Influence of Functionalized Polyolefin on Interfacial Adhesion of Glass Fiber-Reinforced Polypropylene

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ABSTRACT: Several types of functionalized polyolefins, grafted with maleic anhydride, were synthesized and used to modify the surface of fiberglass in reinforced polypropylene composites. The influence of maleated polyolefin, matrix, and compounding conditions on the interfacial bonding strength of composite were studied by measuring interfacial shear strength. The results showed that strong interactions, e.g., chemical bonding, were formed between maleated polyolefin and fiber surface. When the modified fibers were compounded with polypropylene, firm entanglements of molecular chain were formed due to the segmental interdiffusion between maleated polyolefin and matrix polypropylene. As a result, the degree of fiber-matrix adhesion was improved. The extent of such improvement depended on the grafting degree, chain length of maleated polyolefin, and the compatibility between maleated polyolefin and matrix resin. At the same time, the compounding temperature and the cooling procedure affected the interfacial adhesion too. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1359–1365, 2000

Key words: glass fiber; polypropylene; interface; interfacial shear strength; functionalized polyolefin

INTRODUCTION

The degree of adhesion between fiber and matrix plays an important role in determining the mechanical properties of fiber-reinforced composites. However, poor compatibility of glass fiber and polypropylene (PP) leads to poor adhesion, which results in composites with poor mechanical properties. Hence, the full utilization of reinforcement was restricted. In order to improve the level of adhesion many attempts, e.g., modifications of matrix and fiber, have been made.[1–12] One method is to add the functionalized polyolefin grafted with polar groups into the matrix. The similarity of the additive and the matrix struc-

tures permits the occurrence of segmental crystallization, which is desirable for cohesive coupling between the additive and the PP matrix, whereas the polar groups provide chemical bonding or other interactions to the coupling agent coated onto the fiber surface. However, the introduction of functionalized polyolefin into the matrix leads to difficulty of the compounding process at the same time as the interfacial adhesion is promoted, and the utility factor of the additive is relatively low.

In this study, glass fibers were surface modified with polyolefin–maleic anhydride copolymer. The modified fibers were used as reinforcements of PP matrix to increase adhesion with the matrix. The interfacial shear strength was measured by introducing a single-filament fragmentation technique, and the effects of different factors on interfacial adhesion were studied.

EXPERIMENTAL

Materials

PP (types Y600, Y1200, Y2600, and M700R) and polyethylene (PE) were purchased from the Plastics of Shanghai Petrochemical Complex (China). Ethylene-propylene diene monomer (EPDM) was kindly supplied by DSM (Dutch State Mine Co. Ltd., The Netherlands). Benzoyl peroxide (BPO), maleic anhydride (MAH), and all the solvents were chemically pure grade and were used without further purification. Glass fiber having no surface treatment came from Nanjing Fiberglass Research & Design Institute (China); its average diameter was 21 μm.

Functionalized Polyolefin Synthesis And Purification

Each of the polyolefins (PP, PE, and EPDM) with MAH was dissolved in xylene in an atmosphere of nitrogen. When the dissolution was complete, the temperature was allowed to rise to 130°C, and the initiator BPO was added to the system in 130 min. If using the two-step feeding, resin, MAH, and BPO were replenished at constant proportion during the reaction process.

After the reaction stopped, the copolymeric products of PP or PE were cooled to room temperature. The precipitated products were filtered, repeatedly washed with acetone, dried at 80°C and finally extracted with acetone for 12 h. The copolymeric product of EPDM needed to be precipitated in acetone and filtered, followed by washing with acetone. Then the mixture was dried at 40°C and heated with reflux in toluene (2 g EPDM/ 100 mL toluene) at 110°C for 30 min, followed by filtering to eliminate the gel. The filtrate was precipitated in acetone, washed several times, and finally dried in a vacuum at 35°C.

Measurement of Grafting Degree

In a typical procedure, 0.1 ~ 0.2 g maleated polyolefin was heated to 110°C with reflux in 50 mL xylene for 30 min, followed by cooling to 60°C. One hundred milliliters potassium hydroxide (KOH)/ethanol standard solution was added, and the mixture was heated under reflux for 15 min. The alkali concentration was determined by acid titration using a known concentration of hydrochloride (HCl)/isopropanol standard solution. The indicator was 0.1% phenolphthalein/ethanol solution. A blank was carried out by the same method.

Grafting degree G_d is expressed by the following equation:

$$G_d = \frac{N(V_0 - V) \times 98.06}{2 \times W \times 1000} \times 100\%$$

where N is the concentration of HCl/isopropanol (mol/L), W is quantity of sample (g), V is the volume of HCl/isopropanol used by titration, V_0 is the volume of HCl/isopropanol used in a blank assay, and 98.06 is the molecular weight of MAH.

Infrared Spectra For Functionalized Polyolefin

Infrared (IR) spectra were taken with a Nicolet Magna-IR 550 spectrometer. The specimens of EPDM and EPDM-g-MAH were obtained by dissolving them with toluene, followed by casting films and drying. The specimens of PP, PE, and their grafting products, having eliminated additives, were taken using the KBr (potassium bromide) pellet method.

Surface Treatment Of Glass Fiber

After immersing in a solution of coupling agent in water, fibers were dried at 80°C for 90 min. When most water was evaporated, the temperature was allowed to rise to 130°C, at which point coupling agent reacted with fiber for 30 min. Then the fibers were coated with functionalized polyolefin in xylene solution. After drying they were reacted with each other at 120°C for 60 min. The concentrations of functionalized polyolefin and coupling agent solutions were 2%, unless otherwise specified.

Preparation Of Tensile Specimens

The matrix materials were rolled out in films of 1 mm thickness. A filament was carefully aligned within two films sandwiched between two flat steel plates. Then the mold was placed in a molding press, and pressure was raised to 1MPa at a temperature of 210°C and maintained for 4 min unless otherwise specified. After cooling to room temperature, the tensile specimens were cut from the pressed plates with the filament aligned in the centerline.

Measurement Of Interfacial Shear Strength

Interfacial Shear Strength (IFSS) (τ) was measured by using a single-filament fragmentation technique. In order to deduce the relationship
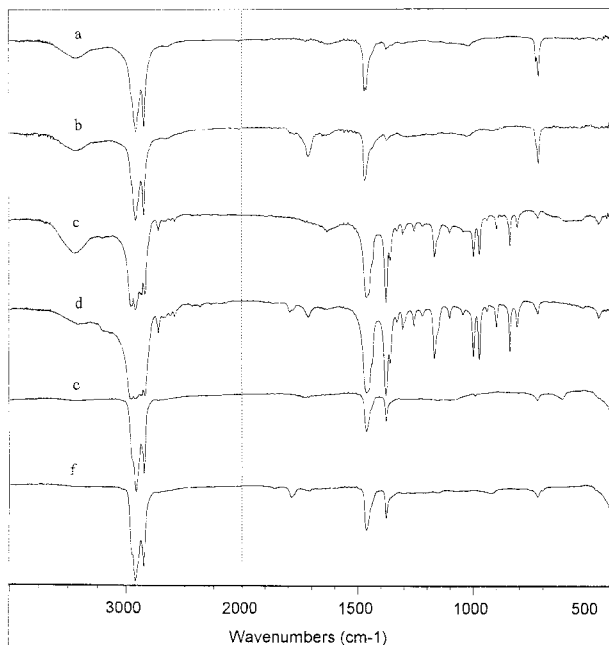
Figure 1 IR Spectra of polyolefin before and after grafting MAH. (a) PE; (b) PE-g-MAH; (c) PP; (d) PP-g-MAH; (e) EPDM; (f) EPDM-g-MAH.

between arbitrary length L_a and tensile strength at break σ_{La}, the tensile strength at break was measured at gage lengths of 30, 20, and 10 mm on monofilaments randomly extracted from a bundle of the fiber to be tested. For each type of fiber 100 tests were used to determine the value.

The specimens were subjected to a tensile test at a test speed of 10 mm/min to yield. Measurements of the fragment length were made by an optical microscope, heating PP to be transparent. For each kind of specimen 100 fragments were needed at least. Then IFSS was calculated according to the equation[13]:

$$\tau = \frac{K\sigma D}{2L}$$

where D is filament diameter(μm), L is the average fragment length (mm), σ is the tensile strength at the length L(GPa), K is Kelly constant (in this paper $K = 0.75$).

RESULTS AND DISCUSSION

Graft Reaction Of Polyolefin

In Figure 1, IR spectra of polyolefin before and

after the grafting reaction are shown. The absorption band at $1740\sim1860$ cm^{-1} corresponds to the absorption of anhydride and can be seen in the spectra of graft products. The difference between the spectra is evidence that MAH is grafted to the polyolefin chain.

The products of PP grafted with MAH can be summarized as follows[9]:
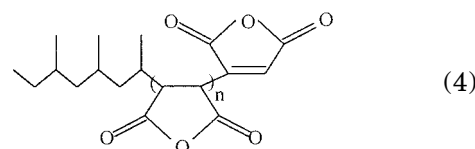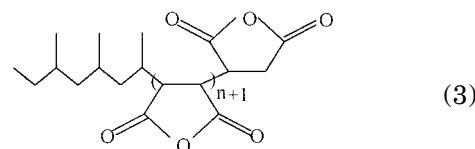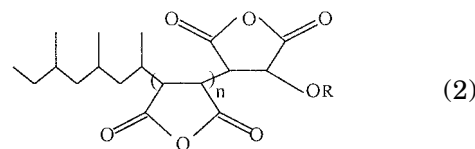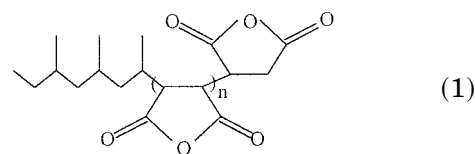
When treating fiber surface with maleated polyolefin, fiber–polyolefin interaction is related to the grafting degree because the interactive sites would increase with increasing grafting degree, i.e., the number of anhydride groups. The effects of the reaction conditions such as temperature, concentration of initiator, and MAH on the grafting degree are widely reported.[14–19] Controlling these conditions achieves different grafting degree. The work described here investigated the effect of the feeding method on the grafting degree. The results show that the grafting degree with two-step feeding is relatively higher than that with one-step feeding under the same conditions (as be seen in Table I), especially at low addition levels of initiator. In such a way, the concentration of reactants and the viscosity of reaction system are relatively lower in the initial reaction, which is beneficial to mass transferring and reaction. The low initial concentration of initiator should decrease the loss of free radicals due

Table I   Effect of the Method of Feeding on the Grafting Degree

| Addition Level of Initiator (%) | Grafting Degree (SD) (%) | |
	One-Step Feeding	Two-Step Feeding
0.8	0.43 (0.04)	1.14 (0.11)
1.6	0.52 (0.03)	1.21 (0.11)
4.7	0.57 (0.08)	1.23 (0.13)
6.2	0.65 (0.05)	1.17 (0.12)

SD = standard deviation.

to coupling and disproportionation reaction, and enhance the initiating efficiency. The second feeding maintains the concentration of initiator, which increases the reactive sites of polymer chains and the probability of MAH grafting onto polyolefin chain.

MAH can graft onto EPDM chain by the addition reaction with double bonds, but the cross-linking reaction between EPDM chains will result in cross-linked gel at the same time. In order to decrease the quantity of gel and increase the grafting degree, it is necessary to control the reaction conditions.

Effect of the Kind of Fiber Coating and the Grafting Degree on the Interfacial Adhesion

Fibers were coated with coupling agent and different functionalized polyolefin solution, and the treated fibers were compounded with different PP matrices. IFSS of the composite systems are shown in Table II.

When the coupling agent A-1100 ($H_2NCH_2CH_2$-$CH_2Si(OCH_2CH_3)_3$), supplied by Shanghai Yaohua Glass Company (China), is dissolved in water, the -OCH_2CH_3 group linking with Si-, will hydrolyze to Si-OH. The produced Si-OH condenses with the Si-OH of fiber surface, whereas the NH_2- groups in A-1100 react chemically with the anhydride groups of functionalized polyolefin, which can be illustrated as follows[20]:
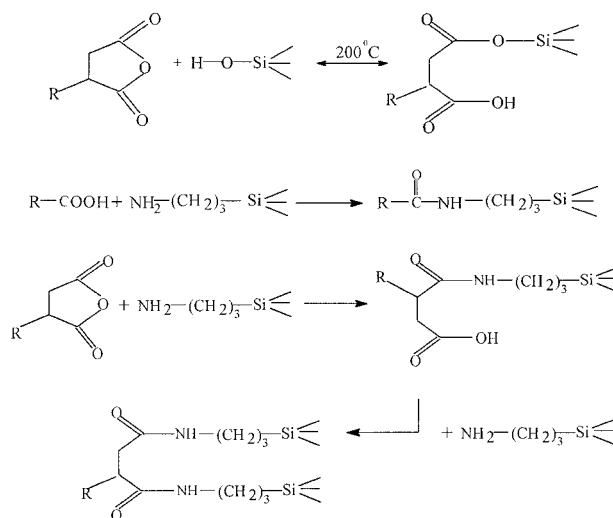
Using the modified fibers compounded with PP, a good compatibility between the functionalized polyolefin and PP matrix leads to their firm chain entanglement. The chemical and polar interac-

Table II   The Effect of the Kind of Coating and the Grafting Degree on IFSS

| Kind of Coating | Grafting Degree (SD) (%) | IFSS (SD) MPa Matrix | |
		Y1200	M700R
C_1(A-1100 + PP_1-g-MAH)	0.65(0.05)	7.28 (1.44)	7.07 (1.35)
C_1	1.21(0.11)	8.19 (1.50)	7.79 (1.38)
C_2(A-1100 + PP_2-g-MAH)	0.85(0.07)	7.27 (1.58)	7.04 (1.35)
C_2	1.13(0.10)	7.70 (1.51)	7.22 (1.48)
C_3(A-1100 + PP_3-g-MAH)	0.34(0.04)	6.17 (0.92)	6.09 (0.86)
C_3	0.44(0.03)	6.35 (0.97)	6.18 (0.92)
C_4(A-1100)		3.49 (0.50)	3.04 (0.41)

PP_1-g-MAH means Y600 grafting with MAH; PP_2-g-MAH means Y2600 grafting with MAH; PP_3-g-MAH means M700R grafting with MAH. SD = standard deviation.

Table III   Effect of Compounding Time on IFSS

Compounding Time (Min)	IFSS (SD) MPa Matrix	
	Y1200	M700R
2	5.81 (1.44)	4.72 (1.20)
4	8.19 (1.50)	7.79 (1.38)
6	8.27 (1.63)	8.20 (1.60)
8	8.24 (1.60)	8.22 (1.64)

SD = standard deviation.

tions of fiber-maleated polyolefin–PP improve the interfacial adhesion between fiber and matrix.

With the increasing of grafting degree, the number of chemical bonds between functionalized polyolefin and coupling agent will increase. Consequently, IFSS increases.

The molecular structure of Y600 is similar to Y2600, except its chain length is longer and its molecular weight is higher. The former grafted MAH is easier to entangle with matrix resin chain than the latter. As expected, stronger IFSS of the specimen using Y600 was found at the same grafting degree.

For a matrix resin with low melt viscosity, the wettability of matrix on fiber, and chain interdiffusion between matrix and functionalized polyolefin, are better than when a high melt viscosity resin is used. So IFSS of the specimen using M700R is lower than that using Y1200 at the same conditions.

Effect of Compounding Time on Interfacial Adhesion

The filament was treated with A-1100 and PP-g-MAH (G_d = 1.21%). The specimens of the treated filament and two different matrices (Y1200, M700R) were prepared at different times. IFSS of single filament specimens are shown in Table III.

In the case of Y1200 matrix, IFSS increases rapidly up to 4 min and then has no detectable change with further prolongation of compounding time. This is due to the fact that wettability and interdiffusion increase with rise in the compounding time from 2 to 4 min. Above this time, the wettability balance between matrix melt and fiber surface is reached, and the chain interdiffusion between PP matrix and maleated polyolefin tends to saturation, so further prolongation of compounding time has no detectable effect on IFSS.

In the case of M700R, a longer time is required for the wettability balance and the chain interdiffusion because of the high melt viscosity of the matrix. So IFSS will increase with prolonging time until 6 min.

Effect of Compounding Temperature on Interfacial Adhesion

IFSS of the specimens molded at 195°C (the other conditions as before) are shown in Table IV.

Comparing Table IV with Table II, we can find that IFSS of specimens molded at 195°C are much lower than that at 210°C. Compounding at 195°C, IFSS of specimens increase with increasing the grafting degree. For the low compounding temperature, the viscosity of matrix is high and the fluidity is poor, so the wetting of fiber by matrix melt decreases. At the same time, the limited chain diffusion leads to the weak chain entanglement between matrix and maleated polyolefin.

Effect of Coupling Agent on Interfacial Adhesion

The filament was treated with PP-g-MAH (G_d = 1.21%) and different coupling agents. The spec-

Table IV   IFSS of Specimens Molded at 195°C (Matrix is M700R)

Kind of Coating	Grafting Degree (SD) (%)	IFSS (SD) MPa
C_1	0.65 (0.05)	3.97 (1.07)
C_1	1.21 (0.11)	4.28 (1.16)
C_2	0.85 (0.07)	3.26 (0.77)
C_3	0.44 (0.03)	3.02 (1.00)
C_5(A-1100 + PE-g-MAH)	2.06 (0.16)	3.92 (1.02)
C_6(A-1100 + EPDM-g-MAH)[a]	2.28 (0.18)	2.63 (0.53)
C_6	3.12 (0.26)	3.51 (0.91)

[a] Concentration of EPDM-g-MAH is 0.2%. SD = standard deviation.

imens of the treated filament with PP (Y1200) were prepared. Table V shows IFSS of the specimens.

When using A-1100 and PP-g-MAH as surface treatment agent of glass fiber, A-1100, which reacts chemically with fiber surface, can link to PP-g-MAH through the reaction of amino groups with anhydride groups.[20] After the modified fibers were compounded with PP matrix, better interfacial adhesion can be obtained. When using A-174 to treat fiber surface, the polymerization of double bonds and ester exchange will occur between methylacrylate $=CHC(CH_3)COOM$ and PP-g-MAH.[21] In addition, A-174 can graft with tertiary carbon atom in PP on thermal condition,[22] so good interfacial adhesion can be obtained too.

Effect of Cooling Procedure on Interfacial Adhesion

IFSS of specimens, by means of different cooling procedures, are shown in Table VI.

In all cases, higher IFSS was found by rapid cooling. For a matrix of high crystallinity (e.g., Y1200), the degree of crystallinity of the interface region and matrix upon slow cooling is higher than that upon rapid cooling; hence, the corresponding compressive stress at interface generated by the shrinkage of the matrix resin is higher. Moreover, during the slow cooling procedure chain entanglement between matrix and functionalized polyolefin will untwist by means of the molecular chain motion caused by thermal stress. So the lower the crystallinity of the matrix and the better the compatibility between matrix and functionalized polyolefin, the weaker is the effect of the cooling procedure on IFSS.

CONCLUSION

Using stepwise feeding increased the grafting degree of maleated polyolefin at the low addition level of initiator. The interfacial bonding strength of composite system can be enhanced by surface

Table V   Effect of Coupling Agent on IFSS

Type of Coupling Agent	IFSS (SD) (MPa)
A-1100	8.19 (1.50)
A-174	5.77 (1.28)

SD = standard deviation.

Table VI   Effect of Cooling Procedure on IFSS

Kind of Coating	Grafting Degree (SD) (%)	Matrix	IFSS (SD) (MPa)	
			Rapid Cooling	Slow Cooling
C_1	1.21(0.11)	Y1200	8.19(1.50)	7.07(1.63)
C_2	0.85(0.07)	Y1200	7.27(1.58)	6.35(1.46)
C_2	0.85(0.07)	M700R	7.05(1.35)	6.31(1.60)
C_3	0.44(0.03)	Y1200	6.35(0.97)	5.72(1.30)
C_3	0.44(0.03)	M700R	6.18(0.92)	6.13(1.26)

SD = standard deviation.

modification of fibers with maleated polyolefin. This behavior was favorable as:

1. grafting degree of maleated polyolefin was relative higher;
2. compatibility of maleated polyolefin with matrix resin was better; and
3. chain length of maleated polyolefin was longer.

The wetting of fiber by matrix and the chain interdiffusion between matrix and maleated polyolefin required certain times, corresponding to the viscosity of matrix melt. The increase in compounding temperature that benefits such processes can increase the degree of interfacial adhesion. The effect of cooling procedure on the interfacial adhesion is related to the degree of crystallinity of matrix and the compatibility between matrix and functionalized polyolefin. The lower the crystallinity and the better the compatibility, the weaker the effects. A-1100 containing NH_2- groups is more appropriate for fiber modification for the fibers in this work.

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