silanol groups content increases during the initial period of the reaction. This increase is faster at higher temperature. The number of unsaturated groups formed by the reaction of silanol groups with allylglycidylether (AGE) is also shown in Table I. The amount of unsaturated groups introduced is generally larger than silanol groups.

$$-Si-O-Si- + H_2O \longrightarrow -Si-O-Si- \qquad (1)$$

$$-Si-O-Si- + CH_2-CH-CH_2-O-CH_2-CH=CH_2 \longrightarrow$$

$$-Si-O-Si- \qquad O-CH_2-CH-CH_2-O-CH_2-CH=CH_2 \qquad (2)$$

Graft Copolymerization of Styrene (St) and Methyl Methacrylate (MMA) onto Glass Fibers

Grafting of the modified glass fiber was performed with different monomers, at various concentrations, first using BPO as the initiator. Figure 1 relates the ratio of the rate of the graft copolymerization (R_g) to the rate of homopolymerization (R_0) against monomer concentration [M].

As can be seen from Figure 1, the effect of MMA on the rate of the graft copolymerization is larger than that of styrene. Similar resuults have been observed by Imoto et al.[20] on the graft copolymerization of poly(vinyl chloride) and by Scanlan[21] on the graft copolymerization of dihydromycene. This can be explained as follows: In the case of the more active monomer, the reinitiating effect of the backbone polymer is so large that the presence of the backbone

TABLE I
Silanol Group Content of Glass Fiber after a Treatment in Boiling Water. Pendant Unsaturated Hydrocarbon Groups of Treated Glass Fibers

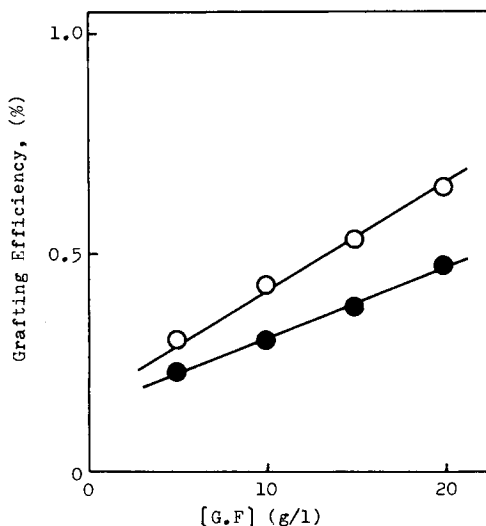| Water temp (°C)	30			60			100		
	1 h	5 h	15 h	1 h	5 h	15 h	1 h	5 h	15 h
Apparent silanol group[a] ($\times 10^4$ mol/g)	6.288	6.466	7.288	7.498	7.607	8.082	8.101	8.125	8.126
Unsaturated groups[b] ($\times 10^4$ mol/g)	6.16	7.15	8.04	9.11	11.26	12.35	12.82	13.06	13.25

[a] ± 0.055.
[b] ± 0.04.

Fig. 3. Relation between treated glass fiber content and grafting efficiency. [BPO] = 0.04 mol/L; [M] = 6 mol/L; t = 60 min; T = 80°C; (O) St; (●) MMA.
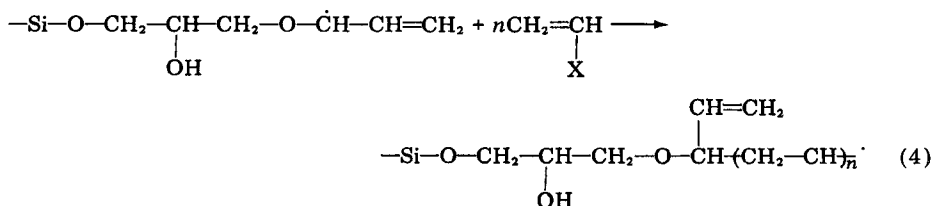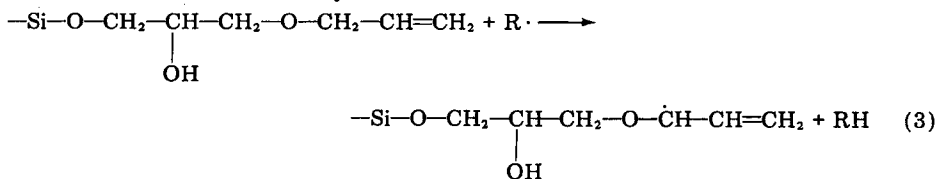
polymer has only a minor effect on the rate of the graft copolymerization, while, in the case of MMA, which is a less active monomer compared to St, the reinitiating reaction is lower and the effect on the rate of the graft copolymerization becomes large.

In Figure 2, the grafting ratio and the grafting efficiency are plotted vs. monomer concentration [M]. The grafting ratio increases in proportion to the monomer concentration, and the rate of increase for St is larger than that for MMA. On the other hand, the grafting efficiency generally decreases with the increase of the monomer concentration [M].

Figure 3 shows the relation between the grafting efficiency and the content of modified glass fiber.

For both St and MMA, the grafting efficiency increases in proportion to the increase of the glass fiber. This suggests that the increase of glass fiber is related to the increase of grafting active points.

Considering that the graft formation is due to a hydrogen abstraction reaction (abstraction of hydrogen at the α-carbon atom of the allyl group of glass fiber) by the primary radical formed from the initiator, the graft copolymerization reaction can be described by known reaction schemes:

$$-Si-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O-CH_2-CH=CH_2 + R\cdot \longrightarrow$$

$$-Si-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O-\dot{C}H-CH=CH_2 + RH \quad (3)$$

$$-Si-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O-\dot{C}H-CH=CH_2 + nCH_2=\underset{\underset{X}{|}}{CH} \longrightarrow$$

$$-Si-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O-\underset{\overset{CH=CH_2}{|}}{CH}(CH_2-CH)_{\overline{n}}^{\cdot} \quad (4)$$

Grafting efficiency generally increases with the increase of backbone polymer concentration and decreases with the increase of the monomer concentration [M]. The results of the present study are in good qualitative agreement with the equation developed by Maekawa et al.[22]

The influence of the polymerization temperature on the grafting ratio and on the grafting efficiency is shown in Figure 4. For both St and MMA, the grafting ratio increases with increasing polymerization temperatures while the grafting efficiency decreases. This suggests that the apparent activation energy of the polymerization initiation may be larger for both St and MMA than the activation energy of the chain transfer reaction.

The influences of the type and concentration of initiator are summarized in Table II. With BPO, the grafting ratio as well as the grafting efficiency, though low, increases with initiator concentration. With CHPO, both grafting ratio and grafting efficiency are considerably larger than those obtained with BPO. In this latter case, the grafting reaction is strongly affected by the concentration of CHPO, and an optimum concentration (in this experiment, 0.02 mol/L) exists. Moreover, in presence of CHPO the graft polymerization behavior depends on the nature of the monomer.

Thus, in the case of St, both the grafting ratio and the grafting efficiency are very large, while for MMA, little effect can be observed. Possibly hydroperoxides, such as CHPO, form radicals relatively more easily with St,[23,24] while such mutual interaction between MMA and CHPO is limited. As reported by Walling and Heaton,[25] the activation energy of the initiation is only 104 kJ/mol for St; consequently, in the case of St, CHPO may react more effectively than BPO.

Using methyl, ethyl, and n-butyl methacrylates for the grafting reaction, the effect of the substituent on the grafting ratio could be investigated. The results of Figure 5 show that the larger the substituent, the more difficult is the graft polymerization. This tendency is similar to that found in the graft polymerization of cellulose.[26]
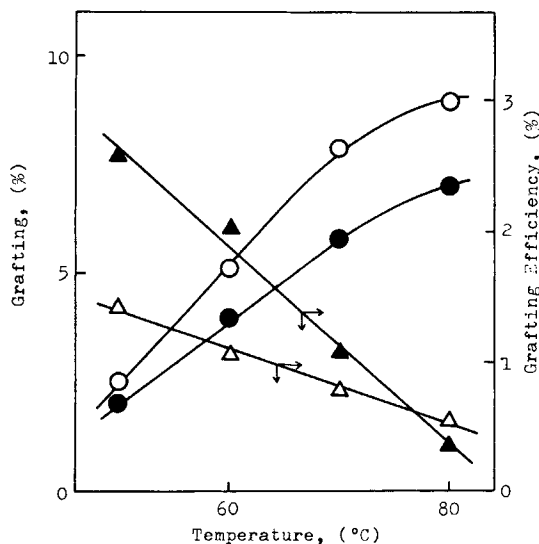

Fig. 4. Effect of the polymerization temperature on grafting ratio and grafting efficiency. [BPO] = 0.04 mol/L; [M] = 6 mol/L; [GF] = 20 g/L; t = 60 min; T = 80°C. Grafting ratio: (O) St; (●) MMA. Grafting efficiency: (△) St; (▲) MMA.

TABLE II
Effect of Type and Concentration of Initiator on Graft Polymerization

		[C] (mol/L)	Time (min)	% Grafting	Grafting efficiency	Total conversion (%)
[GF] = 20 g/L,	BPO	0.02	60	5.3	0.42	6.8
T = 80°C			120	9.0	0.85	14.5
[St] = 6 mol/L			180	9.5	1.55	24.2
			60	8.9	0.65	7.0
		0.04	120	10.4	1.24	15.2
			180	12.8	8.05	25.8
			240	16.3	9.85	38.5
			60	8.8	0.68	10.5
		0.06	120	11.5	2.40	20.8
			180	12.4	5.34	40.5
	CHPO	0.01	30	13.2	8.5	0.3
			60	52.1	19.7	1.7
			90	78.2	43.7	2.6
		0.02	20	50.1	43.4	2.8
			40	88.7	44.8	4.0
			60	140.0	47.9	4.8
			80	160.9	52.8	5.2
		0.04	20	42.3	34.5	3.5
			40	83.0	47.2	4.2
			60	112.8	34.3	7.0
			80	155.0	34.1	9.6
		0.06	20	10.3	2.8	4.0
			40	23.5	4.7	8.8
			60	70.0	10.8	9.2
			80	42.0	5.5	11.0
	BPO	0.04	30	2.4	0.35	9.8
			60	7.0	0.48	25.0
			90	12.0	0.84	40.2
			120	13.2	1.05	52.4
[GF] = 20 g/L,	CHPO	0.04	30	0.6	0.08	0.91
T = 80°C						
[MMA] = 6 mol/L			60	1.4	0.11	1.82
			90	2.1	0.18	2.68
			120	3.8	0.25	4.05

Physical Properties of the Grafted Glass Fiber

Tensile strengths and Young's modulus of the grafted glass fiber were measured (Fig. 6 and 7). The tensile strength generally increases linearly with the increase of the grafting ratio within the experimental conditions. The tendency for the increase of the tensile strength of styrene-grafted glass fiber was somewhat larger than that of methyl methacrylate-grafted glass fiber. Young's modulus generally decreases with the increase of the grafting ratio, especially with the styrene-grafted glass fiber.

Contact angles on various grafted fibers were measured by means of the dropping method; the results are shown in Figure 8. The contact angle with water increases with the increase of the grafting ratio, while, with ethylene glycol and phenyl glycidyl ether, contact angles decrease.

Using grafted glass fibers for composite materials, it is expected that the affinity to epoxy resin, polyester resin, etc. will be improved.
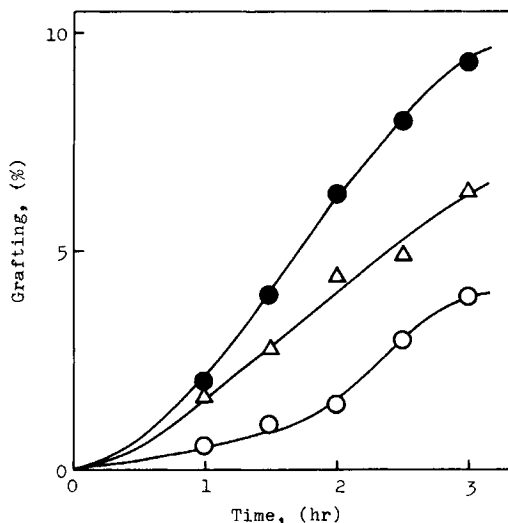
Fig. 5. Effect of the substitutions of monomer on grafting ratio. [M] = 6 mol/L; [BPO] = 0.04 mol/L; [GF] = 25 g/L; T = 80°C; (●) methyl; (△) ethyl; (○) n-butyl methacrylate.

Mechanical Properties of the Composite Materials

Some properties of composite materials consisting of St (or MMA)-grafted glass cloth and epoxy resins are summarized in Table III. The flexural strength and the flexural modulus increase with the increase of the grafting ratio of glass cloth, while the interlaminar shear strength varies little. The decrease of the interlaminar shear strength after the boiling water treatment is similar to that observed with ordinary glass cloth composite materials, and, therefore, it can be stated that the grafting of St or MMA onto the glass cloth has little effect on the interlaminar shear strength.

To overcome this difficulty, glass cloth composite materials grafted with glycidyl methacrylate (GMA) or methacrylic acid (MAA) can be successfully
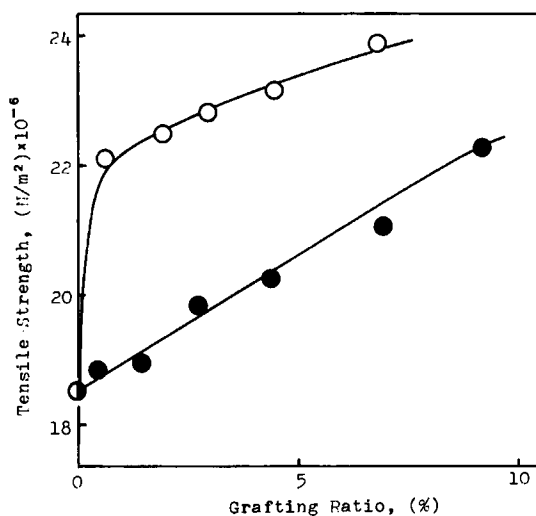

Fig. 6. Relationship between the tensile strength of the grafted glass fiber and grafting ratios: (○) St; (●) MMA.
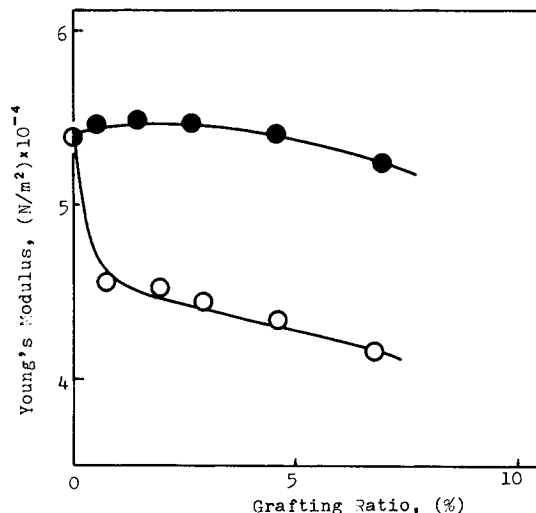
Fig. 7. Relationship between Young's modulus of the grafted glass fiber and grafting ratios: (O) St; (●) MMA.

used. As seen in Table III, this suggests that the glass cloth grafted with GMA or MAA possibly reacts, through epoxy or carbonyl groups of the grafts, with the epoxy matrix to form a crosslinked structure; hence the extent of the increase of the interlaminar shear strength as well as the extent of its decrease after the boiling test may be small. For comparison, the hydrothermal-treated glass cloth just coated with polystyrene or poly(methyl methacrylate) is less efficient as the grafted glass cloth.
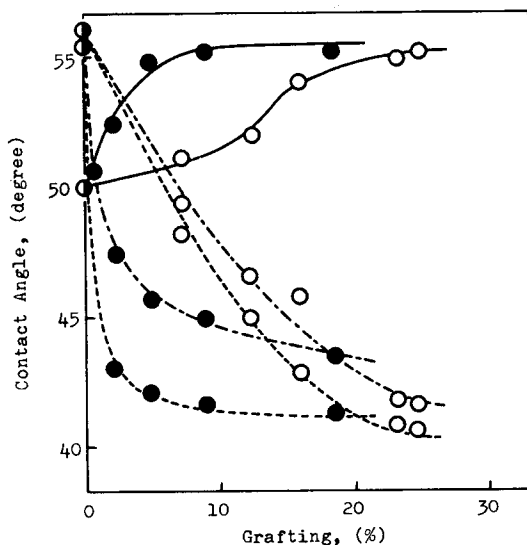

Fig. 8. Contact angle of water, ethylenglycol, and phenylglycidylether on the grafted glass fibers: (——) water; (–··–) ethylenglycol; (– – –) phenylglycidylether; (O) St; (●) MMA.

TABLE III
Mechanical Properties of Grafted Glass Cloth-Reinforced Epoxy Resin Composites[a]

Glass cloth treatment		Flexural strength [(N/m^2) $\times$ 10^{-7}]	Flexural modulus [(N/m^2) $\times$ 10^{-7}]	Interlaminar shear strength [(N/m^2) $\times$ 10^{-7}]
None		53.4 (52.0)	2479 (2355)	4.8 (3.8)
MMA-grafted	(a)	57.8 (53.0)	2508 (2408)	5.4 (4.0)
	(b)	58.2 (54.4)	2530 (2440)	5.8 (4.0)
	(c)	58.0 (57.2)	2558 (2515)	6.0 (5.6)
St-grafted	(d)	56.8 (53.1)	2510 (2410)	5.2 (3.9)
	(e)	58.0 (54.8)	2574 (2430)	5.8 (4.1)
	(f)	60.2 (59.4)	2635 (2594)	6.2 (6.0)
PolyMMA-coated	(g)	55.3 (52.4)	2485 (2360)	5.0 (3.8)
PolySt-coated	(h)	55.6 (52.5)	2490 (2370)	5.0 (3.8)

[a] ( ): Boiling test for 72 h, at 100°C. (a) Grafting 3.2%; (b) grafting 9.5%; (c) MMA–MAA (90:10) grafted; grafting 4.2%; (d) grafting 2.8%; (e) grafting 8.6%; (f) St–GMA (95:5) grafted; grafting 5.6%; (g) coating 7.5 wt % to a hydrothermal-treated glass cloth; (h) coating 8.2 wt % to a hydrothermal treated glass cloth.

Scanning Electron Microscopy of Composite Fracture Surface

An example is shown in Figure 9. For composite materials prepared with untreated glass cloth or a hydrothermal treated glass cloth, the glass fiber is completely separated from the resin, while in the composite materials, prepared with grafted glass cloth, strong bonding between the glass surface and the resin can be clearly observed.

CONCLUSION

Graft copolymerization of glass fiber containing unsaturated hydrocarbon groups is similar to that usually observed with ordinary polymers. Mechanical properties of composites containing the grafted glass cloth are markedly improved. The better shear resistance possibly results from the improvement in the wetting of the fiber by the resin which results from polar interaction and
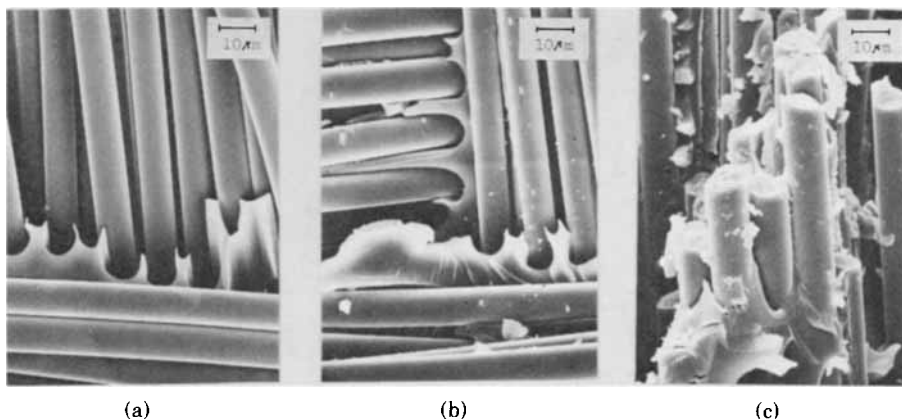

(a)   (b)   (c)

Fig. 9. Electron micrographs of the surface of composites after tensile fracture ($\times$ 1000): (a) untreated glass cloth; (b) hydrothermal treated glass cloth; (c) fracture surface of St–GMA (95:5, grafting = 5.6%).

possibly also from the formation of chemical links between the grafted glass fiber and the epoxy resin.

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