

Performance Improvement of Glass-Fiber-Reinforced Polystyrene Composite Using a Surface Modifier.

I. Synthesis and Characterization of Poly(γ -MPS-co-styrene)

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SYNOPSIS

Poly(γ -MPS-co-styrene), as a surface modifier of glass-fiber-reinforced polystyrene composite, was synthesized to improve the adhesion between glass fiber and polystyrene matrix. The copolymerization was carried out using AIBN as the initiator at 70°C. The reactivity ratios of γ -MPS and styrene were determined by the Finemann–Ross method. The result was r_1 (styrene) = 0.10, r_2 (γ -MPS) = 0.86. Judging from these results, the copolymerization of γ -MPS and styrene was azeotropic copolymerization and the synthesized copolymer was a random one. Thermal stability of the copolymer was improved as the content of silane in the copolymer was increased and the glass transition temperature decreased. The surface-modified glass fiber was investigated with Fourier transform infrared spectroscopy (FTIR). The glass fiber surface was effectively modified with the copolymer. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Fiber-reinforced thermoplastic composites have gained considerable interest since the mid-1980s for their unique characteristics. Thermoplastic composites have an advantage over thermoset composites in that they are tough and easily processable and low cost manufacturing is possible. Engineering plastics such as poly(phenylene sulfide) (PPS), poly(ether ether ketone) (PEEK), poly(phenylene oxide) (PPO), and poly(ether sulfone) (PES) and general purpose plastics such as polypropylene (PP), polyethylene (PE), and polystyrene (PS) are used as the matrix of thermoplastic composites. Recently, much interest has been concentrated on general-purpose plastics which have the advantage of low cost.^{1–3}

The mechanical properties of fiber-reinforced composites largely depend on the interphase between the reinforcement and the matrix. Adhesion between the reinforcement and the matrix plays an

important role in improving the mechanical properties of composites and therefore much interest is focused on the adhesion promotion of thermoplastic composites. Coupling agents, which have bifunctionality, are used to improve the adhesion between the reinforcement and the matrix. Among them, silane coupling agents are generally used because of their range of molecular structures and their effectiveness.⁴ By introducing γ -aminopropyltrimethoxysilane (γ -APS) into glass fiber/poly(butylene terephthalate) and glass fiber/epoxy composites, flexural strength and tensile strength of their composites were improved considerably while cationic vinylbenzyltrimethoxysilane was effective in promoting the mechanical properties of glass fiber/PP composite.^{4–6} Mechanical properties of glass fiber/PE and glass fiber/PS composites were improved by modifying the glass fiber surface with γ -methacryloxypropyltrimethoxysilane (γ -MPS) and β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane was also effective in adhesion promotion in glass fiber/SAN and glass fiber/ABS composites.^{4,7} In glass fiber/polyester and glass fiber/epoxy composites, silane coupling agents can form a chemical bond with the reinforcement and are compatible with the polymer

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matrix. Therefore, the mechanical properties of polymer composites can be improved considerably. However, in the case of glass fiber/PE and glass fiber/PP composites, mechanical properties were not increased drastically since silane coupling agents were not compatible with the polymer matrices. To improve the compatibility between the reinforcement and the polymer matrix, silane-modified copolymer was introduced into glass fiber/PE and glass fiber/PP composites. It proved to be effective in promoting the mechanical properties of these composites.⁴

The purpose of this research paper was, therefore, to investigate the surface modification of glass fiber using a copolymer as an adhesion promoter. Poly(γ -MPS-*co*-styrene) was synthesized through radical copolymerization and the glass fiber surface was modified with this synthesized copolymer. We determined the reactivity ratio of each monomer and the thermal properties of poly(γ -MPS-*co*-styrene) and surface-modified glass fiber was analyzed with diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

EXPERIMENTAL

Materials

Styrene used in the copolymerization was supplied by Kanto Chemical Co. It was purified by washing with a 1N NaOH solution to remove the inhibitor, then washed with distilled water and dried over anhydrous CaCl₂. Vacuum distillation was performed under 10 Torr, at 40°C before use. γ -Methacryloxypropyltrimethoxysilane (γ -MPS) was obtained from Dow Corning Co. and purified under 1.5 Torr, at 90°C, by fractional distillation. Azobisisobutyronitrile (AIBN) was recrystallized from methanol at 30°C. Benzene was dried over P₂O₅ and distilled before use. The glass fiber fabric used as reinforcing material was supplied by Hankook Fiber Co. and dried at 200°C for 10 h. Fabric thickness was 0.12 mm, and filament diameter, 10 μ m.

Preparation of Poly(γ -MPS-*co*-styrene)

Copolymerization of styrene and γ -MPS was carried out in a 500 mL four-necked round-bottomed flask fitted with a mechanical stirrer, condenser, thermometer, and N₂ inlet system. The copolymer was synthesized in benzene solution under N₂ atmosphere using AIBN as the initiator. The monomer concentration in copolymerization was 3M and the

initiator concentration was 5×10^{-4} M. Several copolymers were prepared by varying the mol ratio of γ -MPS and styrene in the initial feed. Polymerization temperature was kept at 70°C and polymerization time was 20 h. The copolymer was precipitated in methanol. The precipitated copolymer was filtered and dried at room temperature under vacuum for 24 h. Figure 1 shows the molecular structures of the monomers and copolymer. Poly(γ -MPS-*co*-styrene) was hydrolyzed in pH 3.5 THF/benzene (50 wt %/50 wt %) cosolvent for 1 h. Figure 2 shows the hydrolysis reaction scheme and hydrolyzed copolymer structure.

Surface Modification of Glass Fiber

Surface modification of the glass fiber was carried out in THF/benzene (50/50) solution for 30 min. Copolymer concentration was varied from 0.025 to 0.5 wt %. Surface-modified glass fiber was dried at room temperature for 48 h before use.

Analyses

Copolymer compositions were determined by elemental analysis using a YANACO MT-2 analyzer. Transmission and DRIFT FTIR spectra were obtained from a Perkin-Elmer 1725-X FTIR spectrometer. A hemispherical diffuse reflectance attachment was mounted into the spectrometer and was used at a resolution 2 cm⁻¹ combining 64 scans. The Kubelka-Munk function was plotted to obtain linear diffuse reflectance spectra and Lorentzian curve-fitting routines were used for spectral analysis.

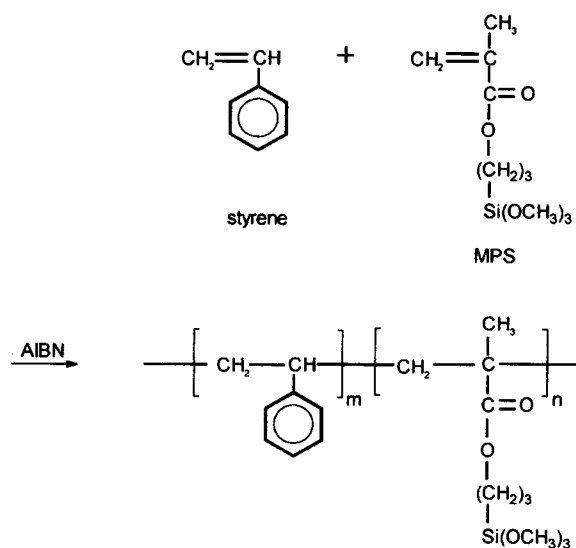


Figure 1 Reaction scheme of γ -MPS and styrene.

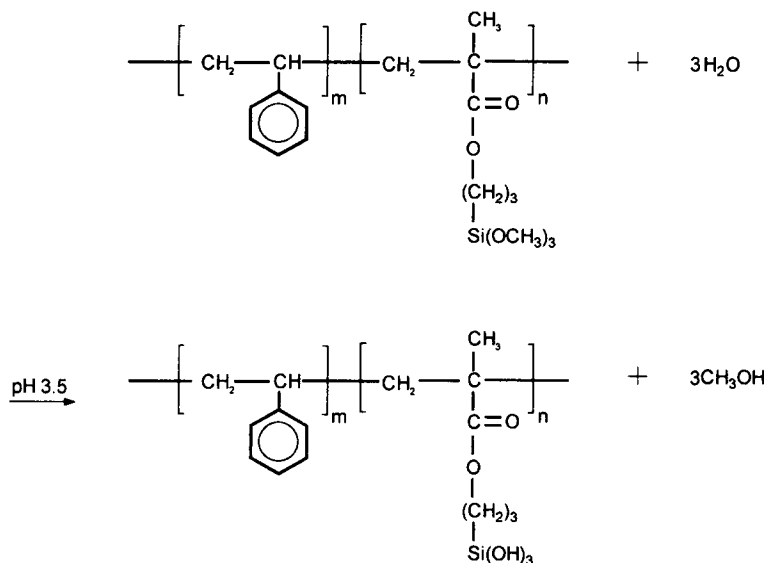


Figure 2 Reaction scheme of poly(γ -MPS-co-styrene) hydrolysis reaction.

The $^1\text{H-NMR}$ spectrum of copolymers was recorded in CDCl_3 using a Bruker AC 80 FT-NMR. Tetramethylsilane (TMS) was used as an internal standard. The glass transition temperature (T_g) of the copolymer was determined by using a DuPont 2100 DSC at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere. The sample weight was 9 ± 1 mg. The thermal stability of the copolymer was investigated using a DuPont 1950 TGA at a heating rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Table I represents the instantaneous copolymer composition and conversion with different mol ratios of γ -MPS and styrene in the feed. The copolymer composition was determined by elemental analysis. Conversion was fixed below 10% to minimize drift in the comonomer composition. The method of Finemann and Ross was used to determine the reactivity ratios of γ -MPS and styrene at low conversion.

The copolymer composition is given by the equation of Finemann and Ross as

$$\frac{F(f-1)}{f} = r_1 \frac{F^2}{f} - r_2$$

where r_1 is the reactivity ratio of styrene, and r_2 , the reactivity ratio of γ -MPS; F represents the mol ratio of styrene and γ -MPS in the feed, and f , their instantaneous compositions in the copolymer. A plot of the left-hand side of the above equation vs. F^2/f gives a straight line with a slope equal to r_1 and intercept equal to $-r_2$. The least-square Finemann-Ross plot is given in Figure 3. The two monomer reactivity ratios calculated are $r_1 = 0.10$ and $r_2 = 0.86$. Experimental data of the reactivity ratio reveal that copolymerization of styrene and γ -MPS is azeotropic copolymerization and that the produced copolymer is a random copolymer. Monomer feed and copolymer composition are the same when the mol fraction of styrene in the feed is 0.13. The mole

Table I Copolymer Composition as a Function of Feed Mol Ratio by Elemental Analysis

Sytrene : γ -MPS Feed Mol Ratio	C (Wt %)	H (Wt %)	O (Wt %)	Si (Wt %)	Copolymer Composition	Conversion (%)
90.0 : 10.0	75.43	8.94	8.31	7.32	63.9 : 36.1	9.83
80.0 : 20.0	71.46	9.24	10.28	9.02	51.6 : 48.4	8.02
70.0 : 30.0	69.76	9.36	11.12	9.76	45.7 : 54.3	8.36
50.0 : 50.0	66.73	10.00	12.39	10.88	41.3 : 58.7	7.49
30.0 : 70.0	65.48	9.66	13.24	11.62	28.4 : 71.6	5.85

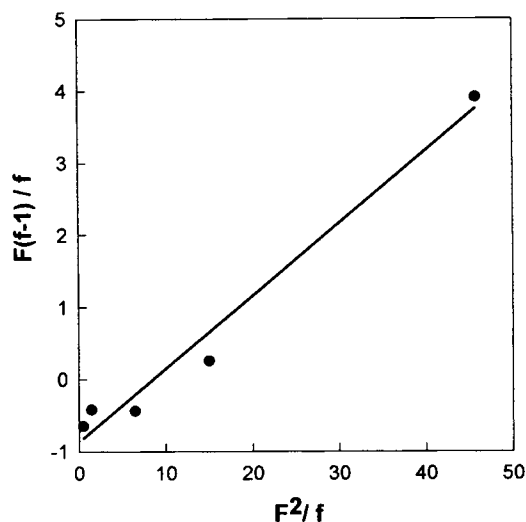


Figure 3 Finemann-Ross plot for the determination of the reactivity ratio.

fraction of styrene in the copolymer is less than that in the feed when the mol fraction of styrene in the feed is less than 0.87 and vice versa. The azeotropic composition can be calculated as follows:

$$f_{\text{styrene}} = \frac{1 - r_{\text{MPS}}}{2 - r_{\text{MPS}} - r_{\text{styrene}}}$$

γ -MPS is more reactive than is styrene toward the radical because r_{MPS} is larger than is r_{styrene} , and as r_1 and r_2 are less than unity, cross-propagation is preferable to homopropagation. The increased reactivity of γ -MPS toward the radical is due to its increased monomer reactivity caused by the polar side chain and enhanced stability of the resulting radical through hyperconjugation with the methyl group. However, conversion is restricted to a certain maximum value due to the steric hindrance of the 1,1-disubstituted structure. Conversion is kept at 23.3% when the mol fraction of γ -MPS in the feed is 5 mol % and it decreases with the increase of γ -MPS content.

Figure 4 represents the transmission FTIR spectra of styrene, γ -MPS, and the radical copolymerized poly(γ -MPS-co-styrene). The peak at 1640 cm^{-1} , which is present in γ -MPS and styrene, disappears in the copolymer. From this result, it can be assumed that γ -MPS and styrene are copolymerized. The peaks at 1087 and 807 cm^{-1} result from antisymmetric and symmetric stretching modes of Si—O—CH₃. The strong peak at 1720 cm^{-1} is the C=O stretching mode, while the band at 2970 cm^{-1} is the aliphatic C—C stretching mode. The bands

at 1300 and 1325 cm^{-1} are associated with ester functionality and the bands at 1463, 1492, and 1684 cm^{-1} are assigned to the in-plane aryl C—C stretching mode. The peak at 3000 cm^{-1} results from the aryl stretching mode present in styrene. The bands at 1812, 1880, and 1953 cm^{-1} are caused by the monosubstituted benzene ring. These results demonstrate that the two monomers effectively copolymerize through radical copolymerization.

Figure 5 is the NMR spectrum of poly(γ -MPS-co-styrene). The peaks at $\delta = 1.0$ –2.4 result from the proton attached to a C—C single bond and the peak at the $\delta = 3.5$ band is due to Si—O—CH₃ protons. The peaks at $\delta = 4.2$ and $\delta = 0.8$ are associated with the protons of O—CH₂ and Si—CH₂, respectively. The peaks at $\delta = 6.5$ –7.0 result from protons of the benzene ring of styrene. From the disappearance of peaks $\delta = 5.0$ –6.0 caused by protons attached to the C—C double bond, it can be shown that the two monomers are radical-copolymerized.

DSC thermograms of the copolymer are presented in Figure 6. Glass transition temperatures (T_g) of the copolymer increase as the content of γ -MPS in copolymer decreases. An increase in the γ -MPS mole fraction in the feed from 0.05 to 0.15 results in a T_g decrease from 75 to 59°C. This trend is due to a free-volume increase as the content of γ -MPS with a long side chain in the copolymer increases. Increase in the mol fraction of styrene in the copolymer results in a corresponding increase in T_g . This indicates that the copolymers produced are random copolymers.

Figure 7 represents the TGA thermograms of copolymers with different mol fractions of γ -MPS. The thermal stability of the copolymer tends to increase with increasing γ -MPS content. Maximum weight loss temperatures were 400, 409, and 414°C when the mol fractions of γ -MPS were 0.05, 0.10, and 0.15. An almost complete weight loss in most of the copolymers occurred above 500°C and the residual weight was dependent on the silicon content in the copolymer. This can be explained by a crosslinking reaction occurring between hydrolyzed γ -MPS molecules. The crosslinking reaction between silane molecules results in network formation and this improves the thermal stability of the copolymers. The crosslinking reaction in this copolymer is facilitated by water being hydrogen-bonded to γ -MPS which is produced during thermal decomposition of the γ -MPS unit.⁸ Therefore, the thermal stability of the copolymer was improved with increasing γ -MPS mol fraction in the copolymer.

FTIR spectra of the copolymer, unhydrolyzed and hydrolyzed in a pH 3.5 solution for 1 h, are presented

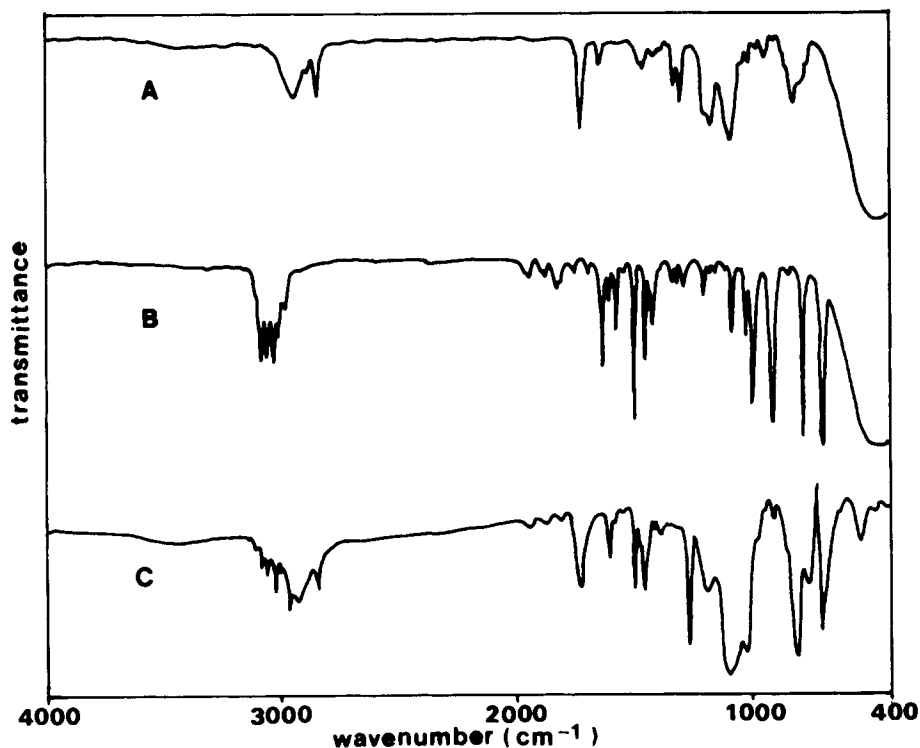


Figure 4 Transmission FTIR spectra of monomer and copolymer: (A) γ -MPS; (B) styrene; (C) poly(γ -MPS-co-styrene).

in Figure 8. The peak intensity of Si—O—C at 1087 and 807 cm^{-1} decreased after hydrolysis and that of Si—OH at 907 cm^{-1} increased after hydrolysis. From this result, it can be suggested that the hydrolysis of Si—O—CH₃ resulted in Si—OH.

Figure 9 shows the DRIFT spectra of heat-treated glass fiber and the poly(γ -MPS-co-styrene)-treated

glass fiber surface. The glass fiber surface was heat-treated at 200°C for 10 h and 0.5 wt % copolymer solution was used for the surface modification of the glass fiber. The strong absorption at 1450 cm^{-1} is assigned to Si—O—Si and the peaks at 1274 and 900 cm^{-1} are assigned to Si—OH. The characteristic peak of C=O stretching at 1720 cm^{-1} and

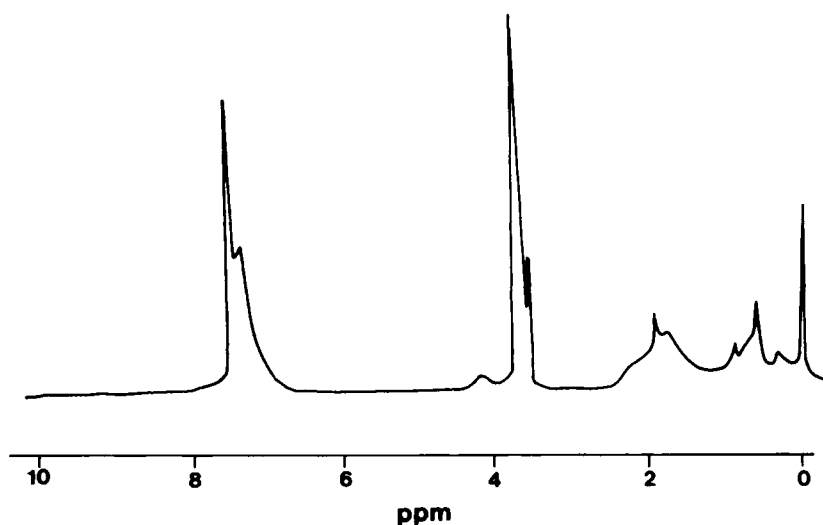


Figure 5 NMR spectrum of poly(γ -MPS-co-styrene).

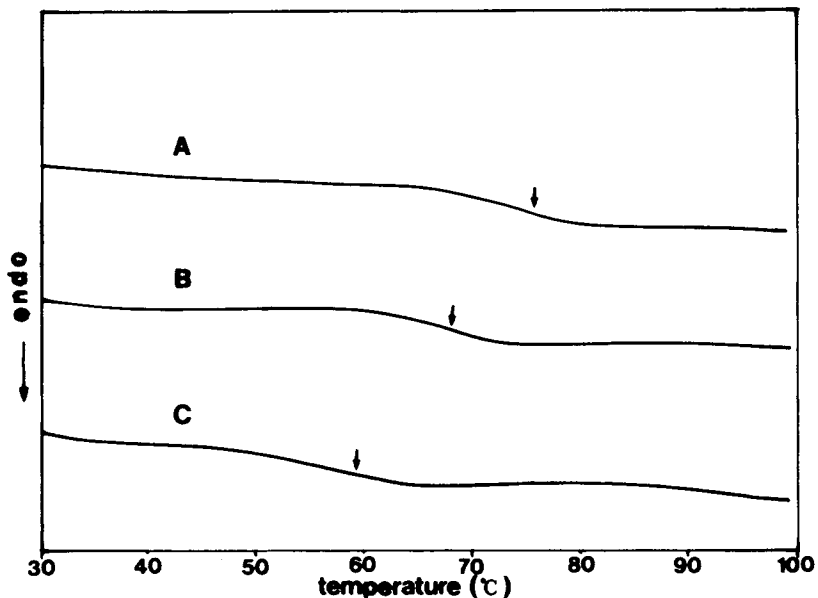


Figure 6 DSC thermograms of poly(γ -MPS-*co*-styrene) as a function of copolymer composition: (A) γ -MPS : styrene = 5 : 95; (B) γ -MPS : styrene = 10 : 90; (C) γ -MPS : styrene = 15 : 85.

C—H stretching at 2970 cm^{-1} appeared in the spectrum of copolymer-treated glass fiber. This means that the copolymer was adsorbed onto the glass fiber surface.

Figure 10 represents DRIFT spectra of the glass fiber treated with the poly(γ -MPS-*co*-styrene) solution with different copolymer concentrations. This

figure focuses on the C=O stretching region. The band at 1720 cm^{-1} is due to the free carbonyl stretching mode and that at 1697 cm^{-1} is from the hydrogen-bonded carbonyl stretching mode. The relative intensity of the free carbonyl stretching peak to the hydrogen-bonded carbonyl stretching peak increases with increase of the copolymer concentra-

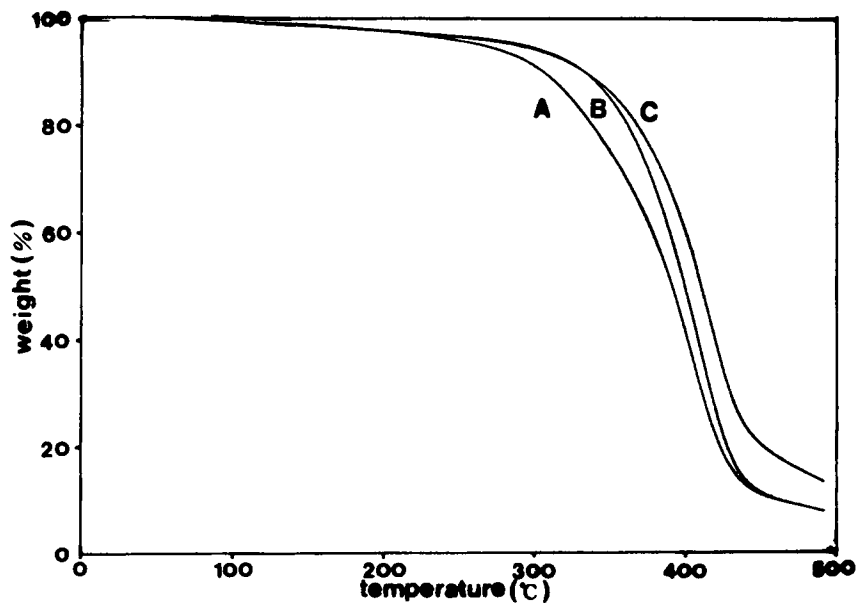


Figure 7 TGA thermograms of poly(γ -MPS-*co*-styrene) as a function of copolymer composition: (A) γ -MPS : styrene = 5 : 95; (B) γ -MPS : styrene = 10 : 90; (C) γ -MPS : styrene = 15 : 85.

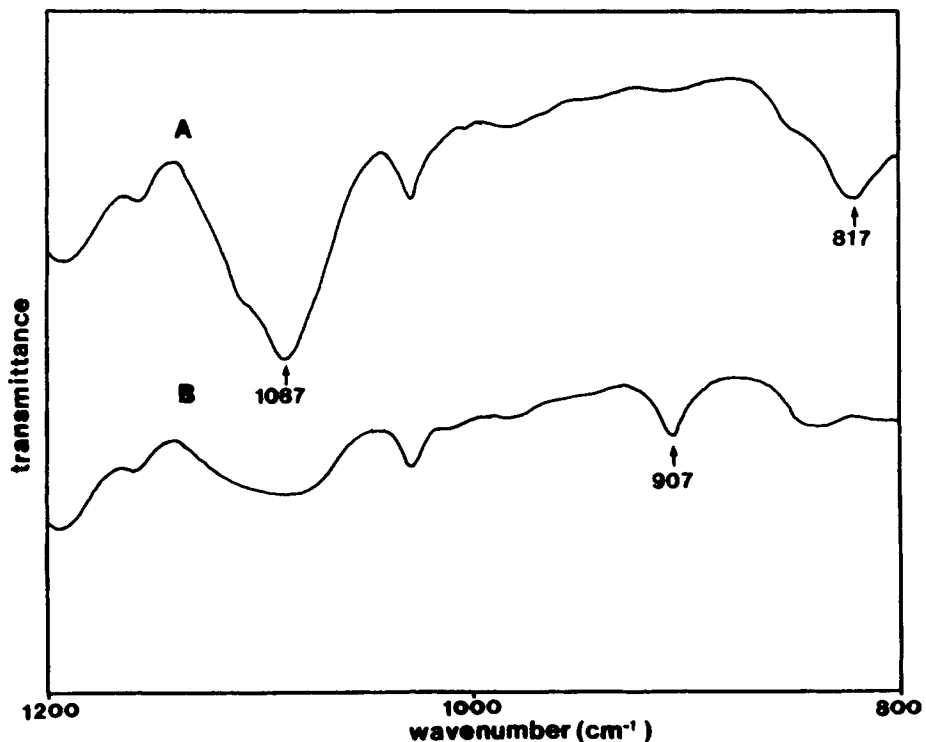


Figure 8 Transmission FTIR spectra of hydrolyzed and unhydrolyzed poly(γ -MPS-co-styrene): (A) unhydrolyzed; (B) hydrolyzed.

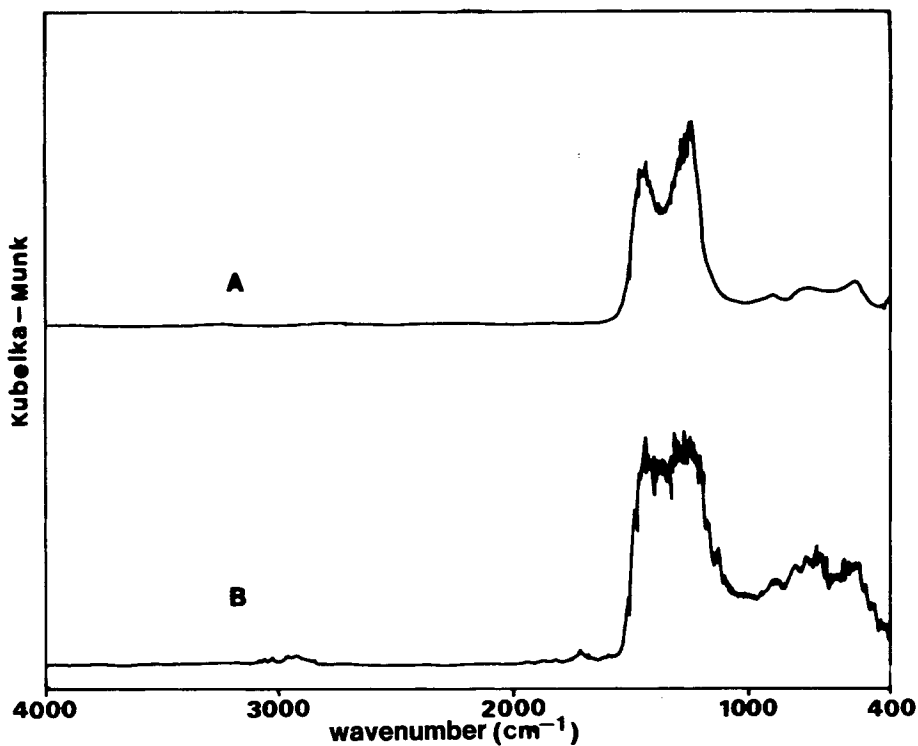


Figure 9 DRIFT spectra of glass fiber surface: (A) heat-treated; (B) poly(γ -MPS-co-styrene)-treated.

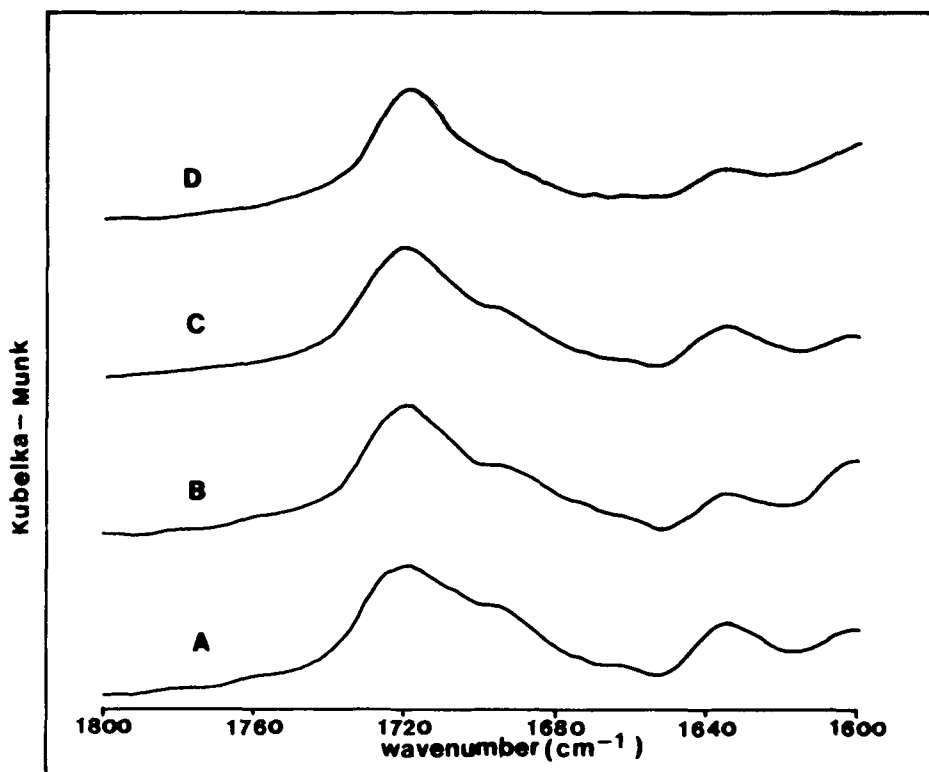


Figure 10 DRIFT spectra of the glass fiber surface treated with poly(γ -MPS-co-styrene) as a function of copolymer concentration: (A) 0.1 wt %; (B) 0.2 wt %; (C) 0.5 wt %; (D) 1.0 wt %.

tion. This indicates that most of the silane in the copolymer is hydrogen-bonded to the glass fiber surface at low copolymer concentration. At high copolymer concentration, only a little of the silane in the copolymer is hydrogen-bonded to the glass fiber surface. At low copolymer concentration, silane is easily adsorbed to the glass fiber surface through condensation and hydrogen bonding with the glass fiber. In the case of high copolymer concentration, silane-modified copolymer forms a multilayer over the glass fiber surface through physical adsorption. So, the amount of the carbonyl group hydrogen-bonded to the glass fiber surface decreases as the copolymer treatment concentration increases. The hydrogen-bonding mechanism between glass fiber and silane in the copolymer is presented in Figure 11.

Figure 12 shows the relative intensity of the free carbonyl peak to the hydrogen-bonded carbonyl peak according to copolymer concentration. The peak intensity was calculated using Lorentzian curve fitting. The intensity of the free carbonyl peak to the hydrogen-bonded carbonyl peak increases with copolymer concentration and the slope decreases with copolymer concentration. This is attributable

to the fact that the quantity of the copolymer adsorbed to the glass fiber surface is not proportional to copolymer concentration. In general, it is reported that the amount of silane adsorbed to the glass fiber surface is proportional to silane concentration at low silane concentration. However, at high silane concentration, it is nearly constant or slightly in-

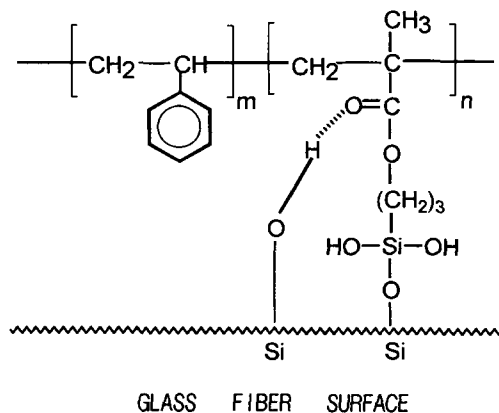


Figure 11 Surface structure of the glass fiber treated with poly(γ -MPS-co-styrene).

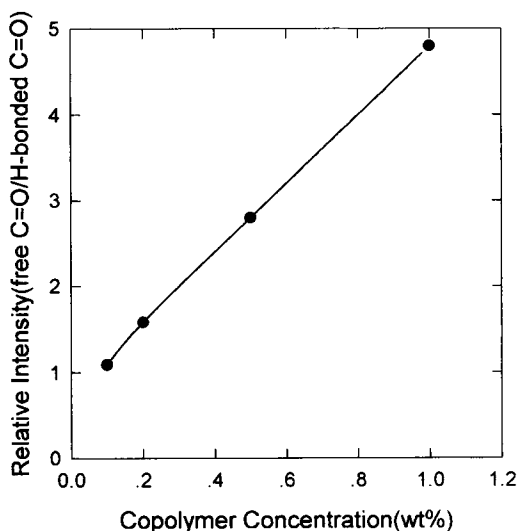


Figure 12 Relative intensity of the free C=O to the hydrogen-bonded C=O as a function of copolymer concentration.

creases with the silane concentration.^{9,15} So, the above result coincides with the general trend.

Figure 13 represents the DRIFT spectra of glass fiber treated with poly(γ -MPS-*co*-styrene) with dif-

ferent copolymer compositions. The copolymer concentration was fixed at 0.1 wt % and the spectra was focused on the 1600–1800 cm^{-1} region. The mol fraction of γ -MPS in the copolymer increased from 5 to 15 mol %. The relative intensity of the free carbonyl stretching band at 1720 cm^{-1} to the hydrogen-bonded carbonyl stretching band at 1697 cm^{-1} decreases as the mol fraction of γ -MPS in the copolymer increases. This is due to the fact that at low copolymer concentration the silane unit which can be hydrogen-bonded to glass fiber surface increases as the silane mol fraction in the copolymer increases. The relative intensity of the free carbonyl band to the hydrogen-bonded carbonyl band calculated by the Lorentzian curve fitting is presented in Figure 14.

CONCLUSIONS

Poly(γ -MPS-*co*-styrene), as a surface modifier of glass-fiber-reinforced polystyrene composite, was synthesized through radical copolymerization. The reactivity ratios of monomers were r_1 (γ -MPS) = 0.86 and r_2 (styrene) = 0.10 and the synthesized

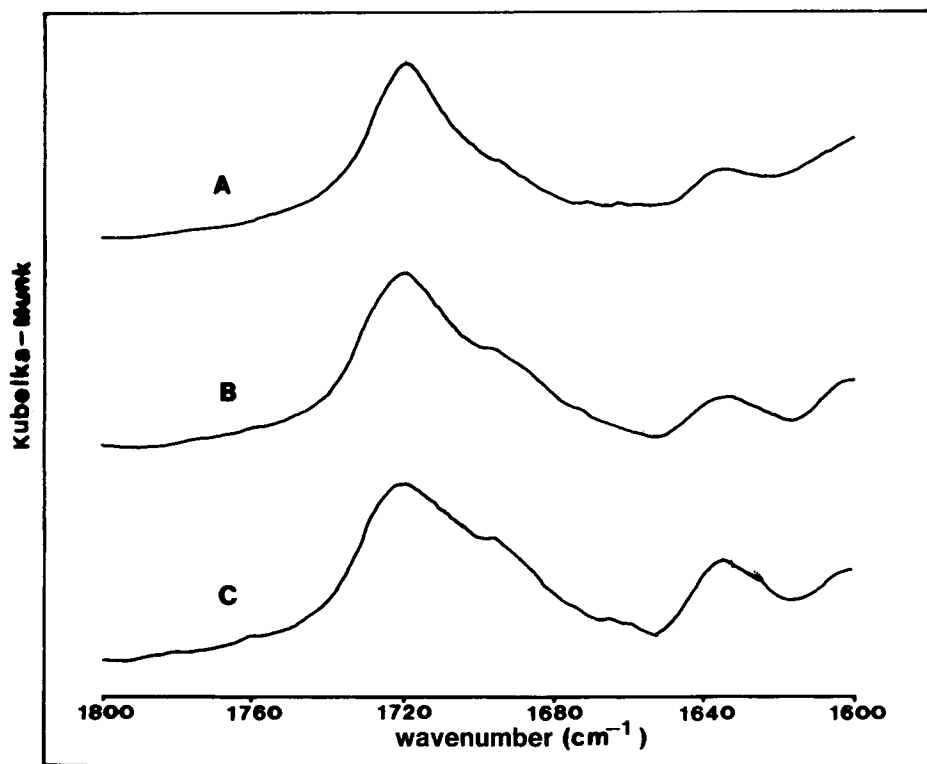


Figure 13 DRIFT spectra of glass fiber surface as a function of copolymer composition: (A) γ -MPS : styrene = 5 : 95; (B) γ -MPS : styrene = 10 : 90; (C) γ -MPS : styrene = 15 : 85.

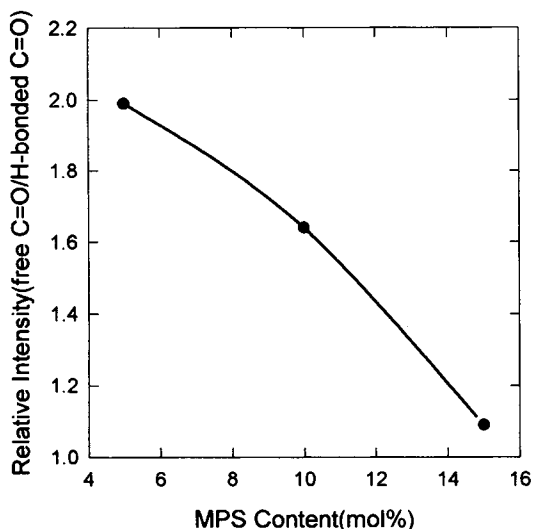


Figure 14 Relative intensity of the free C=O to the hydrogen-bonded C=O as a function of copolymer composition.

copolymer was a random one. The thermal stability of the copolymer increased with the silane content in the copolymer. The glass transition temperature of the copolymer decreased with increase of silane content in the copolymer. This is attributed to a free-volume increase in the copolymer. The glass fiber surface was surface-modified with the copolymer through chemical and physical adsorption, and hydrogen bonding was increased with increasing the silane content in the copolymer.

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