

Use of Silane Agents and Poly(propylene-*g*-maleic anhydride) Copolymer as Adhesion Promoters in Glass Fiber/Polypropylene Composites

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ABSTRACT: Two organofunctional silanes and a copolymer were used to increase the interfacial adhesion in glass fiber polypropylene (PP) reinforced composites. The performance of the coupling agents was investigated by means of mechanical property measurements, scanning electron microscopy (SEM), and dynamic mechanical analysis. The increased adhesion between the glass fibers and PP matrix observed with SEM resulted in an improvement of the mechanical and dynamic mechanical properties of the composites. Coupling achieved with the copolymer poly(propylene-*g*-maleic anhydride) (PP-*g*-MA) proved to be the most successful compared with 3-aminopropyltriethoxysilane and 3-aminopropyltriethoxysilane. The combination of PP-*g*-MA with the silanes resulted in further property improvements because of the ability of the MA groups to react with the amino groups of the silanes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 701–709, 2001

Key words: polypropylene; glass fiber; silane; copolymer; adhesion

INTRODUCTION

Glass fiber reinforcement provides an attractive means of enhancing the mechanical and thermal properties of polymers required for engineering applications. Incorporation of short glass fibers in thermoplastic matrices imparts stiffness, strength, and thermal stability to these materials with some sacrifice of strain to failure.

The importance of good adhesion between the fiber and matrix has long been recognized. Good

adhesion between the fibers and matrix results in efficient stress transfer from the continuous polymer matrix to the dispersed fiber reinforcement and can increase the ability of the material to absorb energy.^{1,2}

The development of methods for controlling the interfacial adhesion between chemically and physically different, incompatible phases has been the subject of considerable research efforts. It is well known that interfacial agents, such as organofunctional silane compounds, are capable of promoting adhesion in fiber reinforced plastics. It has also been demonstrated that for some types of composites and polymer blends the concept of adhesion is operationally the same. For instance, graft or block polyolefin copolymers can be equally effective as

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adhesion promoters in composites or blends containing a polyolefin component.³ The use of a silane compound as a glass fiber surface modifier is based on the reactivity or compatibility of its segments with the fibers and the polymer matrix.⁴ The choice of a copolymer as an adhesion promoter is based on similar considerations.^{3,5}

Dynamic mechanical analysis is a powerful and widely used analytical tool for the understanding of the viscoelastic behavior of polymeric and composite materials. In addition to measuring the dynamic storage, loss modulus, damping characteristics, and glass-transition temperature of a material, it can also be used to study different aspects of multiphase systems such as the adhesion between components of a composite material.^{6,7}

In the near future a high consumption rate has been predicted for fiber, especially glass fiber reinforced polypropylene (PP) composites because of their favorable cost to property performance. Thus, the choice of a suitable adhesion promoter, an understanding of the coupling mechanism, and its effect on the material property of PP composites is of paramount importance.

The objective of this work was to investigate the use of silane agents, a copolymer, and their combination as adhesion promoters in PP/short glass fiber reinforced composites. Mechanical and dynamic mechanical measurements, scanning electron microscopy (SEM), and FTIR spectroscopy were used to evaluate the adhesion effect on these materials.

EXPERIMENTAL

Materials

A Montell PP with a melting point of 168°C and a degree of crystallinity of 48.8% was used as the matrix material. Short glass fibers (GF, E glass, Cristaleria Espanola, Madrid) with an average length and diameter of 6 mm and 13 μm , respectively, were used as reinforcement. The typical strength and stiffness levels were about 3450 MPa for the tensile strength and 72.4 GPa for the Young's modulus.¹ Two silane agents purchased from Aldrich were used to modify the glass fiber surface: 97% (w/v) 3-aminopropyltrimethoxysilane [$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, APTMS] and 99% (w/v) 3-aminopropyltriethoxysilane [$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, APTES]. The fibers according to the surface treatment were classified as follows: F1

was the as-received glass fiber that was heat cleaned for 4 h at 500°C; F2 was a treated F1 fiber with APTMS; and F3 was a treated F1 fiber with APTES. The silane agents were dissolved in pure alcohol and placed with the fibers in 1-L round-bottomed flasks. After a 6-h heating at 40°C under stirring, the alcohol was slowly distilled and the fibers were cured for 12 h at 100°C. The silane content was 10% of the fiber weight. The copolymer poly(propylene-*g*-maleic anhydride) (PP-*g*-MA) was kindly supplied by Du Pont Canada (MD-353). It had 0.8 mol % MA content, which was measured using a titration technique, and was used as an interfacial adhesion promoter. The copolymer content was 10% of the fiber weight.

Preparation of Composites

A series of glass fiber/PP (GF/PP) composites was produced with each of the three types of fiber (F1–F3) at a fiber content of 20 wt %. Another series was also prepared using the same fiber content but with the addition of the copolymer (PP-*g*-MA). The fibers and the polymer were mixed in a Haake Buchler Rheomixer (model 600) with roller blades and a mixing head with a volumetric capacity of 69 mL. Prior to mixing the F1 fibers and all polymers were dried in a vacuum oven for 24 h at 75°C. The F2 and F3 fibers were also dried under a vacuum for 6 h at 50°C. The components were physically premixed before being fed into the Rheomixer. Blending was performed at 200°C and 60 rpm for a period of 15 min. The melt temperature and torque were continuously recorded during the mixing period on a Haake Rheocord (model 5000). After preparation the blends were immediately removed from the mixer, cooled to room temperature, and placed in tightly sealed plastic containers to prevent any moisture absorption.

FTIR Measurements

FTIR measurements for the three types of fiber (F1–F3) were acquired in a Bio-Rad FTS-75A FTIR spectrometer connected to a UMA 500 microscope. The spectra were recorded using a germanium crystal in the attenuated total reflection mode, which was placed at the bottom of a 15 \times objective. For each spectrum 64 consecutive scans with 4 cm^{-1} resolution were coadded.

Mechanical Properties

The tensile strength, Young's modulus, and elongation at break were measured on an Instron

mechanical tester (model 1122) according to the ASTM D638 method. The crosshead speed was 5 mm/min. Six measurements were conducted for each material, and the results were averaged to obtain a mean value. The specimens for the mechanical property measurements were prepared by hot press molding at 200°C for 5 min at a pressure of 250 bar.

The Izod impact measurements were performed on a Tinius Olsen instrument according to ASTM D256. Six measurements were conducted. Prior to mechanical measurements, the samples were conditioned at $50 \pm 5\%$ relative humidity for 48 h at ambient temperature in a closed chamber containing a saturated solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in distilled water (ASTM E-104).

Dynamic Mechanical Thermal Analysis (DMTA)

The DMTA measurements were performed with a Rheometric Scientific Analyzer (model MKIII). The experiments were carried out using the tensile mode of the DMTA instrument over a temperature range of -50 to 150°C at a rate of $3^\circ\text{C}/\text{min}$ under a nitrogen flow. The samples were scanned at a frequency of 1 Hz, and a strain level of 0.071% was applied. A static force was applied to prevent buckling of the sample. Its value was determined so that the experiments could be held in the area of the linear viscoelastic behavior of the samples. The storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) were recorded as a function of temperature. The testing was performed using rectangular bars measuring approximately $8 \times 5 \times 0.5$ mm. The exact dimensions of each sample were measured before the scan.

SEM Analysis

The impact specimens were fractured and the exposed surfaces were observed with a scanning electron microscope (model JSM-840A, Jeol). The three types of fiber were also examined under SEM. All surfaces were coated with gold to avoid charging under the electron beam.

RESULTS AND DISCUSSION

Characterization of Fiber Coating

Organofunctional silanes have R groups that can react or interact with the resin, whereas hydroxyl groups bond to the mineral surfaces by means of

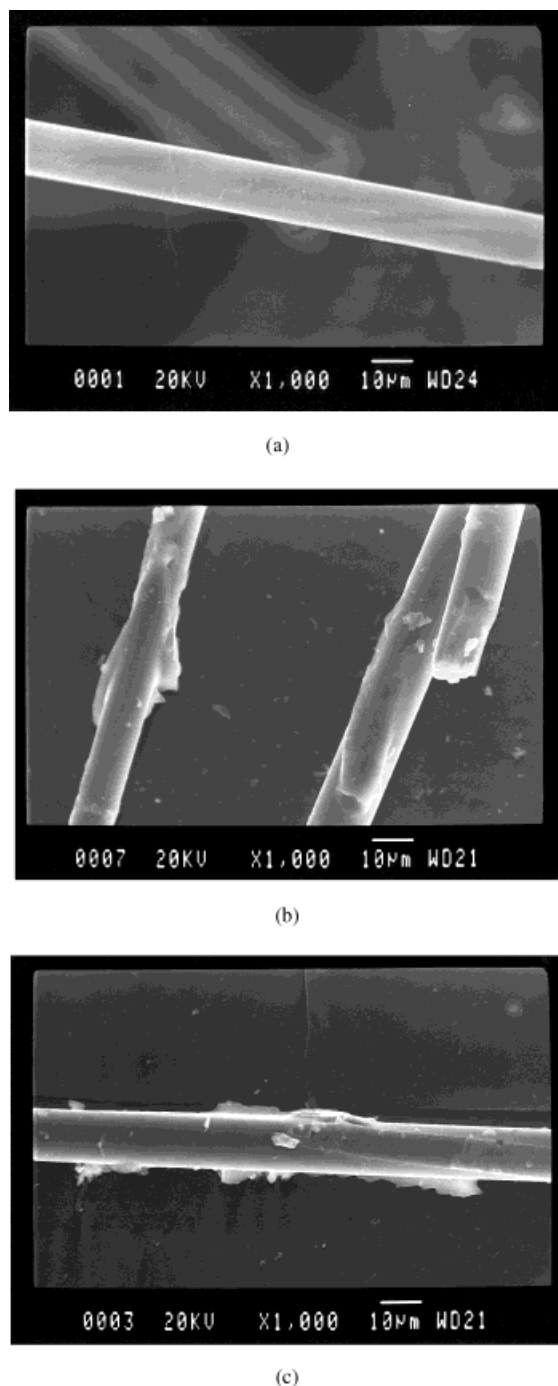


Figure 1 SEM micrographs of uncoated and coated fibers: (a) F1, (b) F2, and (c) F3.

oxane bond formation.⁸ The uncoated and coated fibers are shown in Figure 1. The formation of a silane film on the surface of the treated fibers can be seen in the micrographs of Figure 1(b,c).

The film was not uniform in thickness because of the coating mechanism, as seen in Figure 1.

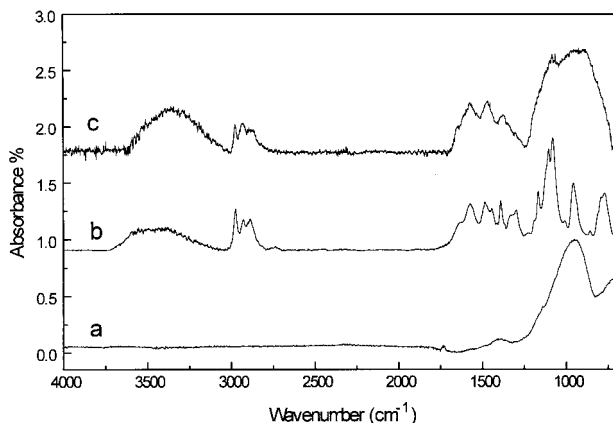


Figure 2 FTIR spectra of uncoated and coated fibers: (a) F1, (b) F2, and (c) F3.

The fiber's —OH groups reacted with the —Si groups of the organofunctional silanes by means of nucleophilic attack and simultaneous methanol evolution. With the progression of the reaction a layer was formed on the surface of the fibers. The formation of the silane layer was optically confirmed by the yellowish color of the fibers, as well as by FTIR spectroscopy. In the FTIR spectra for the uncoated and coated fibers presented in Figure 2 the peaks of the —Si—O— bonds of the glass fiber material at $850\text{--}1050\text{ cm}^{-1}$, the peaks of the —C—O— groups in the fingerprint area at $1000\text{--}1200\text{ cm}^{-1}$, and the peaks of the —CH₂ and —CH₃ groups at $2800\text{--}3050\text{ cm}^{-1}$ can be clearly seen.

The coating was completed by curing the silane-covered fibers at 100°C for 12 h. The amino groups could have possibly reacted intramolecularly with the —Si— groups, forming stable five-membered rings.⁸ It was also probable that some —NH₂ groups could have reacted intermolecularly with the —Si— groups, leading to fiber agglomerations as seen in Figure 1(b).

Mechanical Properties

The tensile strength, elongation at break, and impact strength of GF/PP composites prepared with different silane agents and their combination with the copolymer are presented in Table I.

Fiber incorporation in a rather brittle polymer matrix such as PP resulted in increased tensile and impact strength as expected, while the elongation at break decreased drastically. Composites prepared with coated fibers displayed higher tensile and impact strength values as compared to those prepared with uncoated fibers, while the

decrease in elongation at break was higher for the coated-fiber composites. This improvement in the tensile and impact strength could possibly be attributed to improved adhesion achieved between the PP matrix and the coated fibers.

The use of untreated fibers (F1) resulted in an increase in the tensile strength of PP from 18.1 to 24.4 MPa, while the impact strength increased from 6.0 to 23.5 J/m. Fiber incorporation was associated with a significant decrease from 120.0 to 27% in the elongation at break.

The significant reinforcing capability of the fibers was better realized in materials containing a coupling agent. Stronger and tougher materials were produced with silane modified fibers. The tensile and impact strength of the composites increased when treated fibers (F2, F3) were used, the best result being observed with the F2 fiber. For the F2 fiber composite the tensile strength increased to 27.1 MPa as compared to 24.4 MPa for the untreated F1 fiber (11% improvement). The increased strength for both treated fibers was associated with decreased elongation at break. The impact strength increased significantly for both fibers: 23.5 J/m for F1 to 31.0 J/m for F2 (32% improvement) and 29.0 J/m (23% improvement) for the F3 fiber.

The increase in mechanical properties of treated-fiber composites could apparently be attributed to improved interfacial adhesion achieved between the fiber and matrix that was due to the coupling effect of the silane compounds. The PP

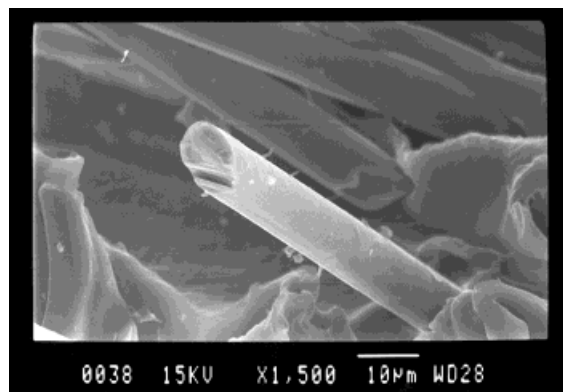
Table I Mechanical Properties of Polypropylene Composites

	Tensile Strength (MPa)	
	PP- <i>g</i> -MA Absent	PP- <i>g</i> -MA Present
PP	18.1	—
F1	24.4	31.6
F2	27.1	33.5
F3	25.2	29.7
	Elongation at Break (%)	
PP	120.0	—
F1	27.0	12.0
F2	15.0	20.0
F3	13.0	16.0
	Impact Strength (J/m)	
PP	6.0	—
F1	23.5	41.0
F2	31.0	46.0
F3	29.0	43.0

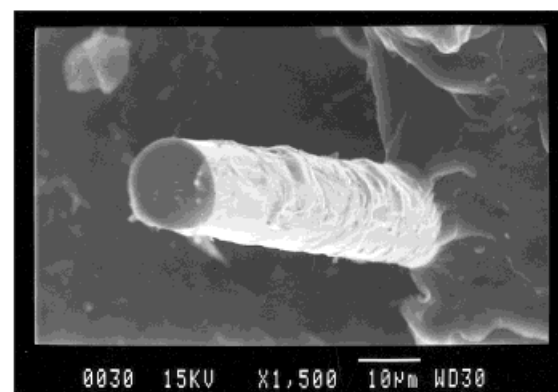
cannot react with the glass fiber and did not exhibit any compatibility with it. The hydrophilic nature of the glass fiber, because of its surface hydroxyl groups, adversely affected the adhesion to the hydrophobic thermoplastic matrix; as a result, the fiber/matrix adhesion was poor. To promote adhesion the fiber should be treated with a coupling agent that contains functional groups, which can bridge the interface between the resin and reinforcement. As mentioned, organofunctional silanes contain hydroxyl and R groups; the former bond to the mineral whereas the latter can form covalent bonds with the resin or in a nonreactive resin, such as PP, promote adhesion through the formation of a pseudointerpenetrating polymer network at the interface region.⁸ Because of the silane layer formed at the fiber surface, a treated fiber may wet out more readily in the polymeric matrix, resulting in improved interfacial adhesion. Furthermore, silanes may have the tendency to reduce fiber agglomeration and improve the distribution within the polymer matrix, thus resulting in improved mechanical properties. Untreated fibers tend to form clusters.⁹

Micrographs of fracture surfaces of GF/PP composites made with untreated and treated fibers are presented in Figure 3. Figure 3(a) shows that failure occurs at the fiber–matrix interface in composites prepared with F1 fiber as a result of the poor interfacial adhesion existing between the fiber and matrix. In comparing the fracture surface of the F2 fiber [Fig. 3(b)] with that of the untreated glass fiber it can be seen that failure increasingly occurred within the matrix, suggesting that the fiber–matrix interfacial adhesion was improved with APTMS treatment. The micrograph in Figure 3(c) shows that composites prepared with F3 fiber had failure within the matrix to a lesser extent than materials prepared with F2 fiber, reflecting the lower interfacial adhesion achieved with APTES. The extent of interfacial adhesion was also reflected in the mechanical properties of the material. These results suggested that APTMS exhibited better performance as a coupling agent compared to the APTES.

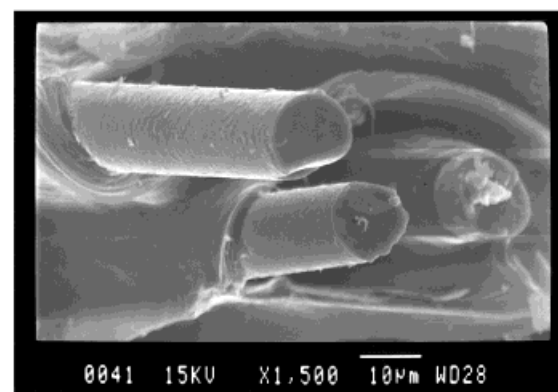
In addition to increasing the strength of the composite (because stress transfer from the matrix to the fiber becomes more effective), interfacial adhesion is also associated with energy absorbing mechanisms. Such mechanisms include fiber debonding and failure within the matrix, which lead to increased toughness and impact strength.¹⁰ It is worth noting that, unlike the



(a)



(b)



(c)

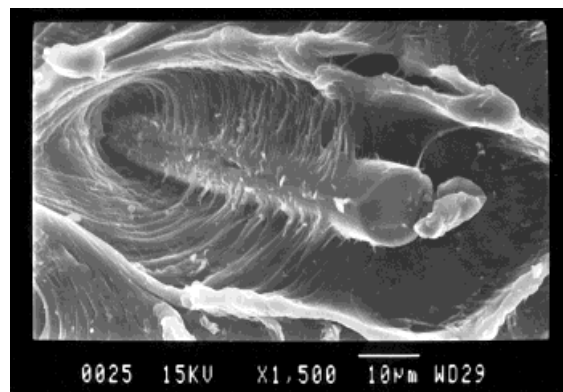
Figure 3 SEM micrographs of the fracture surfaces of GF/PP composites containing different types of fibers: (a) F1, (b) F2, and (c) F3.

APTMS treatment, which raised the tensile and impact strength of the material, treatment with the APTES had a significant influence on the impact strength only. It would appear that, although the fiber/silane/matrix bridging system formed by the APTES was not very efficient at

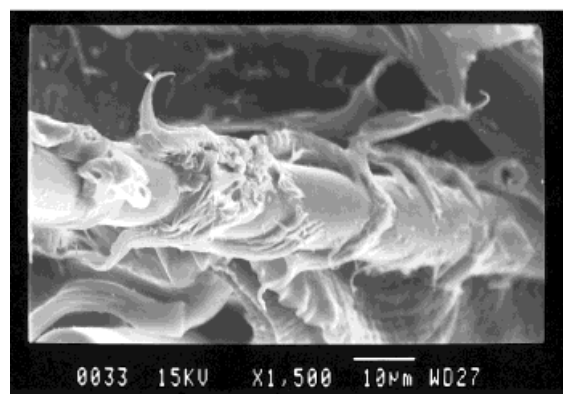
transferring stress, it was however effective in consuming energy, which resulted in increased impact strength.

The addition of the maleated copolymer PP-g-MA as a coupling agent in composites prepared with each of the three fibers (F1–F3), independent of surface treatment, resulted in increased mechanical properties, the best result being achieved for the functionalized fiber F2. A comparison of the coupling performance of PP-g-MA, APTMS, and APTES with uncoated fibers showed that the use of PP-g-MA resulted in increased mechanical properties, demonstrating the high compatibility of PP-g-MA with both phases of the material (i.e., PP and the inorganic fiber). The tensile and impact strength of the composite increased from 24.4 MPa and 23.5 J/m to 31.6 MPa (30%) and 41.0 J/m (74%), respectively (Table I). These mechanical property improvements were a reflection of strong interfacial adhesion achieved with PP-g-MA. The excellent performance of PP-g-MA as a coupling agent in GF/PP composites could be attributed to the following two factors: the ability of the MA groups to react with the hydroxyls of the glass fiber and the excellent compatibility of the grafted copolymer PP chains with the main PP phase. The use of PP-g-MA with the functionalized fibers caused a further increase in the tensile and impact strength of the composites from 27.1 MPa and 31.0 J/m to 33.5 MPa (24%) and 46 J/m (48%) for the F2 fiber and from 25.2 MPa and 29.0 J/m to 29.7 MPa (18%) and 43 J/m (48%) for the F3 fiber. This significant increase in the mechanical properties of the composites could apparently be attributed to the synergism of the two coupling agents, which is the ability of the anhydride group to react with the —NH_2 groups, thereby promoting further adhesion between the glass fibers and the polymeric matrix. Of course, additivity in the action of the two coupling agents (i.e., the reaction of the anhydride group with the —OH groups of the fiber, which may not have reacted with the silanes), could not be excluded. Although based on the data of this study it could not be unequivocally concluded which effect was dominant (synergistic or additive) with regard to adhesion and property promotion, we believed that the synergistic effect was probably the most important.

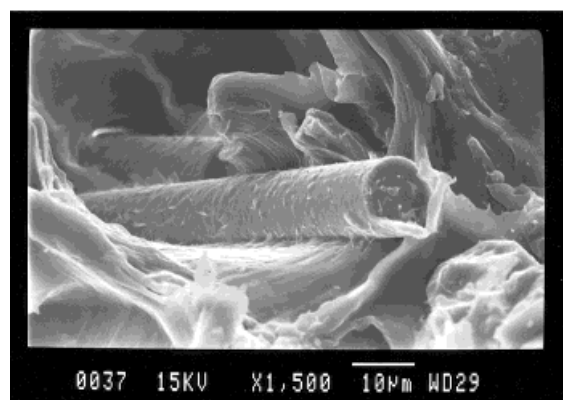
The SEM images of the fracture surfaces from composites containing PP-g-MA are shown in Figure 4. Figure 4(a, F1 fiber) shows that there was a large contact area between the matrix and the fiber surface. It was interesting to note that the



(a)



(b)



(c)

Figure 4 SEM micrographs of the fracture surfaces of GF/PP composites containing PP-g-MA and different types of fiber: (a) F1, (b) F2, and (c) F3.

adhered matrix usually ended in quite long strips of material. This suggested that the polymer network formed between the grafted PP and main PP phase through solubility and interdiffusion⁸ not only affected a few polymeric chains but also a

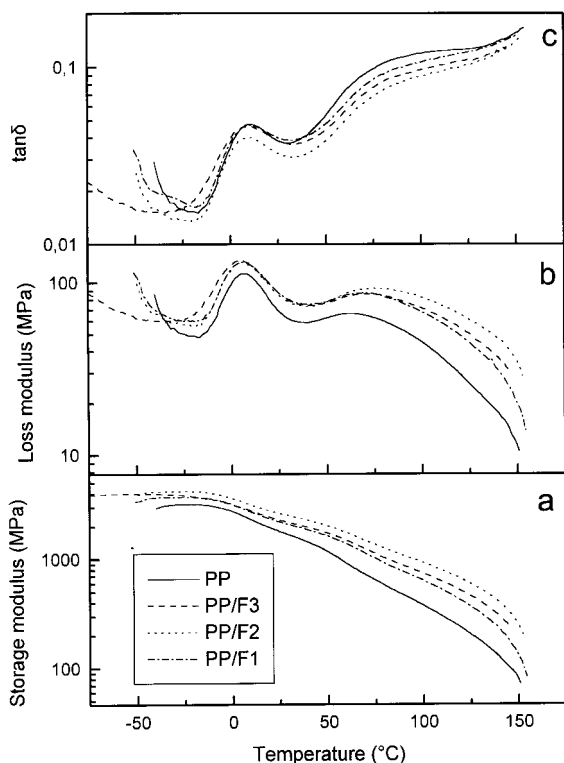


Figure 5 DMTA thermographs of GF/PP composites made with F1, F2, and F3 fibers: (a) the storage modulus, (b) loss modulus, and (c) $\tan \delta$.

considerable part of the matrix resin. Comparing the fracture surfaces shown in Figure 4(b,c) for the respective F2 and F3 fibers with the corresponding surfaces of Figure 3(b,c), it appeared that improved interfacial adhesion occurred in the presence of PP-g-MA, which was also reflected in the mechanical properties of the material.

Dynamic Mechanical Analysis

The temperature dependence on the dynamic mechanical properties for materials investigated in this study is presented in Figures 5–8. The values of E' at selected temperatures are presented in Table II.

Figure 5 shows data for the E' , E'' , and $\tan \delta$ of PP and composites prepared with F1, F2, and F3 fibers as a function of temperature. As expected, the $\tan \delta$ curve of PP [Fig. 5(c)] in the temperature range investigated in this study exhibited two relaxations located in the vicinity of 8°C (β), and 100°C (α). It is well known that a third relaxation also exists in the vicinity of -80°C (γ).¹¹ The nature of these relaxations was reviewed by McCrum and coworkers.¹¹ The γ peak is assigned

to relaxation of a few chain segments in the amorphous phase. The β relaxation is the dominant relaxation, which corresponds to the glass-rubber transition of the amorphous portions. The temperature of the peak maximum is assigned to the glass-transition temperature (T_g). The small α -relaxation peak appears as a shoulder and can be attributed to a lamellar slip mechanism and rotation within the crystals. It is clear from Figure 5 that at relaxation temperatures in the vicinity of 8 and 100°C the E' decreases [Fig. 5(a)] while the E'' [Fig. 5(b)] and $\tan \delta$ [Fig. 5(c)] pass through a maximum.

The introduction of glass fiber in the PP matrix had profound effects on the dynamic mechanical properties of the material. The stiffness and heat resistance of the composite were both increased over the whole temperature range, but the damping factor decreased.

Figure 5(a) shows that the drop in modulus on passing through α - and β -relaxation temperatures was comparatively less for reinforced materials than for PP alone, and this drop was less as the temperature increased. In other words, the effect of the glass fiber on the modulus was larger

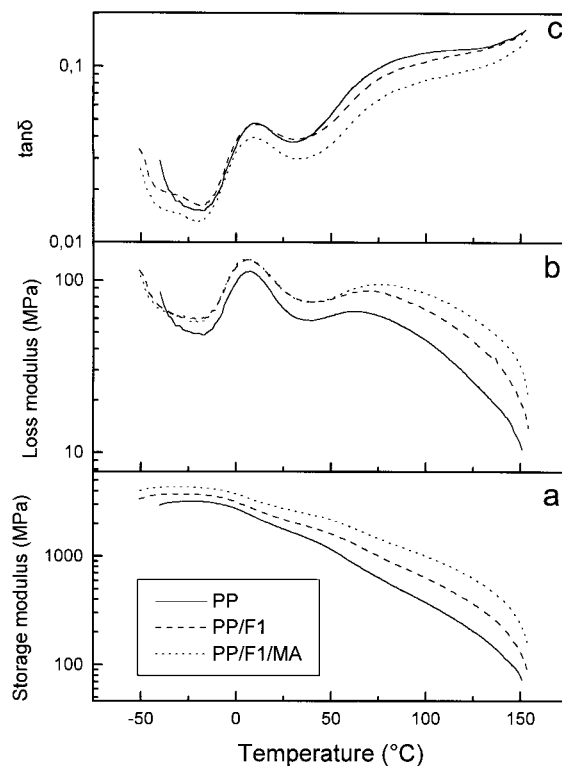


Figure 6 DMTA thermographs of GF/PP composites made with F1 fiber containing PP-g-MA: (a) the storage modulus, (b) loss modulus, and (c) $\tan \delta$.

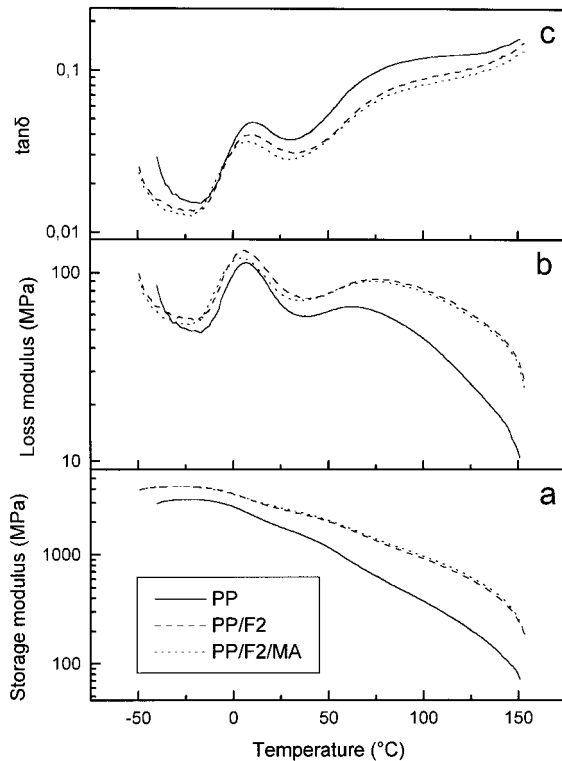


Figure 7 DMTA thermographs of GF/PP composites made with F2 fiber containing PP-g-MA: (a) the storage modulus, (b) loss modulus, and (c) $\tan \delta$.

at higher temperatures than at lower temperatures. Thus, a material with a relatively higher modulus was produced at higher temperatures. This was probably due to the fact that the incorporation of glass fiber reduced the flexibility of the material by introducing constraints on the segmental mobility of the polymeric molecules or by retarding the lamellar movement at relaxation temperatures^{12,13} effects, which become more pronounced with increasing temperature.

The plot of the E'' as a function of temperature [Fig. 5(b)] shows that the most pronounced effect of glass fiber reinforcement was the broadening of the relaxation regions, especially the α relaxation. It appeared that the glass fibers significantly affected the lamellar movement and rotation in the crystalline phase. Decreased mobility of the PP segments due to the interaction with the high energy glass fiber surface, which resulted in a wider distribution of their relaxation times or retardation of the relative motion of the lamellae, may be some of the factors causing the observed broadening of the relaxation peaks.¹²

A comparison of the $\tan \delta$ curves presented in Figure 5(c) shows that fiber incorporation led to a

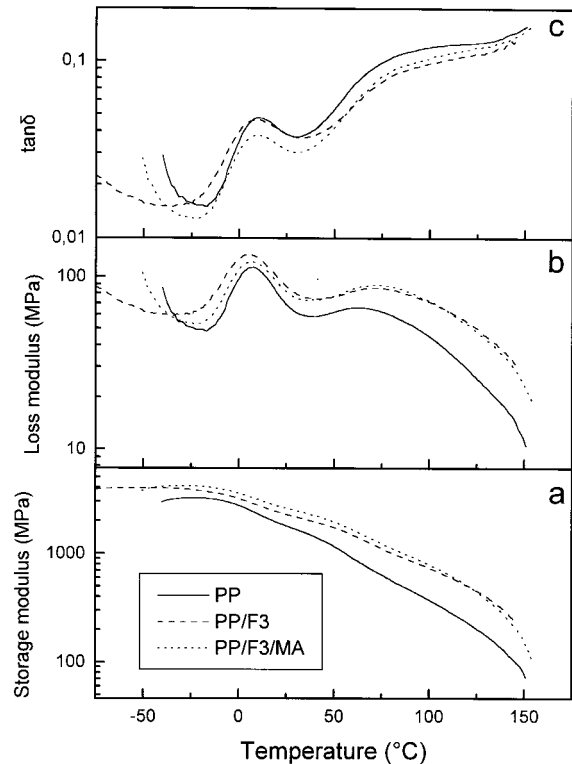


Figure 8 DMTA thermographs of GF/PP composites made with F3 fiber containing PP-g-MA: (a) the storage modulus, (b) loss modulus, and (c) $\tan \delta$.

reduction in magnitude of the peak intensity for both α and β relaxations. However, the position of the peaks practically remained unchanged. This would suggest that glass fiber incorporation did not significantly influence the crystallization or percentage of matrix crystallinity, because such processes are related to peak location change.¹²

Table II Storage Modulus of Polypropylene Composites at Different Temperatures

	Temperature (°C)			
	25	50	100	150
	Storage Modulus (MPa)			
PP	1789	1169	376	78
PP/F1	2195	1627	634	131
PP/F2	2620	2023	928	247
PP/F3	2283	1737	738	176
PP/F1/MA	2762	2179	1005	239
PP/F2/MA	2691	2078	975	258
PP/F3/MA	2600	1949	796	157

The existence of interfacial adhesion results in a material with an increased E' , resistance to elevated temperatures, decreased damping, and broader peaks. The best results were observed with APTMS treated fibers (F2), which were in agreement with the mechanical property results obtained and microscopic evidence. It appeared that the presence of interfacial adhesion hindered the molecular motion, as well as the relative motion of the lamellae, leading to a stiffer, stronger, tougher material.^{14,15}

The effect of PP-g-MA on the thermomechanical properties of the material is shown in Figures 6–8. In all cases the use of PP-g-MA resulted in a further increase of the E' and lowering of the damping factor.

A comparison of the E' at selected temperatures for composites prepared with the three types of fiber (F1–F3) and use of the copolymer PP-g-MA is shown at Table II. The best results (higher E' and lower damping factor, Figs. 6–8) were achieved for the composite made with the functionalized fiber F2 and the uncoated fiber F1, which agreed with the mechanical property results and microscopic evidence. The ability of the MA groups to react with the amino groups of the APTMS coated glass fiber or the hydroxyl groups of the uncoated glass fiber, as well as the compatibility of the grafted PP chains with the main PP phase, all translated to better composite properties.

CONCLUSIONS

Glass fiber reinforced PP composites can be effectively coupled by standard organofunctional silane coupling agents. Adhesion is promoted through the formation of a pseudointerpenetrating polymer network at the interface region⁸ of the polymeric matrix and the fiber. Increased interfacial adhesion results in a material with increased mechanical properties. Materials coupled with the APTMS show improved properties compared to those coupled with the APTES. A possible reason may be that the methoxy groups, which are smaller than the ethoxy, can more effectively react with the fiber's hydroxyl groups.

Functionalized copolymers may be successfully used as adhesion promoters in thermoplastic composites. Materials coupled with the PP-g-MA co-

polymer show improved properties compared to those coupled with the organofunctional silanes. The excellent compatibility of the grafted PP copolymer chains with the main PP phase and the ability of the MA groups to react with the hydroxyl groups of the mineral explain the superior coupling performance of PP-g-MA.

The use of PP-g-MA with aminosilane coated fibers is very effective. This can be attributed to the ability of the MA groups to react with the amino groups.

In addition to affecting the mechanical properties of the composites, interfacial adhesion also affects their viscoelastic behavior. In general, improved interfacial adhesion in glass fiber composites means an increase in the E' and a lowering of the damping factor.

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