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Graft Copolymerization of Glass Fiber and Its Application

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ABSTRACT

Glass fiber, introduced with unsaturated groups at silanol groups on its surface, was graft copolymerized with styrene and methyl methacrylate by the sealed-tube polymerization method with nitrogen substitution, using benzoyl peroxide (BPO) and cumene hydroperoxide (CHPO) as initiators. The graft copolymerization behavior was investigated. In the case when BPO was used as the initiator, the graft efficiency was extremely low but the graft copolymerization behavior was similar to that of the usual organic polymers. On the other hand, when CHPO was used, both percent grafting and graft efficiency were very high. Further, various properties of composite materials containing grafted glass cloth as a constituent were studied, and it was found that flexural strength, flexural modulus, and interlaminar shear strength increased proportionally to the increase of the percent grafting, and that these values of the composite materials were decreased by only a small extent in the boiling test.

INTRODUCTION

It is well-known that the mechanical, electrical, and water-resisting properties of composite materials containing glass fiber as a constituent are lowered when the cohesion between glass fiber and the matrix is incomplete. At present, various coupling agents such as an alkoxysilane have been developed and put to practical use for the improvement of these properties, but no satisfactory results have been obtained in forced deterioration tests such as the boiling test [1-7].

Recently, various studies on grafted glass fibers, obtained by grafting polymerizable monomers to glass fiber by means of the ion polymerization method, were reported [8-14]. By the use of such grafted glass fibers in composite materials it may be possible to modify the above-mentioned defects of composite materials and also improve their mechanical properties, especially their interlaminar shear strength and their impact strength. In the present study, glass fiber underwent graft copolymerization with styrene or methyl methacrylate by means of the sealed-tube polymerization method and their graft-copolymerization behavior as well as various properties of the composite materials made of the grafted glass fiber were investigated.

EXPERIMENTAL

Glass Fibers and Reagents

E glass fiber (SiO_2 54.5%, Al_2O_3 14.5%, CaO 17.0%, B_2O_3 8.5%, MgO 4.0%, TiO_2 1.0%) was subjected to hydrothermal treatment under various conditions and used as the sample fiber. Monomers of styrene, methyl (ethyl, n-butyl) methacrylate, glycidyl methacrylate, methacrylic acid, allyl glycidyl ether, and benzene (1st grade reagents) were vacuum distilled and used for experiments. Benzoyl peroxide (BPO), purified by recrystallization, and cumene hydroperoxide (CHPO) (special grade reagent), without further purification, were used as the initiators.

Grafting Procedure

Glass fiber, introduced with double bonds, was dipped in benzene solutions of monomers and initiators of various concentrations. Graft copolymerization was carried out at 40-80°C by the sealed-tube polymerization method with nitrogen substitution. After the prescribed reaction time, the reaction was stopped by the addition of methanol. By repeating reprecipitation with acetone-methanol, the homopolymers produced were removed. The remaining homopolymers were extracted with acetone in a Soxhlet extractor for 15-30 h. The graft polymer were dried, and percent grafting and the graft efficiency were calculated:

$$\%\ \text{Grafting} = \frac{\text{weight of grafted polymer}}{\text{weight of original sample}} \times 100$$

$$\text{Grafting efficiency} = \frac{\text{weight of grafted polymer}}{\text{weight of grafted polymer} + \text{weight of homopolymer}} \times 100$$

Measuring Methods for Properties

(a) Tensile strength, breaking elongation, and the Young's modulus of the grafted glass fiber were measured with a K.S.-type fiber tester according to the reported method [15].

(b) The contact angle of the grafted glass fiber was measured by means of the dropping method according to the reported method [15].

(c) Analysis of the formation functional group. Silanol groups on the surface of the glass fiber were measured by means of the method of Boehm et al. [16]. Unsaturated groups were introduced according to the method of Weber et al. [17] by the reaction with allylglycidyl ether at 0°C for 10 h, and the unsaturated groups introduced were determined by means of the method of Weber et al. [18].

(d) Observation with a scanning electron microscope. Fracture surfaces of selected samples were examined in the Mini-SEM-MSM type scanning electron microscope (Akashi Seisakusho Ltd.) for the effects of treatment on the fiber surface and fiber resin bonding.

(e) Composite fabrication. The resin used for the composite characterization was Epcot 828 epoxy, which was cured with meta-phenylenediamine. The grafted glass cloths were carefully aligned in a mold, and 2 g samples of each were made into composite bars measuring 30 mm × 2.5 mm × 1.05 mm which then contained a volume fraction of the grafted glass cloths of 0.52. The mold was heated at 150°C for 1 h.

Flexural strength and modulus were measured by 3-point bending 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.

TABLE 1. Silanol Groups by Boiling Water Treatment and Pendant Unsaturated Groups

	Water temperature (°C)								
	30			60			100		
Time (h):	1	5	15	1	5	15	1	5	15
Silanol group (× 10^4 mol/g)	6.288	6.466	7.288	7.498	7.607	8.082	8.101	8.125	8.126
Unsaturated group (× 10^4 mol/g)	6.16	7.15	8.04	9.11	11.26	12.35	12.82	13.06	13.25

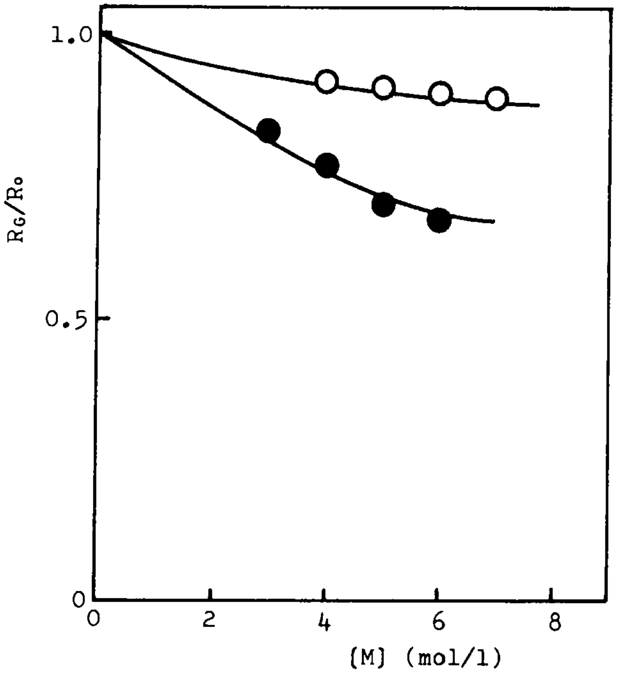

FIG. 1. Influence of monomer concentration on the rate of the graft polymerization. [BPO] = 0.04 mol/L, [GF] = 20 g/L, at 80°C. (○) St, (●) MMA.

RESULTS AND DISCUSSION

Preparation of Unsaturated Group-Introduced Glass Fiber

Silanol groups, formed by the hydrothermal treatment [19] of glass fiber under various conditions, were measured and the results are summarized in Table 1. The formation of silanol groups was likely to increase rapidly at the initial period of the reaction, and the higher the reaction temperature, the more the silanol groups formed. The results of the introduction of unsaturated groups by the reaction of silanol groups formed with allyl glycidyl ether (AGE) are also shown in Table 1. The amount of unsaturated groups introduced is generally larger than the amount of silanol groups. This may be caused by the adsorption of AGE on glass fiber in addition to the reaction of AGE with silanol groups of the glass fiber.

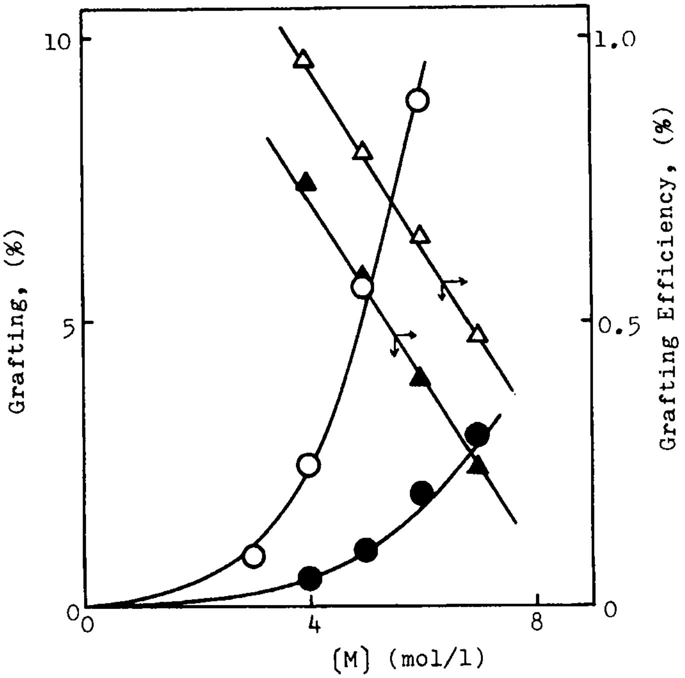

FIG. 2. Influence of monomer concentration on percent grafting and grafting efficiency. [BPO] = 0.04 mol/L, [GF] = 20 g/L, for 60 min at 80°C. Percent grafting: (○) St, (●) MMA. Grafting efficiency: (△) St, (▲) MMA.

Graft Copolymerization of Styrene (St), Methyl Methacrylate (MMA)

Graft copolymerization of unsaturated groups (introduced in glass fibers and used as a backbone polymer) with monomers of various concentrations and with BPO as the initiator was studied. The rate of the graft copolymerization is plotted against the concentration of the monomer in Fig. 1.

As can be seen from Fig. 1, the effect of MMA on the rate of the graft copolymerization is larger than that of St. Similar results have been observed by Imoto et al. on the graft copolymerization of PVC [20] and by Scanlan on the graft copolymerization of dihydromycene [21]. In the case of the more active monomer, the reinitiating effect of the backbone polymer is so large that the presence of the backbone polymer has little effect on the rate of graft copolymerization. In the case of MMA, which is a less active monomer than St, the reinitiating

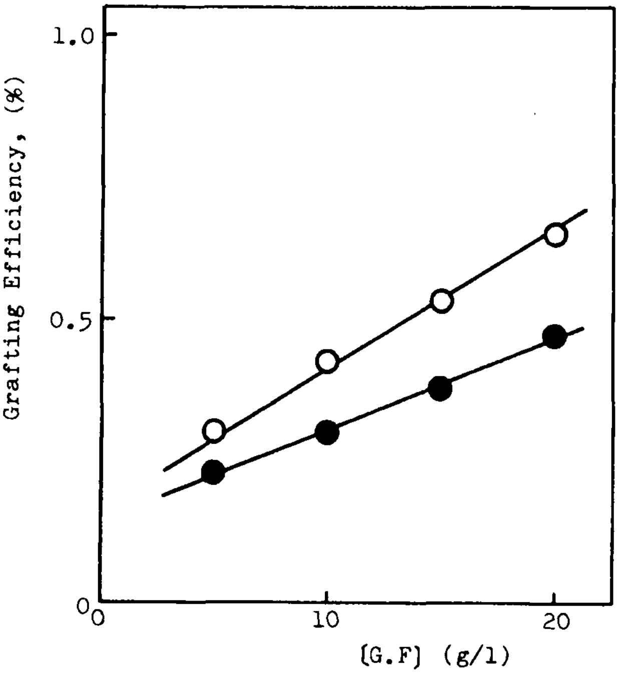

FIG. 3. Effect the backbone glass fiber concentration on grafting efficiency. [BPO] = 0.04 mol/L, [M] = 6 mol/L, for 60 min at 80° C. (○) St, (●) MMA.

reaction is naturally less, and the effect on the rate of the graft copolymerization may be large.

The percent grafting and the grafting efficiency are plotted against the monomer concentration in Fig. 2. The percent grafting increase in proportion to the monomer concentration. The rate of increase for St is larger than for MMA. On the other hand, the grafting efficiency generally decrease linearly with an increase of the monomer concentration.

Figure 3 shows the relation between the grafting efficiency and the backbone polymer concentration. For both St and MMA the grafting efficiency increases in proportion to the increase in the backbone polymer concentration. This suggests that the increase of the backbone polymer is related to the increase of active points for grafting.

By considering the graft-copolymer formation as a hydrogen abstraction reaction (abstraction of hydrogen at the α-carbon atom of the allyl group) of the backbone polymer by the primary radical formed from the initiator, the graft-copolymerization reaction can be written as

$$I \longrightarrow 2R^{\bullet} \qquad K_1 \tag{1}$$

$$R^{\bullet} + M \longrightarrow M^{\bullet} \qquad K_2 \tag{2}$$

$$M^{\bullet} + nM \longrightarrow Mn^{\bullet} \qquad K_3 \tag{3}$$

$$R^{\bullet} + P \longrightarrow P^{\bullet} \qquad K_4 \tag{4}$$

$$Mn^{\bullet} + P \longrightarrow P^{\bullet} + P' \qquad K_5 \tag{5}$$

$$P^{\bullet} + nM \longrightarrow PMn^{\bullet} \qquad K_6 \tag{6}$$

$$\left.\begin{aligned} Mn^{\bullet} + Mn^{\bullet} &\longrightarrow P' \\ PMn^{\bullet} + Mn^{\bullet} &\longrightarrow PP' \end{aligned}\right. \qquad K_7 \tag{7}$$

where I = initiator, M = monomer, P = backbone polymer, P' = homopolymer, PP' = graft polymer, $R^{\bullet}$ = initiator radical, $Mn^{\bullet}$ = growth polymer radical, and $P^{\bullet}$ = backbone polymer radical.

According to Okamura et al. [22], the graft efficiency of such a graft copolymerization can be described by

$$\text{Grafting efficiency} = \frac{[P]}{K_6[M]}\left\{\frac{K_4(fK_1[I]K_7)^{1/2}}{K_2[M]} + K_5\right\} \tag{8}$$

Equation (8) means that grafting efficiency increases with an increase in backbone polymer concentration [P] and decreases with an increase of the monomer concentration [M]. The results of the present study are in good agreement with Eq. (8).

The effects of the polymerization temperature on the percent grafting and on the grafting efficiency are shown in Fig. 4. For both St and MMA, the percent grafting tends to increase with increasing polymerization temperature while the grafting efficiency tends to decrease. This suggests that the activation energy of the initiation of polymerization may be larger for both St and MMA than the activation energy of the chain transfer reaction.

The results of our investigation on the type and the concentration of the initiator are summarized in Table 2. In the case of using BPO as the initiator, the precent grafting as well as the grafting efficiency, though low, tends to increase with an increase of the initiator concentration. In the case of CHPO, both percent grafting and grafting efficiency are considerably larger than with BPO. Also, in this case the graft-copolymerization behavior is strongly affected

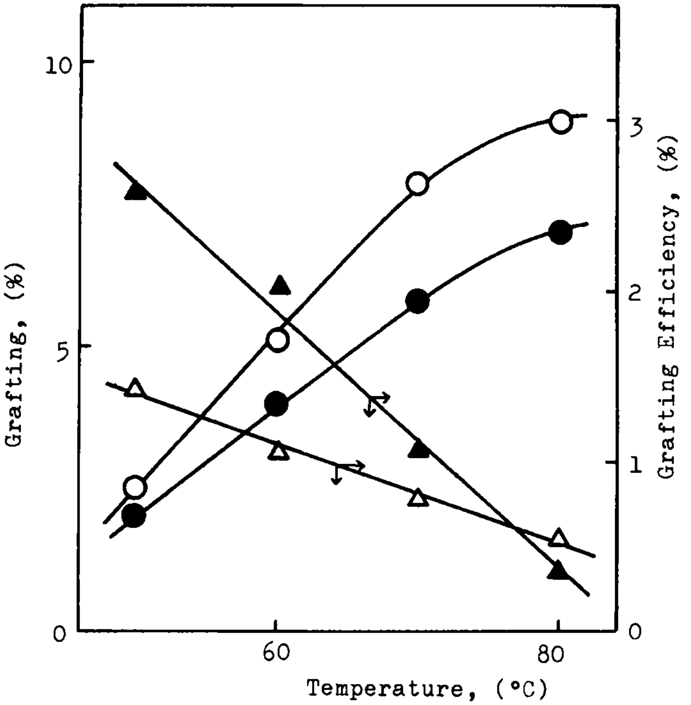

FIG. 4. Effect of the polymerization temperature on percent grafting and grafting efficiency. [BPO] = 0.04 mol/L, [M] = 6 mol/L, [GF] = 20 g/L, for 60 min at 80°C. Percent grafting: (○) St, (●) MMA. Grafting efficiency: (△) St, (▲) MMA.

by the concentration of CHPO, and an optimum concentration (in the present experiment, 0.02 mol/L) exists. Further, graft-copolymerization behavior in the presence of CHPO depends upon the nature of the monomer. That is, in the case of St both the percent grafting and the grafting efficiency are very large, while for MMA little effect can be observed. This is because hydroperoxides such as CHPO, owing to their mutual interaction with St, form radicals relatively easily in the monomer [23, 24] while such mutual interaction between MMA and CHPO is only slight. As reported by Walling et al. [25], the activation energy of initiation is as little as 25 kcal/mol for St. Therefore, when using St, CHPO reacts more effectively than BPO.

Further, by the use of methyl, ethyl, and n-butyl methacrylates for graft copolymerization, the effect of the substituent on the percent grafting was investigated. The results are shown in Fig. 5. As can be seen, the larger the substituent in the monomer the more

TABLE 2. Effect of the Type and the Concentration of the Initiator on the Graft Polymerization

		[C] (mol/L)	Time (min)	% Grafting	Grafting efficiency	Total conversion (%)
[GF] = 20 g/L at 80° C; [styrene] = 6 mol/L	BPO	0.02	60	5.3	0.42	6.8
			120	9.0	0.85	14.5
			180	9.5	1.55	24.2
		0.04	60	8.9	0.65	7.0
			120	10.4	1.24	15.2
			180	12.8	8.05	25.8
			240	16.3	9.85	36.5
		0.06	60	8.8	0.68	10.5
			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
[MMA] = 6 mol/L; [GF] = 20 g/L at 80° C	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
	CHPO	0.04	30	0.6	0.08	0.91
			60	1.4	0.11	1.82
			90	2.1	0.18	2.68
			120	3.8	0.25	4.05

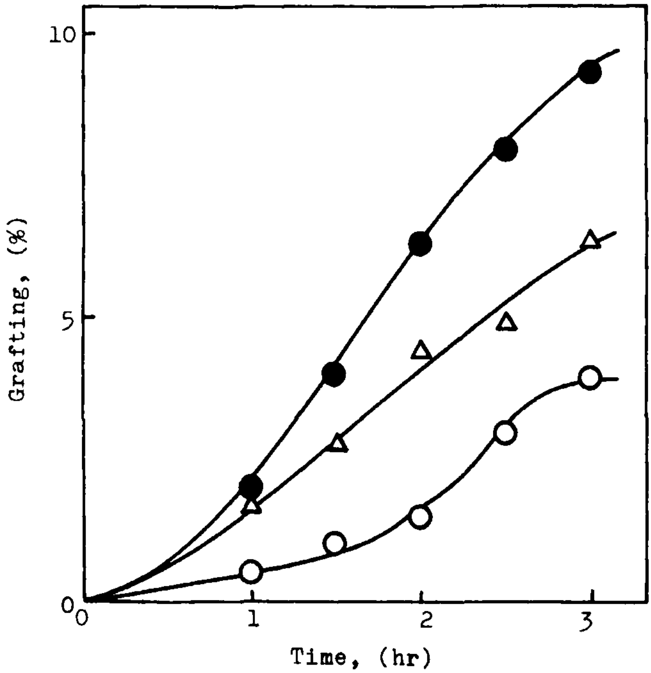

FIG. 5. Effect of the substitutions of monomer on percent grafting. [M] = 6 mol/L, [BPO] = 0.04 mol/L, [GF] = 25 g/L at 80°C. Monomer: (●) methyl, (△) ethyl, and (○) n-butyl methacrylate.

difficult is the graft copolymerization. This tendency is similar to that found in the graft polymerization of cellulose [26].

Physical Properties of the Grafted Glass Fiber

Tensile strengths and Young's modulus of the grafted glass fiber were measured; the results are shown in Figs. 6 and 7. The tensile strength generally increases linearly with an increase of the percent grafting within the experimental conditions. The tendency for an increase of tensile strength of styrene-grafted glass fiber was somewhat larger than that of methyl methacrylate-grafted glass fiber. Young's modulus generally decreases linearly with an increase of percent grafting; this tendency is especially large for styrene-grafted glass fiber.

The contact angles of various grafted glass fibers were measured by means of the dropping method; the results are shown in Fig. 8.

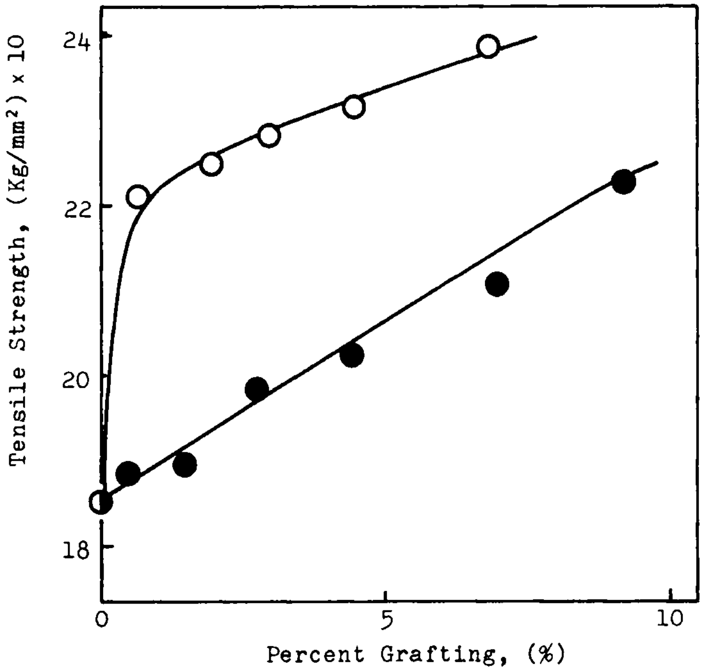

FIG. 6. Relationship between the tensile strength of the graft glass fiber and percent graftings. (○) St, (●) MMA.

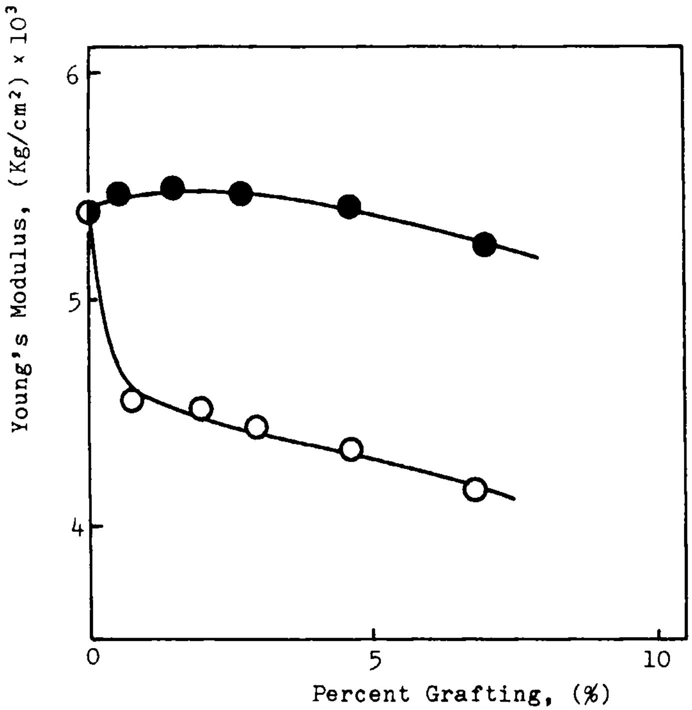

FIG. 7. Relationship between Young's modulus of the graft glass fiber and percent grafting. (○) St, (●) MMA.

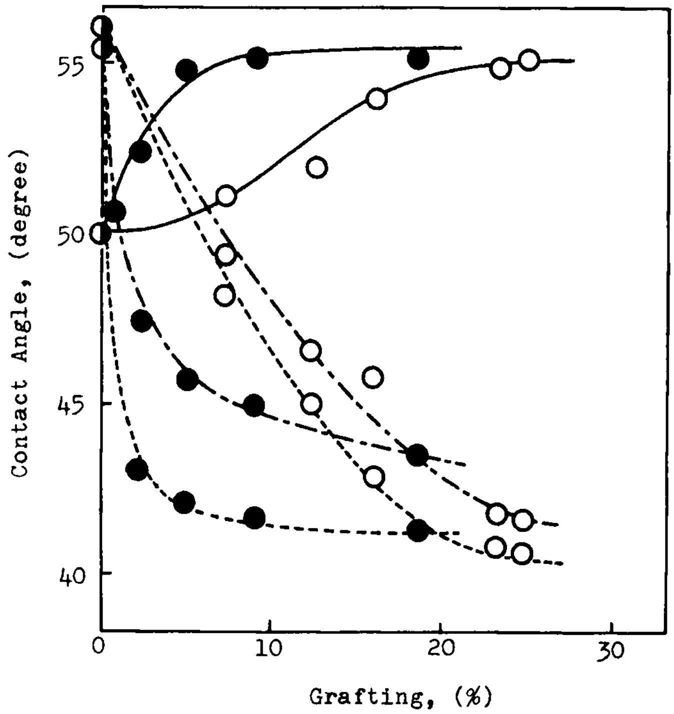

FIG. 8. Contact angle of water, ethylene glycol, and phenylglycidylether on the graft glass fibers. (—) Water, (-•) ethylene glycol, and (- -) phenylglycidylether. (○) St, (●) MMA.

TABLE 3. Mechanical Properties of Grafted Glass Cloth-Reinforced Epoxy Resin Composites[a]

Glass cloth treatment[b]		Flexural strength (kg/mm^2)	Flexural modulus (kg/mm^2)	Interlaminar shear strength (kg/mm^2)
None		53.4 (52.0)	2479 (2355)	4.8 (3.8)
MMa grafted:	(1)	57.8 (53.0)	2508 (2408)	5.4 (4.0)
	(2)	58.2 (54.4)	2530 (2440)	5.8 (4.0)
	(3)	58.0 (57.2)	2558 (2515)	6.0 (5.6)
St grafted:	(4)	56.8 (53.1)	2510 (2410)	5.2 (3.9)
	(5)	58.0 (54.8)	2574 (2430)	5.8 (4.1)
	(6)	60.2 (59.4)	2635 (2594)	6.2 (6.0)

[a] The values in parentheses are for the boiling test for 72 h at 100° C.

[b] (1) % grafting 3.2%; (2) % grafting 9.5%; (3) MMA-MAA (90:10) grafted, % grafting 4.2%; (4) % grafting 2.8%; (5) % grafting 8.6%; (6) St-GMA (95:5) grafted, % grafting 5.6%.

The contact angle with water generally increases linearly with an increase of the percent grafting, while the contact angles decreases with ethylene glycol and phenyl glycidyl ether.

Mechanical Properties of the Grafted Glass Fiber Composite Materials

Various properties of composite materials consisting of St (MMA)-grafted glass cloth and epoxy resins were measured; the results are summarized in Table 3. The flexural strength and the flexural modulus general increase with an increase of the percent grafting of glass cloth used, while the interlaminar shear strength varies little. The decrease of the interlaminar shear strength after boiling treatment is similar to that of the usual glass cloth composite materials, and it can therefore be considered that the St- and MMA- grafted cloth has little effect on the interlaminar shear strength.

For the improvement of interlaminar shear strength, glass cloth composite materials containing glycidyl methacrylate (GMA) or methacrylic acid (MAA) as a comonomer component can be used owing to the reaction of epoxy or carbonyl groups on the graft branch with the matrix to form a cross-linking structure.

The fracture surfaces of these composite materials were observed

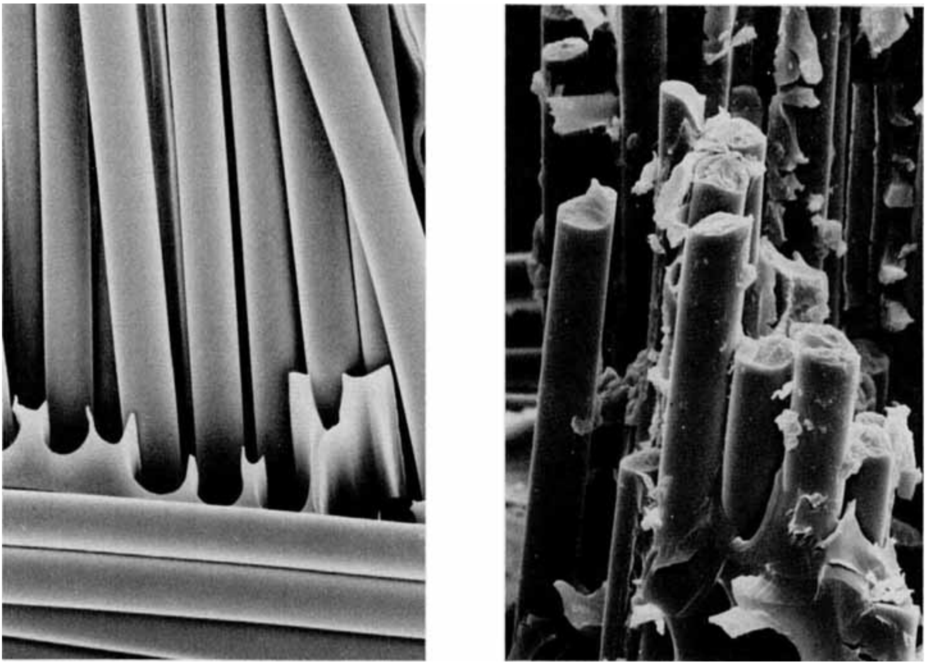

FIG. 9. Electron micrographs of a glass cloth-epoxy composite tensile fracture (×1000). Left: Untreated glass cloth. Right: St-GMA (95:5) grafted glass cloth (grafting 5.6%).

with a scanning electron microscope. Examples are shown in Fig. 9. As can be seen from the fracture surface, in the composite materials prepared by use of untreated glass cloth the glass layer is completely separated from the resin layer, while in the composite materials prepared by use of grafted glass cloth a strong affinity between the glass layer and the resin layer can be clearly observed.

REFERENCES

[1] E. J. Kohn, A. G. Sands, and R. C. Clark, Ind. Eng. Chem., Prod. Res. Dev., 7, 179 (1968).
[2] K. Nelson, SPE Trans., 4, 124 (1964).
[3] A. S. Kenyon, J. Colloid Interface Sci., 27, 761 (1968).
[4] B. M. Vanderbilt and R. E. Clayton, Ind. Eng. Chem., Prod. Res. Dev., 4, 18 (1965).

[5] H. Ishida and J. L. Koeving, J. Polym. Sci., Polym. Phys. Ed., 17, 1807 (1979).

[6] J. L. Koeving and P. T. K. Shih, J. Colloid Interface Sci., 36, 247 (1971).

[7] D. A. Scola, Ibid., 64, 480 (1978).

[8] H. Yoshida and F. Higashide, J. Appl. Polym. Sci., 18, 939 (1974).

[9] E. Papirer and V. T. Ngugen, J. Polym. Sci., Polym. Lett., 10, 167 (1972).

[10] E. Papirer, V. T. Ngugen, and J. B. Donnet, Ibid., 9, 195 (1971).

[11] N. Fery, R. Laible, and K. Hamaum, Angew. Makromol. Chem., 34, 81 (1973).

[12] T. E. Lipatova and I. S. Skorynina, J. Polym. Sci., C, 16, 2341 (1967).

[13] F. Runge, H. Ehrhardt, and G. Penndorf, Makromol. Chem., 81, 68 (1965).

[14] S. Yamashita and S. Kohjiya, J. Appl. Polym. Sci., 17, 2935 (1973).

[15] A. Tanaka, T. Fujiisawa, and R. Yosomiya, J. Polym. Sci., Polym. Chem. Ed., 18, 2267 (1980).

[16] H. P. Boehm and M. Schneider, Z. Anorg. Allgem. Chem., 301, 326 (1959).

[17] K. Gutread and H. S. Weber, Proceedings of the 16th Annual Technical and Management Conference, Reinforced Plastics Industry, SPI, February 1961, 8-C.

[18] F. E. Critchfield, G. L. Funk, and J. B. Jonson, Anal. Chem., 28, 76 (1956).

[19] V. Ya. Dauydov, A. V. Kiselev, and L. T. Zhuravlev, Trans. Faraday Soc., 60, 2254 (1964).

[20] M. Imoto, Y. Minoura, and T. Hayashi, High Polym. Jpn., 15, 26 (1958).

[21] J. Scanlan, Trans. Faraday Soc., 50, 756 (1954).

[22] T. Maekawa, K. Hayashi, K. Uno, and S. Okamura, High Polym. Jpn., 21, 323 (1964).

[23] C. Walling and Y. W. Change, J. Am. Chem. Soc., 76, 4875 (1954).

[24] G. Schröder, J. Polym. Sci., 31, 309 (1958).

[25] C. Walling and L. Heaton, J. Am. Chem. Soc., 87, 38, 48 (1965).

[26] M. Negishi, Y. Nakamura, T. Kakinuma, and Y. Iizuka, J. Appl. Polym. Sci., 9, 2227 (1965).

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