Effect of Macromolecular Coupling Agent on the Property of PP/GF Composites

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ABSTRACT: Silane-grafted polypropylene manufactured by a reactive grafting process was used as the coupling agent in polypropylene/glass-fiber composites to improve the interaction of the interfacial regions. Polypropylene reinforced with 30% by weight of short glass fibers was injection-molded and the mechanical behaviors were investigated. The results indicate that the mechanical properties (tensile strength, tensile modulus, flexural strength, flexural modulus, and Izod impact strength) of the composite increased remarkably as compared with the noncoupled glass fiber/polypropylene. SEM of the fracture surfaces of the coupled composites shows a good adhesion at the fiber/matrix interface: The fibers are coated with matrix polymer, and a matrix transition region exists near the fibers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1537–1542, 1999

Key words: macromolecular coupling agent; silane-grafted polypropylene; polypropylene; glass fiber; composite

INTRODUCTION

Polypropylene (PP) is one of the most important engineering polymers with its relatively low cost, versatility, recyclability, and good processability. Glass fiber (GF)-reinforced PPs are engineering thermoplastic materials with good mechanical properties. It is well known that the interaction and adhesion between the fiber and matrix has a significant effect in determining the properties in fiber-reinforced materials.[1,2] A good interfacial adhesion between the matrix and the fiber is essential to transfer the stresses from the matrix to the fibers and thus improve the mechanical strength of the composite. Unfortunately, the minimal reactivity of PP and GF results in weak bonds at the interface and low mechanical properties of the composite.[3] To improve the interfacial adhesion, coupling agents such as silane coupling agents were used formerly.[4,5] Although there exists good adhesion between the coupling agents and GF, there is little interaction between the coupling agents and the nonpolar chain of PP. Furthermore, the small molecular coupling agents may not very well distribute in the composite. Maybe the chemically modified PP with polar active groups can overcome the shortcoming of the usual coupling agents.

An acrylic acid-modified PP/GF composite[6,7] and maleic anhydride-modified PP/GF composite[8] was investigated. The results show that the mechanical properties were improved. It is considered that the coupling of chemically modified PP on the GF surface is based on the cocrystallization of chemically modified PP wit the rest of the PP matrix,[3] thus improving the properties of the composite.

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Table I Feed Compositions of PP/GF Composites

	Percentage by Weight			
Sample Code	PP	PP-*g*-Si	AO	CaSt
M_0	100	0	0.2	0.2
M_1	90	10	0.2	0.2
M_2	80	20	0.2	0.2

(PP+PP-*g*-Si): GF = 70 : 30 by weight.

In the present work, vinyltrimethoxysilane-modified PP (PP-*g*-Si) was manufactured and was used as the macromolecular coupling agent in PP/GF composites. The mechanical behavior and the morphology indicate that PP-*g*-Si enhanced the interfacial adhesion between the PP matrix and the GFs of the composites.

Table II Processing Parameters

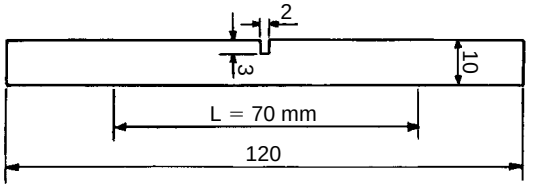
Injection time (s)	45 (25)
Injection pressure (MPa)	115
Screw speed (rpm)	60
Cooling time (s)	28 (20)
Mold temperature (°C)	60
Melt temperature (°C)	
Zone I	230
Zone II	230
Zone III	220

The parameters in parentheses are for the tensile-testing specimens, and others, for flexural- and impact-testing specimens.

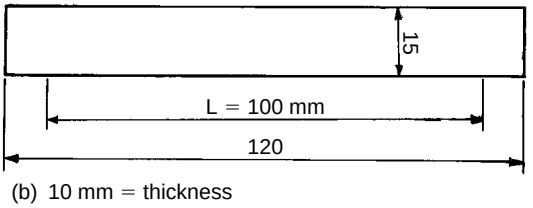
EXPERIMENTAL

Materials

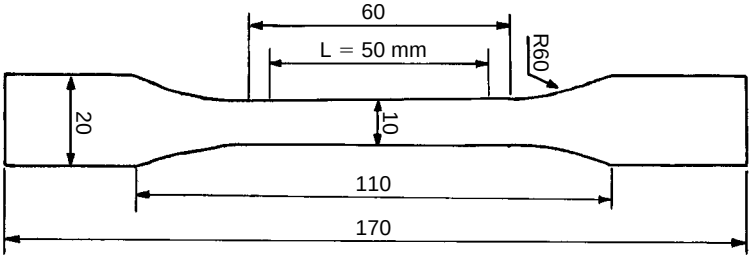
The PP was the commercial product F-401, a product of Guangzhou. Vinyltrimethoxysilane (A-



(a) 15 mm = width



(b) 10 mm = thickness



(c) 4 mm = thickness

Figure 1 Size of the test specimens: (a) for izod impact testing; (b) for flexural testing; (c) for tensile testing.

Table III Mechanical Properties of PP/GF Specimens

Specimen	M	M_0	M_1	M_2
Tensile strength (MPa)	33.0 ± 0.1	36.7 ± 0.1	74.9 ± 0.6	90.9 ± 0.2
Tensile modulus (GPa)	1.8 ± 0.1	5.4 ± 0.3	6.8 ± 0.2	7.3 ± 0.4
Elongation at break (%)	>250	1.7 ± 0.2	0.8 ± 0.1	1.4 ± 0.1
Flexural strength (MPa)	53.5 ± 0.5	59.5 ± 0.4	97.9 ± 0.5	122.3 ± 0.4
Flexural modulus (GPa)	1.6 ± 0.1	5.2 ± 0.2	6.5 ± 0.1	6.3 ± 0.2
Izod impact strength (MPa)	4.9 ± 0.3	6.2 ± 0.1	8.9 ± 0.2	10.4 ± 0.4

M: PP parents' matrix without glass fiber in it.

171) was obtained from OSI Specialtics Asia Ltd. Alkali-free long FGs were supplied by Tongxiang Glass Fiber Factory of Hunan Province. Chemical-grade dicumyl peroxide (DCPO) was used. The antioxidant 1010 (AO) and calcium stearate (CaSt) were all commercial products.

Preparation of the Macromolecular Coupling Agent

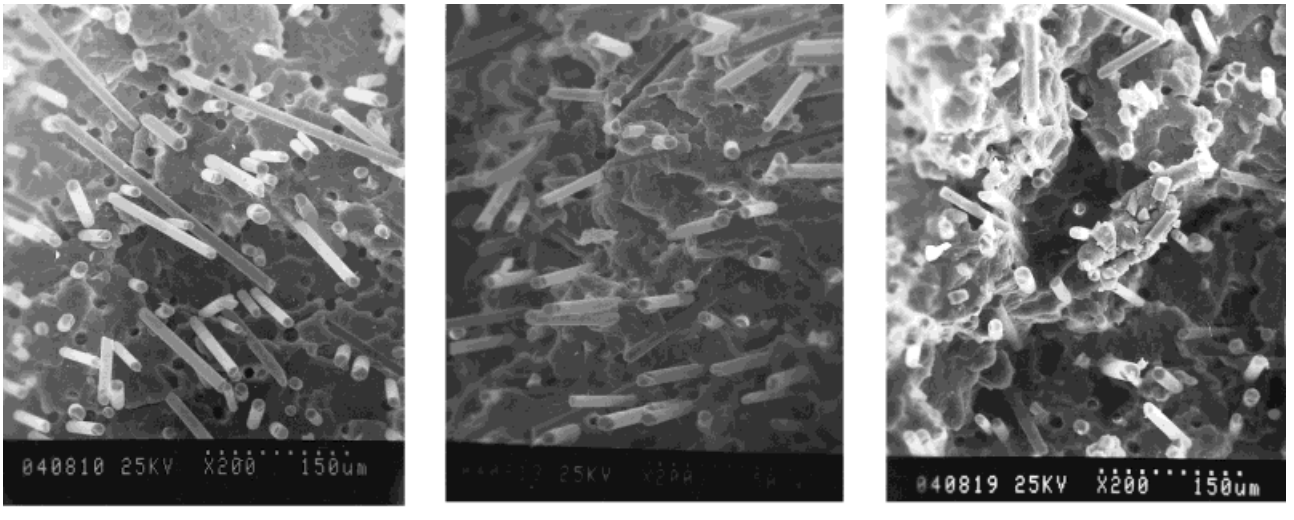
A premix of the PP, A-171, DCPO, and CaSt in the mass ratio of 100 : 6 : 1 : 0.2 was continuously fed to an SHF-53 twinscrew compounding extruder (L/D = 28/1, D = 18.9 mm). The temperature in the five successive zones of the extruder was increased along its length from 200 to 220°C. The product was cooled and cut to the pellets, and the masterbatch of the silane-grafted PP (PP-*g*-Si) was obtained. After extruding, the melt flow index of the polymer increased from 3.2 to 8.7 g/10 min. This is helpful for the PP-*g*-Si to be used as the macromolecular coupling agent.

Preparation of GF/PP Composites

The GF roving was impregnated with the polymer matrix and additives in a Siemens WP40 twinscrew extruder. The feed compositions are given in Table I. The feed ratio of PP (including PP-*g*-Si) to the GF was 70 : 30 by weight. The temperature in the extruder was controlled as described above, and the final blends extruded were frozen in-line in a water bath, dried, and granulated to less than 3 mm.

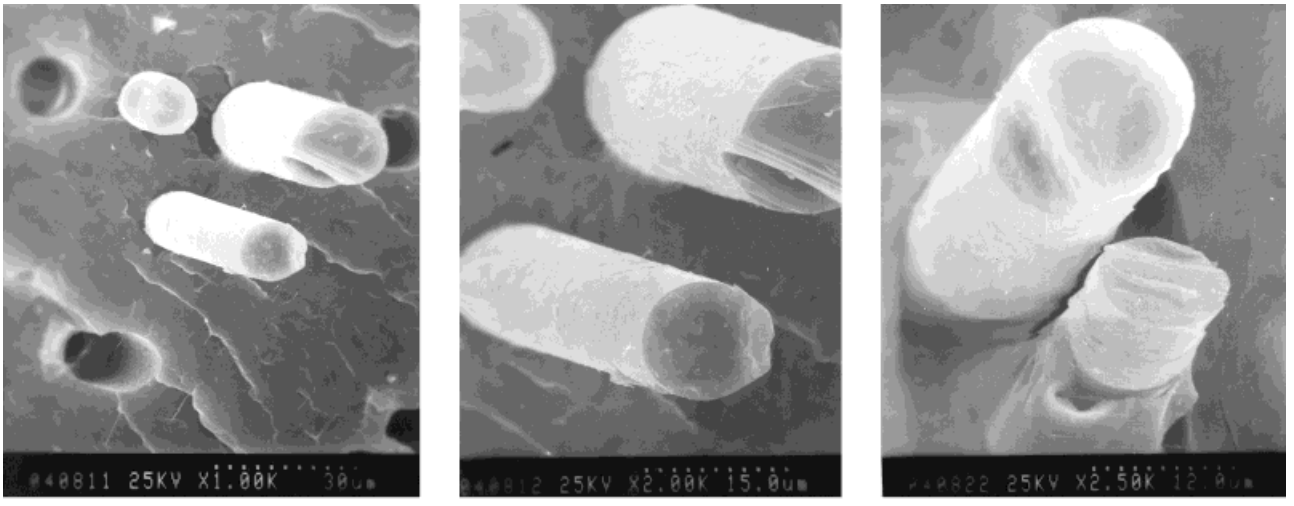
Preparation of the Test Specimens

The prepared fiber-reinforced PP composite granules were dried at a temperature of 80°C for 8 h



(a) (b) (c)

Figure 2 SEM of impact fracture surface of (a) M_0 (noncoupled GF/PP), (b) M_1, and (c) M_2 (coupled GF/PP).



(a) (b) (c)

Figure 3 SEM of impact fracture surface of (a,b) M_0 and (c) tensile fracture surface of M_0.

before injection molding. The granules were injection-molded using a CJ-150M^2-NC in-line screw injection-molding machine. The processing conditions are specified in Table II. The shape and size of the test specimens are shown in Figure 1.

Test Methods

Tensile Tests

The tensile test was performed according to GB/T1040-92 with a WD-5A electronic universal testing machine. The tensile test speed was 5 mm/s and the results were calculated from the data obtained from six parallel tests.

Flexural Tests

The flexural test was performed according to GB9341-88 with an LWK-5 electronic tension testing machine. The span length was 100 mm and span-to-thickness ratio was 10. The crosshead speed was 5 mm/s. The results were calculated from the data obtained from six parallel tests.

Izod Impact Tests

The Izod impact test was performed according to GB/T 1043-93 with an XJJ-5 impact testing machine with a hammer of 2 J at room temperature. The span length was 70 mm and the notch depth was 3 mm. The results were calculated from six parallel tests.

Electron Microscopy

The morphology of the composites was obtained by scanning electron microscopy (SEM) using a Hitachi S-520 electron microscopy operated at 25 kV. The samples were used as the impacted specimens and tensioned specimens, respectively. The fracture surfaces were sputter-coated with gold before viewing.

RESULTS AND DISCUSSION

IR Spectroscopic Analysis

Silane-grafted PP (PP-*g*-Si) was characterized with a Nicolet 205 FTIR spectrometer using thin film (molded at 220°C) of the polymer. Free silane was removed from the thin film by acetone extraction. Measurements were made immediately after the samples were extruded. Compared with the PP parents' sample, a new absorption peak at 1095 cm^{-1}, which corresponds to the Si—O—C stretching vibration [9] of the Si-containing sample, was recorded. The conclusion is that PP-*g*-Si was obtained.

Mechanical Properties

The mechanical properties of the specimens are shown in Table III. The values of the tensile

strength, tensile modulus, flexural strength, flexural modulus, and Izod impact strength of the GF/PP composites are all higher than those of the PP parents.

In tensile testing, the specimens of the reference PP matrix show necking behavior, while the GF/PP composites exhibit negligible necking. Addition of GF to PP increases the modulus and tensile strength, while its decreases the elongation at break. furthermore, the tensile modulus values and tensile strength values of the composites coupled by the macromolecular coupling agent PP-*g*-Si are higher than those of the noncoupled materials. The increase in the tensile modulus of the GF/PP composites is due to the higher tensile modulus of GF, whereas the presence of the macromolecular coupling agent (PP-*g*-Si) in the GF/PP composites improves the interfacial adhesion of PP and GF, resulting in further improvement in the tensile modulus and tensile strength.

The flexural strengths and the Izod impact strengths of the specimens show a good correlation with the tensile strengths. As shown in Table III, the coupled GF/PP composites produce higher flexural strengths and impact strengths than those of the corresponding noncoupled materials, and the flexural modulus of the coupled composites are also higher than those of the noncoupled materials. Within the present experimental compositions, the mechanical properties of the composites increased as the content of the macromolecular coupling agent (PP-*g*-Si) in the composites increased.

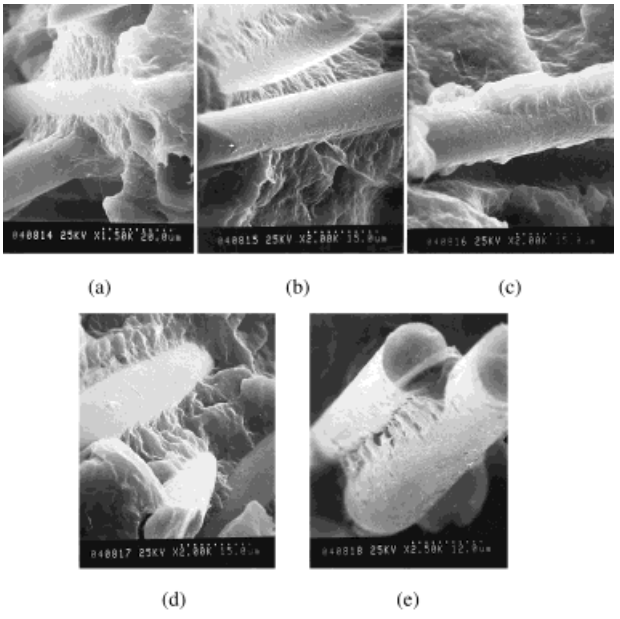


Figure 4 SEM of impact fracture surface of (a–c) M_1 and (d,e) M_2.

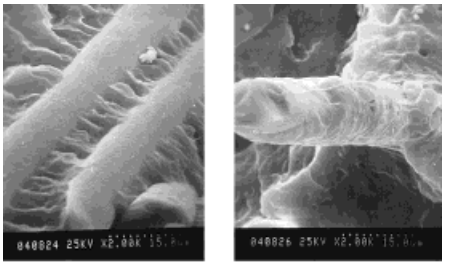
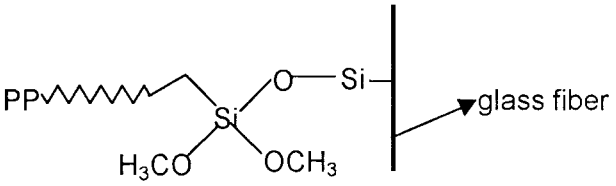


Figure 5 SEM of tensile fracture surface of (a) M_1 and (b) M_2.

Morphology of the GF/PP Composites

The morphology of the GF/PP composites was characterized by SEM studies on the impact fracture surfaces and the tensile fracture surfaces. The fracture surfaces indicate a good correlation with the mechanical properties of the respective GF/PP composites. Figure 2(a) is an SEM micrograph of M_0 which shows many long fiber ends at the surface, known as the classical pullout phenomenon. By contrast, Figure 2(b,c), corresponding to M_1 and M_2, respectively, reveals good tensile properties and short fiber ends with a small number of holes, with the fiber ends becoming shorter as the content of PP-*g*-Si increases in the matrix. Figure 3 (refer to M_0) shows the bare fiber surfaces; a sign of poor adhesion at the GF and PP interface is noted from the boundaries and pullout of the GF during the fracture process. But in Figure 4 [(a,b,c) refer to M_1, and (d,e) refer to M_2] and Figure 5 [(a) refers to M_1, and (b) refers to M_2], fibers are coated with the matrix polymer and connected tightly by the matrix, which indicates good adhesion at the fibers/matrix interface. It can be concluded that the PP-*g*-Si may promote the formation of the PP wrapping layer, thus improving the adhesion and modulus of the fiber/matrix interface. As a result, the mechanical properties of the GF/PP composites are improved. The results obtained show that PP-*g*-Si is an effective macromolecular coupling agent of the PP/GF composite. The reaction between PP-*g*-Si and the GF can be schematically shown as follows:



It can be seen that PP-*g*-Si has a good interaction between the PP matrix as well as the GF.

REFERENCES

1. Harris, B.; Beaumont, P. W. R.; Moncunill de Ferran, E. J Mater Sci 1971, 6, 238.
2. Sanadi, A. R.; Subramanion, R. V.; Manoranjan, V. S. Polym Compos 1991, 12, 377.
3. Peltonen, P.; Paakkonen, E. J.; Jayvela, P. K.; Tormala, P. Plast Rubb Compos Process Appl 1995, 23, 111.
4. Gupta, V. B.; Pandit, S. N.; Singh, R. K.; Subramanlam, K.; Baja, P. Indian J Textile Res 1978, 3, 119.
5. Pape, P. G.; Plueddemann, E. P. ANTEC 1991, 1870.
6. Adur, A. M. SPI National Plastics Exposition Conference, 1992, Chicago.
7. Denault, J.; Vu-Khanh, T.; Tailor, D.; Low, A. ANTEC 1992, 788.
8. Constable, R. C.; Adur, A. M. ANTEC 1991, 1892.
9. Wong, W. K.; Varrall, D. C. Polymer 1994, 35, 5447.