Performance Improvement of Glass-Fiber-Reinforced Polystyrene Composite Using a Surface Modifier. II. Mechanical Properties of Composites

JYONGSIK JANG,[1,*] JUN YEOB LEE,[1] and JONG KOO JEONG[2]

[1]Department of Chemical Technology, College of Engineering, Seoul National University, San 56-1, Shinlimdong Kwanakgu, Seoul, South Korea; [2]Dongbu Advanced Research Institute, 130-2, Moonjidong, Daeduck Science Town, South Korea

SYNOPSIS

The mechanical properties of glass-fiber-reinforced polystyrene composites were investigated with the variation of glass fiber content, surface treatment conditions, and silane coupling agents. γ-MPS, GPS, and poly(γ-MPS-co-styrene) were used for the surface modification of glass fiber. Mechanical properties of glass-fiber-reinforced polystyrene composites increased with increasing the content of glass fiber. Poly(γ-MPS-co-styrene) was superior to γ-MPS and GPS in promoting the interfacial adhesion of glass fiber-reinforced polystyrene composites. The mechanical properties of composites were maximum at a low copolymer concentration when the γ-MPS content in the copolymer was high and vice versa. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Long fiber-reinforced thermoplastic composites have not been widely used due to limitations in the processing technology. In recent years, the processing technique used in thermoset composites has been applied to thermoplastic composites. Therefore, thermoplastic composites have gained considerable interest.

The matrix resin of a thermoplastic composite holds the reinforcing fiber in proper orientation, protects the fibers from wear and abrasive damage, and transfers the load among fibers. Thermoplastic resin has a higher viscosity and requires a higher processing temperature than those of a thermosetting resin. Therefore, thermoplastic composites are manufactured mainly by a hand lay-up using a prepreg material.[1-4] A prepreg material consists of a reinforcing fiber impregnated with the polymer resin. Thermoplastic prepreg materials can be prepared by solvent impregnation and hot-melt resin

impregnation. The solvent impregnation process is composed of three steps:

1. Dissolving the resin with a proper solvent.
2. Fiber impregnation.
3. Solvent vaporization.

The resin content can be controlled by varying either the resin concentration in a resin bath or the pressure during impregnation. The solvent used in the solvent impregnation must dissolve the resin and be volatile. This method cannot be applied to insoluble semicrystalline polymer. Therefore, the solvent-impregnation method can be used to make amorphous polymer soluble in a proper solvent. The solvent plays a role in lowering the resin viscosity and helps to improve the wettability between fiber and resin.

Hot-melt resin impregnation is a method applied to a less soluble semicrystalline polymer matrix. This process has the advantage of simplicity but cannot be applied to a resin with high melt viscosity.

Generally, fiber-reinforced thermoplastic composite materials have higher mechanical properties,
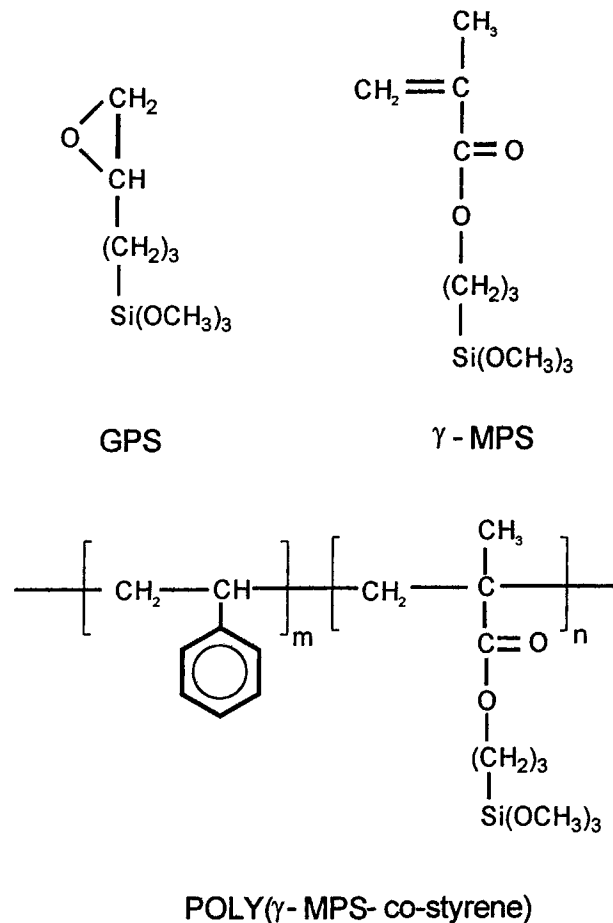
Figure 1 Chemical structures of various surface modifiers.

impact properties, and chemical resistance than those of a matrix resin. In the case of polystyrene (PS), strength and modulus, dimensional stability, and thermal resistance can be improved considerably by introducing glass fiber (GF). However, the interfacial adhesion between glass fiber and polystyrene is poor because glass fiber cannot react with polystyrene and is not compatible with polystyrene. Therefore, the mechanical properties of GF/PS composites can be enhanced by improving the interfacial adhesion between the glass fiber and polystyrene.

In this experiment, GF/PS composites were prepared using the solvent-impregnation method. We investigated the mechanical properties of GF/PS composites with different glass fiber content, surface modification condition, and silane coupling agents. GPS, γ-MPS, and poly(γ-MPS-co-styrene) were used to modify the glass fiber surface.

Table I   Physical Properties of Glass Fiber

Specific gravity	2.57
Tensile strength (MPa)	3433
Tensile modulus (GPa)	10.0
Ultimate elongation (%)	2–4
Refractive index	1.56

EXPERIMENTAL

Materials

γ-Methacryloxypropyltrimethoxy silane (γ-MPS) used in the surface modification of glass fiber was purchased from Dow Corning Co. under the trade name of Z-6030. Glycidoxypropyltrimethoxy silane (GPS) was purchased from Union Carbide Co. under the trade name of A-187. Poly(γ-MPS-co-styrene) was synthesized according to the procedure presented in a previous article.[5] Figure 1 represents the chemical structure of each surface modifier. The E-glass fiber fabric used as the reinforcement in this experiment was obtained from Hankook Fiber Co. The fabric thickness was 0.12 mm and the filament diameter was 10 μm. The physical properties of the glass fiber are presented in Table I. The polystyrene used as the matrix resin of the composites was manufactured by Dongbu Chemical Co. The physical properties of polystyrene are presented in Table II.

Hydrolysis of Poly(γ-MPS-co-styrene), GPS, and γ-MPS

Poly(γ-MPS-co-styrene) was hydrolyzed according to the method described in a previous article.[5] γ-MPS was hydrolyzed in a pH 3.5 aqueous solution for 1 h and GPS was hydrolyzed in a pH 4.0 aqueous solution for 1 h. In general, the hydrolysis rate depends on the silane concentration, solution pH, temperature, organic functional group, etc.[6] The silane coupling agent forms an ion in an alkali solution and reacts with the other silanes through the formation of a siloxane bond in a neutral solution. This resulted in the silane oligomer and polymer, so that

Table II   Physical Properties of PS G116

Melt index	2.3
Elongation at break (%)	2.8
Heat deflection temperature (°C)	85.2
Hardness (Rockwell)	100
Tensile strength (MPa)	53.0
Flexural strength (MPa)	68.7

in this condition silane cannot effectively modify the glass fiber surface. While in an acidic solution, silane can be stabilized since it is present as the free molecule. Therefore, silane is hydrolyzed in an acidic solution.[6,7] However, in the case of GPS, the ring-opening reaction of the glycidyl group can happen in addition to the hydrolysis reaction of the methoxy group. Therefore, GPS was hydrolyzed in the weak acidic condition to prevent a ring-opening reaction and to accelerate the hydrolysis reaction.[6]

Surface Modification of Glass Fiber

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

Preparation of Glass-fiber-reinforced Polystyrene Composites

GF/PS composites were manufactured with the variation of glass fiber content, surface modifier concentration, and surface modifier species. A hand lay-up of the prepreg material was used to prepare the composite materials. Glass fiber prepreg material impregnated with polystyrene was prepared in a 20 wt % polystyrene resin bath using the solvent-impregnation method. Tetrahydrofuran was used to dissolve polystyrene and was vaporized at room temperature. The solvent used in this experiment lowers the viscosity of the resin and helps to improve the wetting between the glass fiber and polystyrene. The prepreg material was pressed on a hot press at 240°C with the pressure of 500 kg/m^2. The pressure was kept for 10 min and cooled at room temperature.

Analyses

The fracture surface of the GF/PS composite was observed with a scanning electron microscope (SEM) manufactured at the JEOL Co. (JSM-35) with a magnification of 5000. Samples of GF/PS composites were fractured in a liquid nitrogen atmosphere. Flexural properties were measured on a Instron tester according to ASTM D 790 with a three-point bending test. The crosshead speed was 2.0 mm/min and a 500 kg compression load cell was used. The span was kept at 50.0 mm and the sample thickness was fixed at 3.0 mm. The flexural modulus was calculated using the initial slope of the stress–strain curve. The interlaminar shear strength (ILSS) of the composite was measured according to ASTM

D 2344. The crosshead speed was kept at 1.3 mm/min and the span was fixed at 15.0 mm. The sample thickness and width was kept at 2 and 10 mm, respectively.

RESULTS AND DISCUSSION

Figure 2 represents the flexural strength and flexural modulus of GF/PS composites with different glass fiber content. The surface of the glass fiber was modified with a 0.025 wt % poly(γ-MPS-co-styrene) solution. The mol fraction of γ-MPS in this copolymer was fixed at 5 mol %. The flexural strength and flexural modulus of the GF/PS composites increased with increasing glass fiber content according to the mixture rule. This is attributed to the fact that glass fiber has a higher strength and modulus than those of polystyrene.

The ILSS and flexural strength of GF/PS composites as a function of γ-MPS concentration are represented in Figure 3. The silane concentration was varied from 0.2 to 1.0 wt %. The ILSS and flexural strength of GF/PS composites increased with increasing γ-MPS concentration. The maximum values of ILSS and the flexural strength of the GF/PS composite were obtained at 0.4 wt % γ-MPS concentration. Above the maximum value, the mechanical properties of GF/PS composites decreased gradually. This is due to the lubrication effect caused by the excess silane layer between the glass fiber and polystyrene matrix. In general, it is known that the silane coupling agent is adsorbed onto the glass fiber surface through chemical bonding and physical adsorption.[6-8] These adsorbed silanes onto the glass
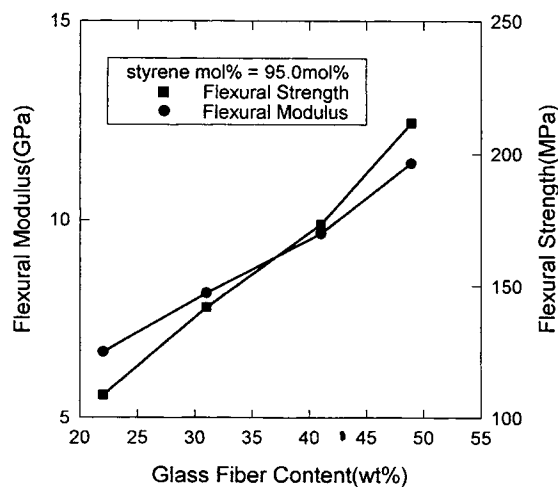
Figure 2 Flexural properties of glass-fiber-reinforced polystyrene composites as a function of glass fiber content.
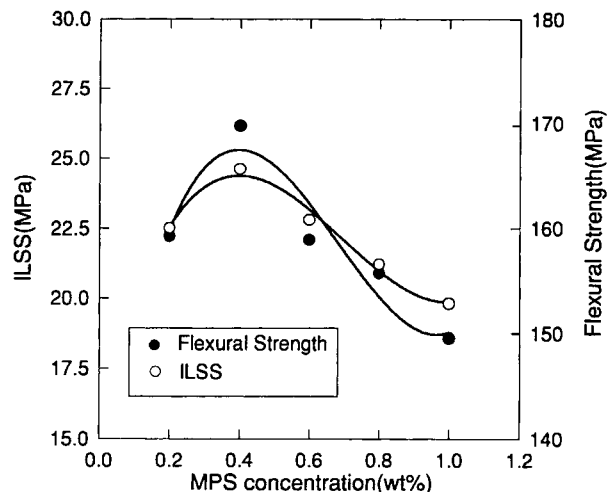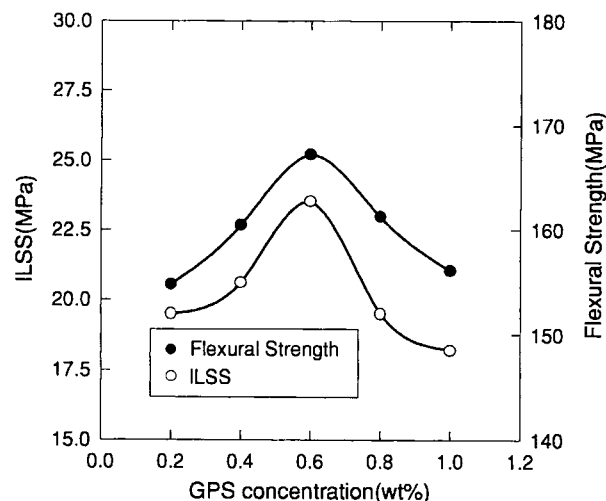
Figure 3   ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of γ-MPS concentration.

Figure 4   ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of GPS concentration.

fiber surface contribute to the adhesion promotion of GF/PS composites. However, excess silane resulted in the formation of a weak boundary layer[6–8] which leads to the decrease of the ILSS and flexural strength of the GF/PS composite.

Figure 4 represents the ILSS and flexural strength of GF/PS composites with the variation of GPS concentration. Mechanical properties of GF/PS composites were maximum at the 0.6 wt % GPS concentration. The overall trend was similar to the case of the GF/PS composite modified with γ-MPS. These results indicate that the excess silane layer forms the weak boundary layer between polystyrene and the glass fiber.

Figure 5 represents the ILSS and flexural strength of the GF/PS composite modified with poly(γ-MPS-co-styrene). The mol fraction of γ-MPS in the copolymer was 2.5 mol % and the copolymer concentration was varied from 0.025 to 0.5 wt %. The ILSS and flexural strength of the composites increased with increasing the copolymer concentration up to 0.2 wt %, reaching a maximum at a 0.2 wt % copolymer concentration, and decreased above 0.2 wt %. This is attributed to the fact that the copolymer chemisorbed onto the glass fiber surface through the siloxane bond formation at a low copolymer concentration (< 0.1 wt %), while the excess silane layer physisorbed onto the glass fiber surface forms the weak boundary layer at a high copolymer concentration (> 0.2 wt %). This excess silane layer may act as a defect in the composite interphase and cause a lubrication effect. Therefore, the mechanical properties of GF/PS composites decreased at a higher copolymer concentration. At an intermediate

copolymer concentration (0.1–0.2 wt %), the copolymer chemisorbed and physisorbed onto the glass fiber surface, which leads to the formation of the siloxane bond with the glass fiber and the interpenetrating polymer network (IPN) with polystyrene. The performance improvements of the GF/PS composites are caused mainly by these two effects. However, interfacial adhesion is largely affected by the chemical bond formation rather than by the IPN in the GF/PS composites. So, the mechanical properties of the GF/PS composites improved considerably even at a low copolymer concentration.
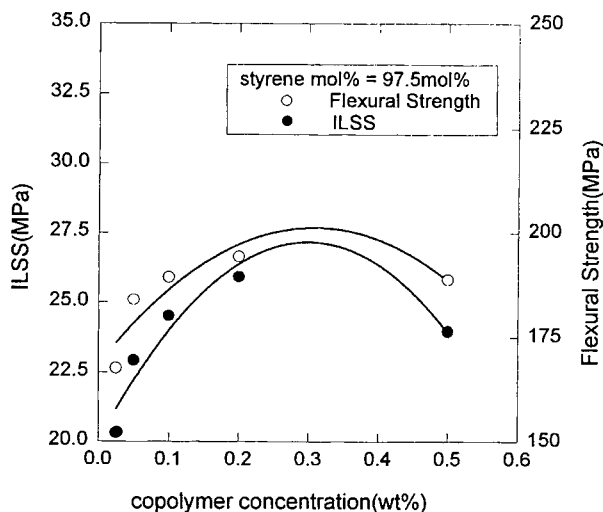
Figure 5   ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of poly(γ-MPS-co-styrene) concentration. γ-MPS : styrene = 2.5 : 97.5.
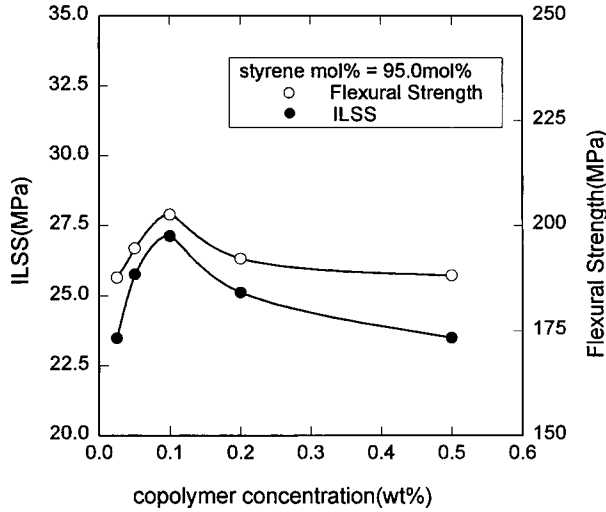
Figure 6 ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of poly(γ-MPS-co-styrene) concentration. γ-MPS : styrene = 5.0 : 95.0.
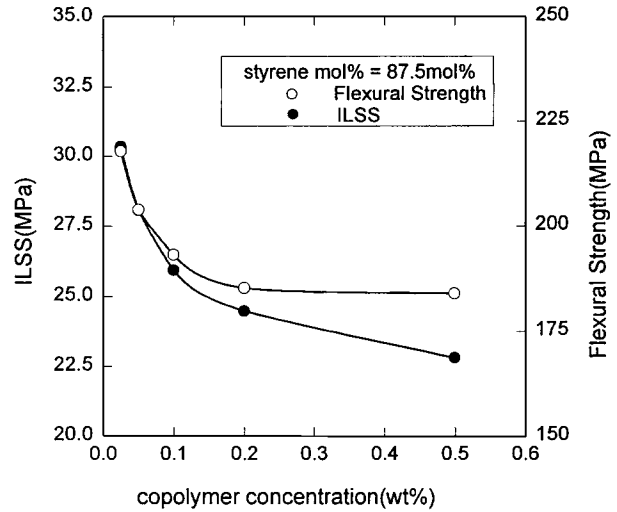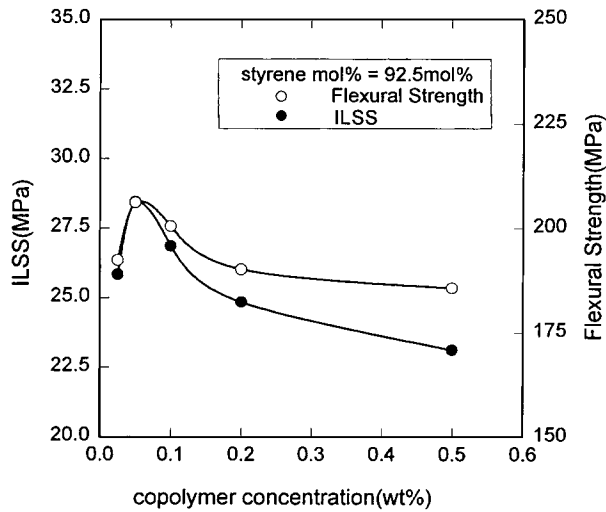

Figure 8 ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of poly(γ-MPS-co-styrene) concentration. γ-MPS : styrene = 12.5 : 87.5.
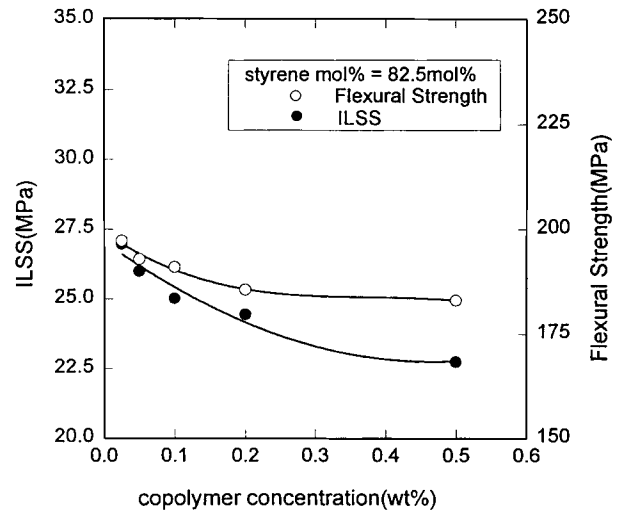
Figure 6 represents the ILSS and flexural strength of a GF/PS composite modified with poly(γ-MPS-co-styrene). The mol fraction of γ-MPS in the copolymer was fixed at 5 mol %. The mechanical properties of the GF/PS composites showed the maximum values when the glass fiber surface was modified with a 0.1 wt % copolymer solution. This indicates that the chemisorbed and physisorbed silane layers were effectively formed at this copolymer concentration. The trend at below and above this

concentration can be explained in the same manner as in the case of Figure 5.

Figure 7 represents the ILSS and flexural strength of the GF/PS composite modified with poly(γ-MPS-co-styrene). The mol fraction of γ-MPS in the copolymer was 7.5 mol %. The mechanical properties of the GF/PS composites improved considerably at the low copolymer concentration and showed the maximum values at 0.05 wt % copolymer concentration. The overall behavior can be also understood by the previous explanation.

Figure 7 ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of poly(γ-MPS-co-styrene) concentration. γ-MPS : styrene = 7.5 : 92.5.

Figure 9 ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of poly(γ-MPS-co-styrene) concentration. γ-MPS : styrene = 17.5 : 82.5.
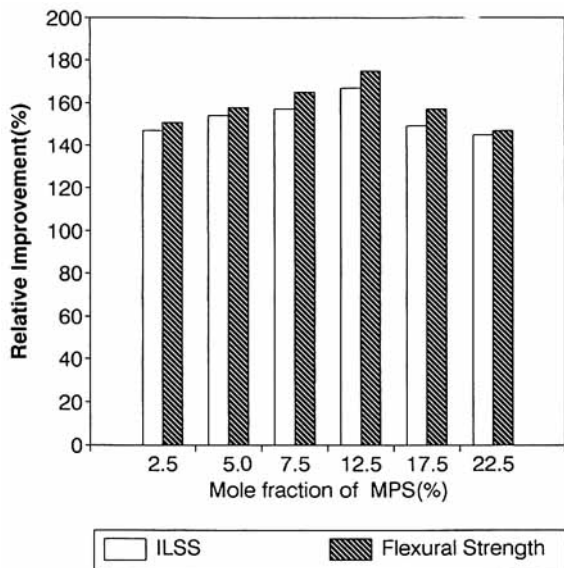
Figure 10 Plot of relative ILSS and flexural strength of glass-fiber-reinforced polystyrene composites as a function of silane content in the copolymer.
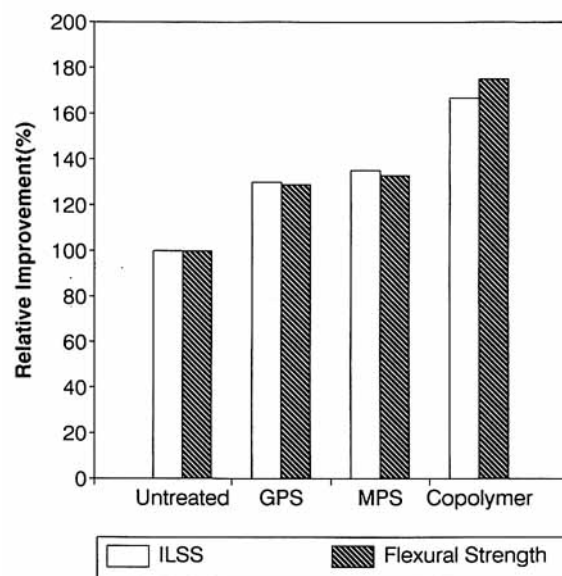
The ILSS and flexural strength of GF/PS composites modified with poly(γ-MPS-co-styrene) are represented in Figures 8 and 9. The mol fractions of γ-MPS in the copolymer were 12.5 and 17.5 mol %, respectively. The mechanical properties of the GF/PS composites showed maximum values at 0.025 wt % copolymer concentration and decreased with increasing copolymer concentration. This is caused by an excess silane layer between the glass fiber surface and the polystyrene matrix resin.

Figure 10 represents the ILSS and flexural strength of the GF/PS composites as a function of the silane content in the copolymer. Maximum values of the ILSS and flexural strength were obtained at 12.5 mol % silane content in copolymer. Above 12.5 mol %, the ILSS and flexural strength of the GF/PS composites decreased considerably. The result indicates that interfacial adhesion of the GF/PS composite can be improved considerably when the silane content in the copolymer is 5–12.5 mol %. This is due to the fact that at a low silane content in the copolymer (< 5 mol %) a chemical bond cannot be formed effectively and that at a high silane content in the copolymer (> 12.5 mol %) the silane unit in the copolymer prevents IPN formation. Therefore, the optimum performance of the GF/PS composites was obtained at 5–12.5 mol %.

From above results, it can be concluded that at higher γ-MPS content in the copolymer the mechanical properties are maximum at a low copolymer concentration and vice versa. In other words, the

interfacial adhesion between the glass fiber and polystyrene is affected mainly by the overall silane content in the copolymer solution. However, if the mol fraction of γ-MPS in the copolymer exceeds 15 mol %, the mechanical properties of composites surface-modified with this copolymer decreased irrespective of copolymer concentration. Therefore, the optimum content of γ-MPS in the copolymer to improve the interfacial adhesion between the glass fiber surface and the polystyrene matrix resin may be 5–12.5 mol %. In addition to these results, the mechanical properties of the GF/PS composites improved considerably at the low (<0.1 wt %) copolymer concentration. It can be inferred from the results that the chemical bond plays a major role in promoting the interfacial adhesion between the glass fiber surface and polystyrene.

Figure 11 represents the ILSS and flexural strength of the GF/PS composite as functions of surface modifiers. The mechanical properties of GF/PS composites modified with GPS, γ-MPS, and poly(γ-MPS-co-styrene) were superior to those of untreated GF/PS composites. Among these surface modifiers, poly(γ-MPS-co-styrene) was the most effective in promoting the interfacial adhesion between the glass fiber surface and polystyrene. γ-MPS was more effective than was GPS in improving the interfacial adhesion of the GF/PS composites. This may be due to the chain-transfer reaction occurring between polystyrene and the silane coupling agent. Generally, it is well known that polystyrene


Figure 11 Plot of relative ILSS and flexural strength of glass-fiber-reinforced polystyrene composites vs. silane compounds.
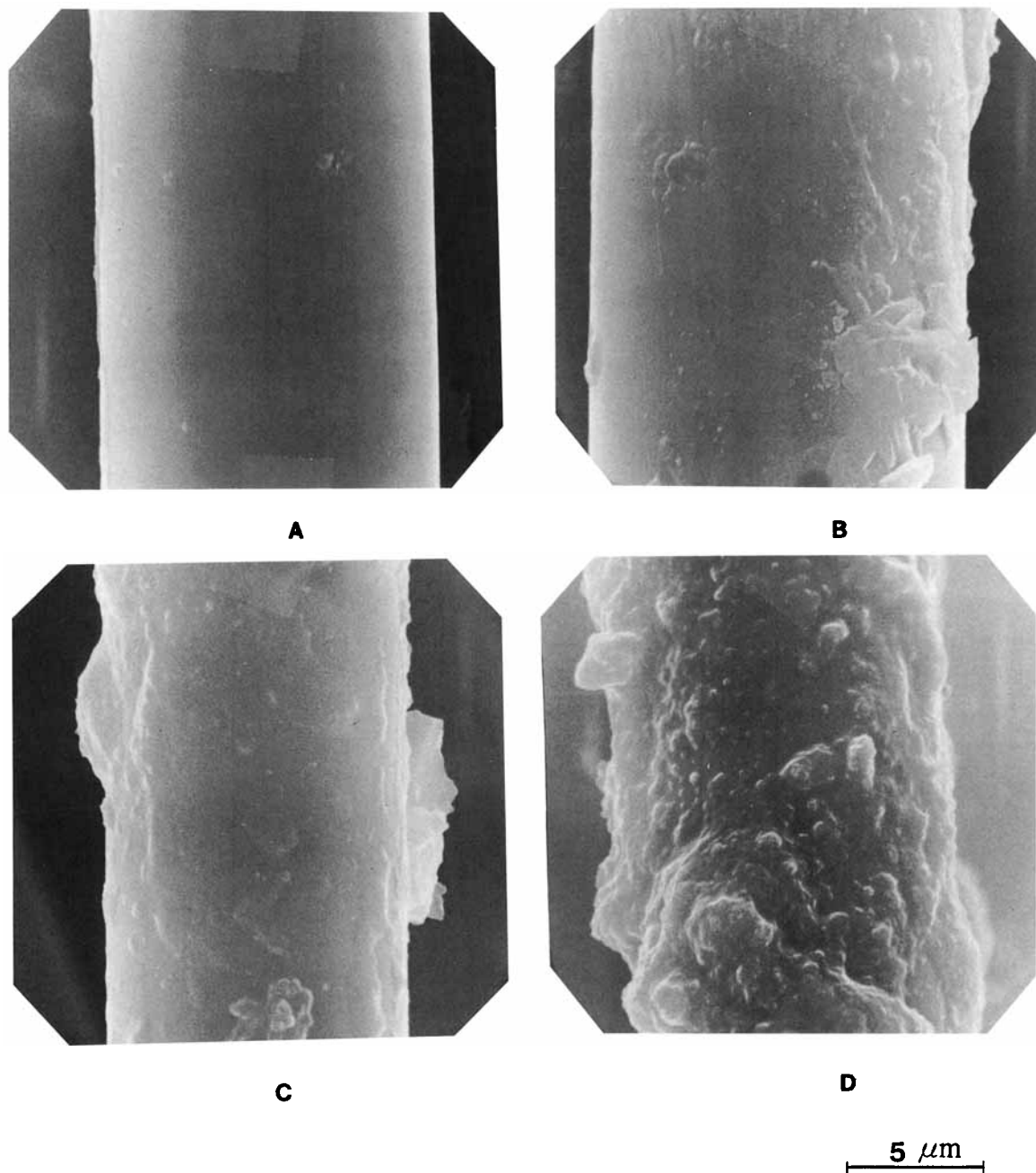
Figure 12   SEM micrographs of the fracture surface of glass-fiber-reinforced polystyrene composites according to silane compounds: (A) untreated; (B) GPS treated; (C) γ-MPS treated; (D) poly(γ-MPS-co-styrene) treated.

is fragmented into a radical at above 200°C.[9–11] Therefore, it is supposed that polystyrene will be fragmented into a radical during GF/PS processing. The produced polystyrene radicals react with the silane through chain transfer and this resulted in the formation of a chemical bond with polystyrene. Compared with GPS, γ-MPS can easily react with the PS radical since it has a large chain-transfer constant.[12] This indicates that γ-MPS is more ef-

fective than is GPS in improving the interfacial adhesion between glass fiber and polystyrene. Poly(γ-MPS-co-styrene) was the most effective in promoting the interfacial adhesion between the glass fiber and polystyrene. This is attributed to the compatibility improvement caused by the styrene unit in copolymer. The silane unit in the copolymer improves the interfacial adhesion through the formation of a chemical bond with the glass fiber, and the
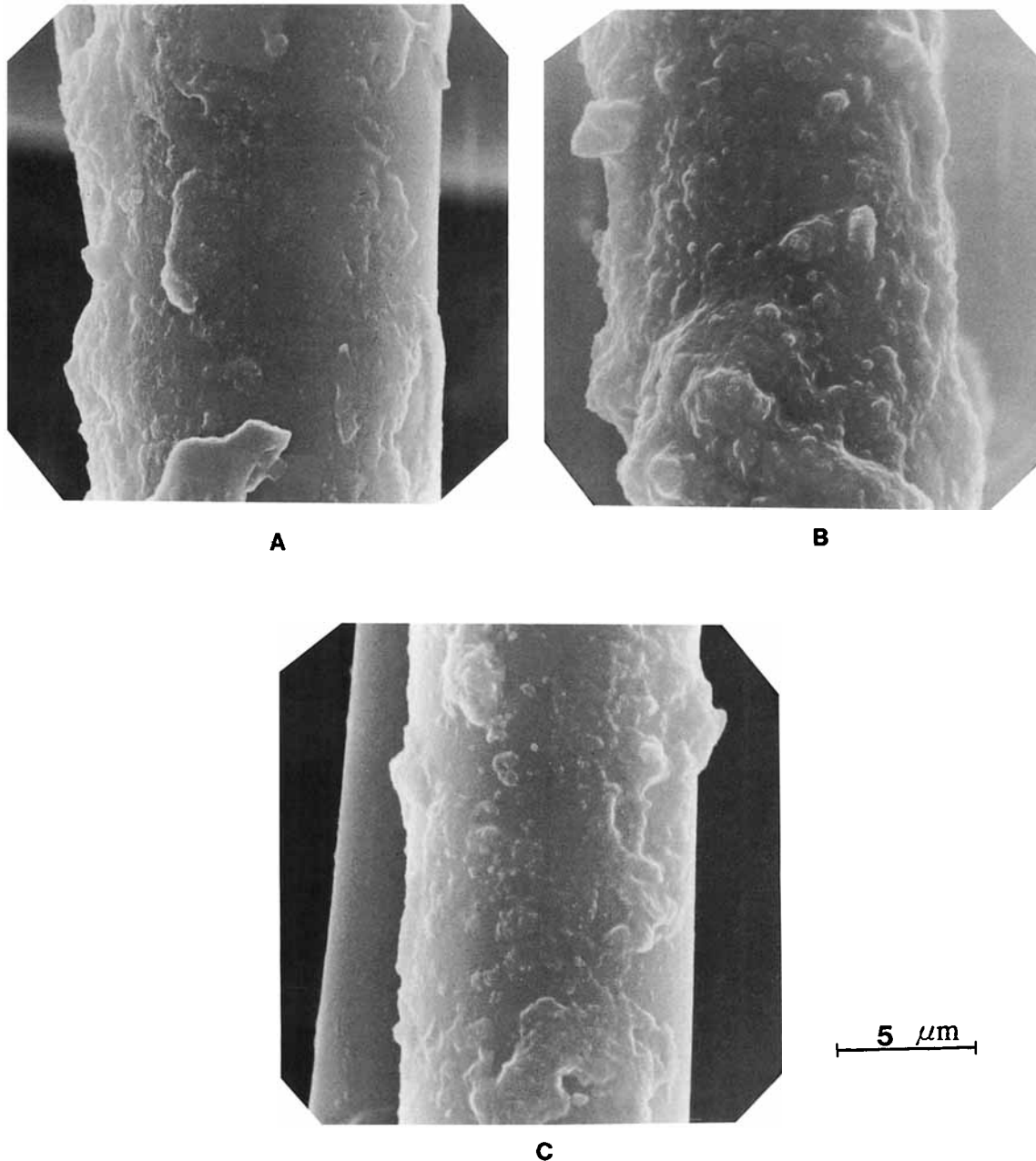
Figure 13 SEM micrographs of fracture surface of glass-fiber-reinforced polystyrene composites according to poly(γ-MPS-co-styrene) concentration: (A) 0.05 wt %; (B) 0.1 wt %; (C) 0.2 wt %.

styrene unit in the copolymer improves compatibility through the formation of an IPN between the glass fiber and polystyrene. Therefore, poly(γ-MPS-co-styrene) was more effective than was any other silane in the promotion of the mechanical properties of the GF/PS composites.

Morphological studies of the GF/PS composites were carried out to analyze the fracture surface of the GF/PS composites with different surface treatment conditions. Samples of the GF/PS composites

were fractured in liquid nitrogen. Figure 12(A) represents the fracture surface of the GF/PS composite. Heat-treated glass fiber was used for the preparation of the GF/PS composite. Without the surface modification of the glass fiber, the GF/PS composites were delaminated at the interface between the glass fiber and polystyrene. This means that the interfacial adhesion between the glass fiber and polystyrene is relatively poor. Polystyrene cannot react with the glass fiber and does not have compatibility with

the inorganic fiber, which resulted in the poor adhesion between the glass fiber and polystyrene. Figure 12(B) shows the fracture surface of the GF/PS composite surface modified with GPS. Compared with the untreated glass fiber surface, the cohesive failure at the polystyrene matrix occurs increasingly and the adhesive failure at the interface diminished. This shows that the interfacial adhesion between the glass fiber and polystyrene was improved by GPS and this result coincides with the ILSS and flexural strength data. Figure 12(C) shows the fracture surface of the GF/PS composite modified with γ-MPS. The cohesive failure at the polystyrene matrix increased and the adhesive failure at the interface diminished compared with the GF/PS composites modified with GPS. This is due to the improvement in interfacial adhesion by γ-MPS in the GF/PS composites and coincided with the ILSS data. Figure 12(D) shows the fracture surface of the GF/PS composite modified with poly(γ-MPS-co-styrene). The cohesive failure at the polystyrene matrix was considerable and the adhesive failure of the GF/PS composite did not occur ʌt the interface. This phenomenon indicates that e interfacial adhesion between the glass fiber and polystyrene is superior to the polystyrene bulk property. Therefore, it is concluded that poly(γ-MPS-co-styrene) in the GF/PS composites improved the interfacial adhesion between the glass fiber and polystyrene considerably.

Figure 13 represents the fracture surface of GF/PS composites modified with poly(γ-MPS-co-styrene) with different copolymer concentrations. The mol fraction of γ-MPS in the copolymer was fixed at 5 mol %. The cohesive failure at the polystyrene matrix increased when the copolymer treatment concentration was increased from 0.05 to 0.1 wt % and decreased at above 0.1 wt % copolymer concentration. From these results, it can be concluded that the interfacial adhesion between the glass fiber and polystyrene depends on the copolymer concentration and shows the maximum value at 0.1 wt % copolymer solution. These results coincided with those of the ILSS and flexural strength.

CONCLUSION

Glass-fiber-reinforced polystyrene composites were manufactured using the solvent impregnation method. We investigated the mechanical properties and fracture surfaces of glass-fiber-reinforced polystyrene composites modified with silane compounds

such as GPS, γ-MPS, and poly(γ-MPS-co-styrene) and obtained the following conclusions:

1. The mechanical properties of GF/PS composites increased with increasing the glass fiber content.
2. Poly(γ-MPS-co-styrene) was superior to GPS and γ-MPS in promoting interfacial adhesion between the glass fiber and polystyrene due to compatibility improvement.
3. The mechanical properties of GF/PS composites modified with GPS and γ-MPS showed the maximum values when the silane concentration was 0.6 and 0.4 wt %, respectively.
4. The mechanical properties of GF/PS composites modified with poly(γ-MPS-co-styrene) showed the maximum values at low copolymer concentration when the mol fraction of γ-MPS was high and vice versa.
5. The silane content in copolymer for optimum performance was 5–12.5 mol %.

REFERENCES

1. L. A. Carlsson, Thermoplastic Composite Materials, Elsevier, New York, 1991.
2. C. C. Ma, C. L. Lee, M. J. Chang, and N. H. Tai, Polym. Comp., 13(6), 441 (1992).
3. C. C. Ma, C. L. Lee, and N. H. Tai, Polym. Comp., 13(6), 435 (1992).
4. Y. Suzuki and J. Saitoh, in 34th International SAMPE Symposium, May 1989, p. 16.
5. J. Jang, J. Y. Lee, and J. K. Jeong, to appear.
6. E. P. Plueddeman, Silane Coupling Agent, Plenum Press, New York, 1989.
7. J. Jang, PhD Dissertation, Case Western Reserve University, 1988.
8. C. R. Choe and J. Jang, Polymer (Korea), 17(6), 703 (1993).
9. H. H. G. Jellinek, J. Polym. Sci., 3, 850 (1948).
10. H. H. G. Jellinek, J. Polym. Sci., 4, 1 (1948).
11. H. H. G. Jellinek, J. Polym. Sci., 4, 13 (1948).
12. C. Walling, Free Radicals in Solution, Wiley, New York, 1981.