Conifer Fibers as Reinforcing Materials for Polypropylene-Based Composites

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ABSTRACT: Conifer fibers were used to reinforce polypropylene (PP). To improve the compatibility between the conifer fibers and the PP matrix, the fibers were either grafted with maleated PP (MAPP), treated by adding MAPP, or mixed with ethylene/propylene/diene terpolymer (EPDM). The treatments resulted in improved processing, as well as improvements in the thermal and mechanical properties of the resultant composites compared with the composites filled with untreated conifer fibers. Moreover, MAPP grafting and MAPP treating displayed more obvious benefits than EPDM treating in terms of thermal properties, processing flowability, and tensile strength improvements. EPDM treating also produced more significant benefits than either MAPP grafting or MAPP treating in terms of impact strength and tensile elongation improvements. These improvements were attributed to surface coating of the fibers when EPDM was used. In addition, the effect of the concentration of the conifer fibers on the properties of the composites and the difference between MAPP grafting and MAPP treating were evaluated. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2833–2841, 2001

Key words: polymer composites; conifer fiber; polypropylene; maleated polypropylene; ethylene/propylene/diene terpolymer

INTRODUCTION

Lignocellulosic fibers are increasingly found in applications in polymer reinforcement because of desirable characteristics such as highly specific properties.[1,2] In comparison with mineral fibers, lignocellulosic fibers are inexpensive, renewable, and biodegradable and have low density and a desirable fiber aspect ratio.[3,4] In addition, lignocellulosic fibers exhibit several attractive mechanical properties when used as reinforcements in thermoplastics. These include high specific strength, high stiffness to weight ratio, and low hardness that minimizes abrasion of equipment during processing.[5,6] Among commodity thermoplastics, polypropylene (PP) possesses outstanding properties like low density, a high Vicat softening point, good flex life, sterilizability, good surface hardness and scratch resistance, very good abrasion resistance, and excellent electrical properties.[7] Lignocellulosic fiber surfaces are hydrophilic in nature. In contrast, PP is hydrophobic. The inherent lack of compatibility between the lignocellulosic fibers and the thermoplastic ma-

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trix has been a key research issue and needs to be improved if properties are to be optimized. The result is composites in which the fibers can be both poorly dispersed and poorly bonded to the polymer matrix. The combination of these factors leads to composites that have less than optimal processing behavior and mechanical properties.

Much previous research focused on efforts to improve the interfacial bonding between lignocellulosic fibers and PP matrix. For example, Felix and Gatenholm[8] and Kazayawoko et al.[9] studied the diffuse reflectance FTIR of bleached kraft cellulose and unbleached thermomechanical pulp treated with maleated PPs (MAPP) and concluded that fibers could be reacted with maleic anhydride with the formation of ester links. Rana et al.[10] concluded from a study of short jute fiber reinforced PP composites that the role of jute fiber was not as a filler but as a reinforcement in a properly compatibilized system. Avella et al.[11] studied broom fibers as reinforcing materials for PP-based composites and concluded that NaOH-extracted fiber MAPP-based composites presented specific mechanical properties comparable to those of analogous short glass fiber reinforced materials. Tjong et al.[12] also concluded from research on composites based on MAPP and methyl cellulosic fiber that improvements in the mechanical properties could be attributed to interaction between the functional group of maleic anhydride and tetrabutyl orthotitanate.

In the present study we investigated the esterification reaction between conifer fibers and MAPP using FTIR spectroscopy. In addition, attempts were made to evaluate the interfacial adhesion between the conifer fibers and PP matrix using scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) techniques. Because the MAPP grafting of fibers would probably be expensive and therefore not be industrially practicable, experiments were also carried out to evaluate composite properties when MAPP was added as a compatibilizer. The effects of the conifer fiber concentration and the different fiber treatments on the thermal properties, heat distortion temperature, processing flowability, and various mechanical properties of the composites were also studied.

EXPERIMENTAL

Materials

Conifer fibers (waste commercial bleached coniferous wood pulp board) were mechanically dispersed to obtain single fibers, and this material was used for the preparation of composites. The original fiber length was in the range of 2–3.5 mm, the width was in the range of 34.2–73.1 μm, and the length to width ratio was 72.6. The selected PP was Fortilene HB 9300 (Solvay) with a density of 900 kg/m^3 and a melt flow index (MFI) of 5 g/10 min (230°C/2160 g). The MAPP was Unite MP880 (Aristech Chemical Corporation) with an average molar mass of 90,000 g/mol. The ethylene/propylene/diene terpolymer (EPDM) was 4015 from Mitsui Petrochemical Co., Ltd.

Conifer Fiber Treatments

The MAPP grafting of conifer fibers was conducted in a reactor with xylene as a solvent and sodium hypophosphite hydrate as an esterification catalyst. Before grafting, the fibers were dried at 70°C in an oven with circulating air for 24 h. The fibers were then immersed in a solution of MAPP in hot xylene and sodium hypophosphite hydrate. The reaction was carried out for 2 h at 135°C. The MAPP concentration was 6 wt % and the concentration of conifer fibers was 4 wt % in the solution. After the reaction, the fibers were Soxhlet extracted with xylene for 24 h to remove all components not covalently bonded to the fibers and oven dried at 70°C for 24 h. The MAPP and EPDM treatments were carried out by simply melt mixing with fibers in a two-roll mill. The EPDM concentration was 8 wt % in the PP matrix.

Sample Preparation

Grafted or treated conifer fibers and PP were mixed at 165°C for 10 min in a two-roll mill and then cooled to room temperature and cut into 5 $\times$ 5 mm^2 pieces. The conifer fiber contents selected were 10, 20, 30, 40, and 50 wt %, respectively. The mixtures were remixed in a Brabender twin-screw extruder with four heating zones. The four zones were heated to 160, 170, 180, and 180°C. The extruded mixtures were granulated to a length of 5 mm. Samples for mechanical property measurements were obtained by compression molding in a press at 180°C under a pressure of 10 MPa followed by cooling in another press.

IR Spectrometric Analysis

The conifer fibers, MAPP, and MAPP-grafted fibers were dried for 24 h at 80°C under a vacuum, ground to mesh size 80, mixed with potassium

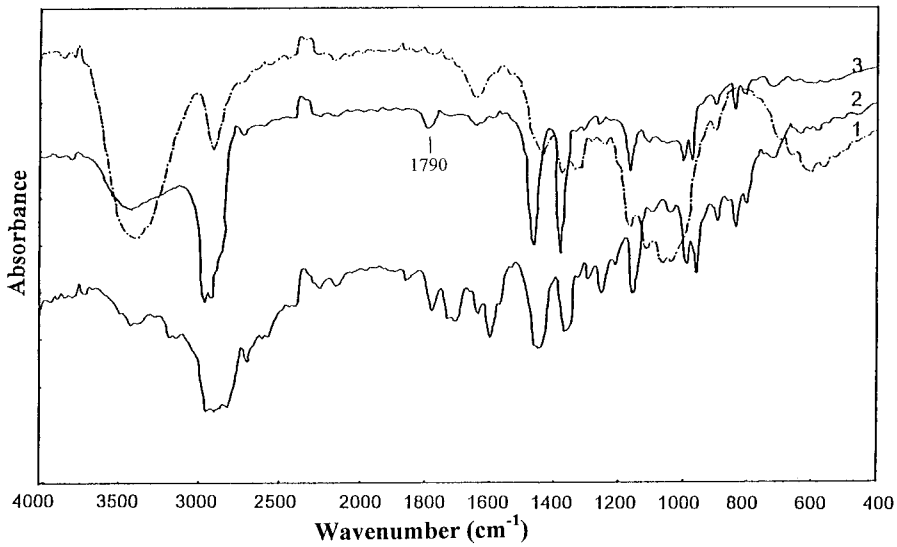


Figure 1 IR spectra of untreated conifer fibers (plot 1), MAPP (plot 2), and MAPP-grafted conifer fiber composites (plot 3, 30 wt % fiber).

bromide, and pressed at room temperature for 10 min for IR spectrometric analysis.

SEM Analysis

For scanning electron microscopy the freeze fractured specimens were prepared by cooling composite specimens in liquid nitrogen, then breaking the samples. Fractured surfaces were coated sequentially with a thin film of carbon and gold to a total thickness of about 25 nm. The SEM images were obtained using an SEM microscope (X-650, Hitachi).

DSC Measurements

The DSC was performed with a Perkin–Elmer DSC-7 calorimeter. Samples were scanned at 10°C/min from −30 to 110°C, then quenched with liquid nitrogen and rescanned at the same heating rate. The glass-transition temperature was taken as the temperature of the inflection point.

Heat Distortion Temperature Measurement

The distortion temperature was measured according to the ISO 075 standard using a Toyo Seiki Seisaku-Sho. Co. test machine.

Torque Rheometer Tests

The torque rheological behavior tests were done in the internal mixer chamber of a Brabender Plasticorder (model PLE 330) during the mixing of the composites. The torque data were taken at the equilibrium stage of each composition mixing at a temperature of 190°C with a a rotor speed of 30 rpm and a mixing time of 8 min.

Table I IR Absorption Bands and Assignments of Bands of Untreated Conifer Fibers

Band Position (cm^{-1})	Assignments
3500–3300	OH stretching
3000–2840	CH stretching of CH_2 and CH_3
1650–1600	Absorbed water
1480–1420	CH_2 deformation
1400–1360	CH deformation of CH_2, CH_3, OCH_3
1350–1320	OH deformation
1170–1150	C—O—C stretching
1100–1000	C—O stretching

Table II IR Absorption Bands and Assignments of Bands of MAPP

Band Position (cm^{-1})	Assignments
3000–2700	CH stretching of CH_2 and/or CH_3
1800–1700	C═O symmetric and asymmetric stretching
1620–1580	C═O stretching of carboxyl groups
1500–1300	CH deformation of CH_2 and/or CH_3

(a)

(b)

Figure 2 SEM micrographs of fractured specimens of PP/untreated conifer fiber composites (40 wt % fiber): (a) original magnification ×200 and (b) original magnification ×2000.

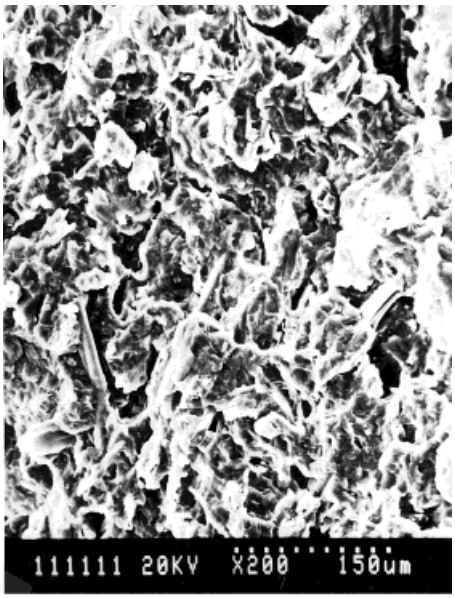
Mechanical Properties

Tensile strength and elongation tests were performed with an Instron tester (model M5K) following the ASTM D 638 method. The Charpy impact strength was measured using both notched and unnotched specimens by the ISO 180-4A method. Each tensile or impact value was the average of five independent measurements.

RESULTS AND DISCUSSION

IR Spectrometric Analysis

Figure 1 shows that the IR absorption spectra of untreated conifer fibers, MAPP, and MAPP-

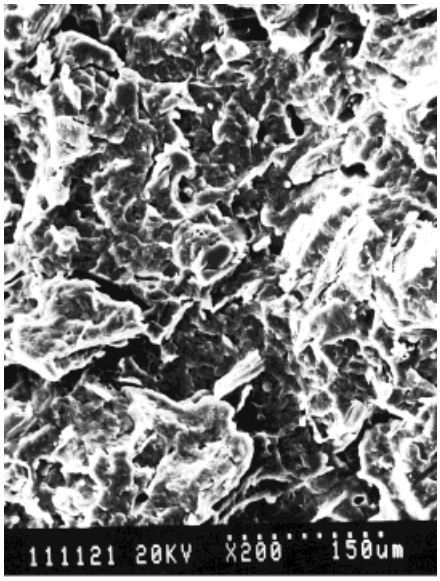


(a)

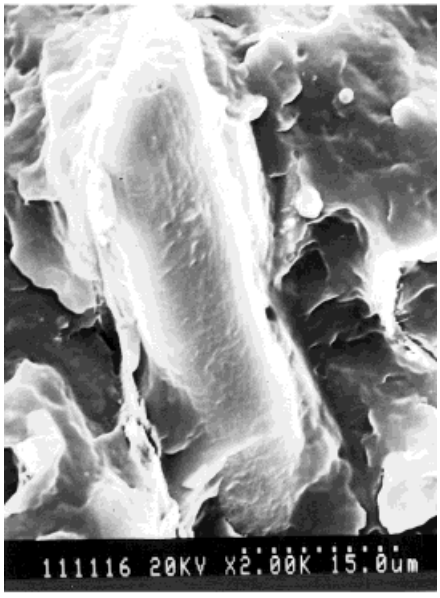
(b)

Figure 3 SEM micrographs of fractured specimens of PP/MAPP-grafted conifer fiber composites (40 wt % fiber): (a) original magnification ×200 and (b) original magnification ×2000.

grafted conifer fibers is in the range of 4000–600 cm^{-1}. The major IR absorption bands and their assignments for conifer fibers and MAPP are summarized in Tables I and II. A new weak absorption band at around 1790 cm^{-1} was found for the MAPP-grafted fibers (Fig. 1, spectrum 3). For comparison the spectra of the ungrafted fibers (spectrum 1) and MAPP (spectrum 2) are also shown in Figure 1. This new absorption may be attributed to the ester functional groups as explained by Felix and Gatenholm[8] and Kazayawoko et al.[9] Furthermore, the OH stretching absorption of grafted fibers in the range of 3500–



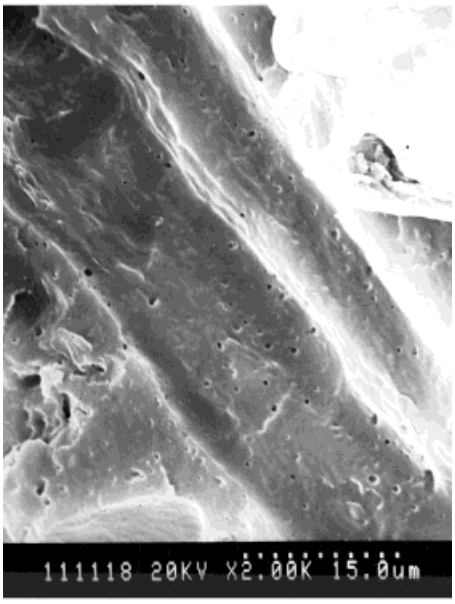
(a)



(b)

Figure 4 SEM micrographs of fractured specimens of PP/MAPP-treated conifer fiber composites (40 wt % fiber): (a) original magnification ×200 and (b) original magnification ×2000.

(a)



(b)

Figure 5 SEM micrographs of fractured specimens of PP/EPDM-treated conifer fiber composites (40 wt % fiber): (a) original magnification ×200 and (b) original magnification ×2000.

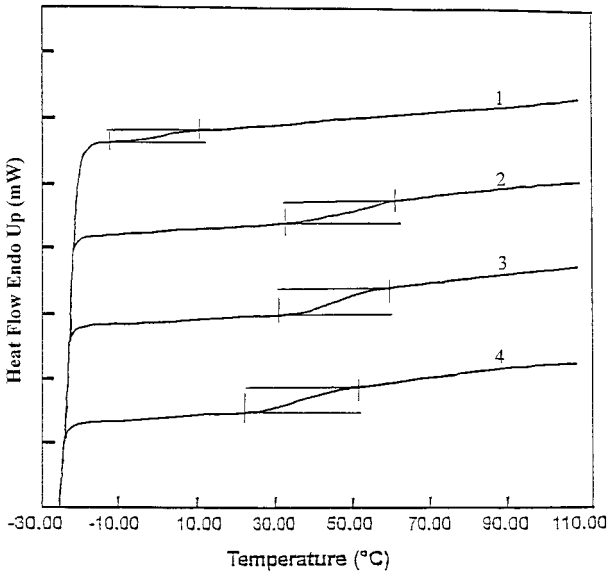


Figure 6 DSC curves for PP (plot 1), PP/MAPP-grafted conifer fiber composites (plot 2), PP/MAPP-treated conifer fiber composites (plot 3), and PP/EPDM-treated conifer fiber composites (plot 4, 50 wt % fiber).

3300 cm^{-1} was much smaller than that of the ungrafted ones, indicating that the numbers of hydroxyl (OH) groups were reduced in the MAPP-grafted fibers. Compared with that in spectrum 2 in Figure 1, the absorption band of the stretching of carboxyl groups of MAPP in the 1800–1700 cm^{-1} region of MAPP-grafted fiber composites disappeared. The stretching band of absorbed water in the 1650–1600 cm^{-1} region of the MAPP-grafted fiber composites was much smaller than that of the ungrafted fibers. An esterification reaction between the conifer fibers' hydroxyl group and the anhydride functional group of MAPP might have occurred, which resulted in better interfacial adhesion between the conifer fibers and the PP matrix as illustrated by the mechanical properties of the composites.

Morphology

Examination of the cryogenically fractured cross-sectional surfaces of the impact test specimens of the composites by SEM gave information about how the surface morphology of the composites changed as a function of the fiber treatment. SEM micrographs of the fracture surfaces of composite samples containing 40 wt % conifer fibers are shown in Figures 2–5. Figure 2 shows the micrographs of the samples of pure PP with untreated fibers. The fibers were not well dispersed in the PP matrix [Fig. 2(a)], and agglomerated fibers were seen in the composites. In Figure 2(b) the microstructure of the composites indicates the poor interfacial adhesion between the fiber surface and the PP matrix with no PP matrix coating around the fiber surfaces. Figure 3 shows the morphology of the samples of PP with MAPP-grafted fibers. Figure 3(a) shows that good dispersion of the fibers in the PP matrix and no agglomerated fibers in the composites were found. In Figure 3(b) the microstructure of MAPP treated fiber composites is different from that of the untreated fiber composites [Fig. 2(b)]. It is difficult to differentiate the interface of the fibers from the PP matrix. The micrographs of the samples treated with MAPP as a compatibilizer [Fig. 4(a,b)] appeared similar to the micrographs shown in Figure 3(a,b). Figure 5 shows the morphology of the sample treated with EPDM as an impact modifier. Figure 5 also shows good dispersion of the fibers in the PP matrix [Fig. 5(a)] and good adhesion between the conifer fibers and PP matrix [Fig. 5(b)]. Because there was good interaction between the PP matrix and EPDM, the fibers were covered by layers of EPDM and the PP matrix. All the above illustrated that the presence of MAPP-grafted fibers and MAPP-treated fibers enhanced the interfacial adhesion of conifer fibers and PP and improved the compatibility of the two phases, therefore leading to better properties.

Thermal Properties

The DSC thermograms for PP and PP/MAPP-grafted conifer fiber composites, PP/MAPP-

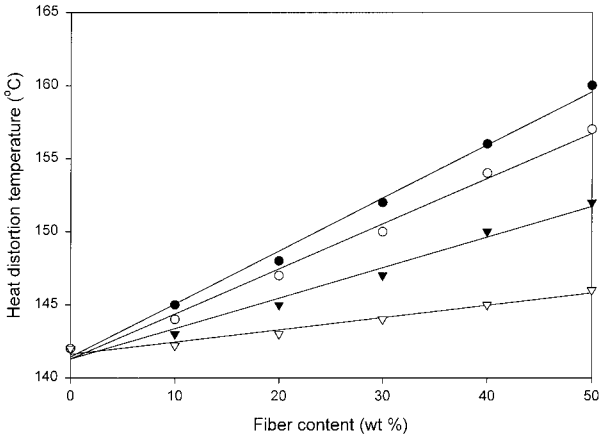


Figure 7 The heat distortion temperatures of (●) PP/MAPP-grafted fiber composites, (○) PP/MAPP-treated fiber composites, (▼) PP/untreated fiber composites, and (△) PP/EPDM-treated fiber composites.

Table III Torque Data of PP/Conifer Fiber Composites

	Torque at Balance Curve (Nm)					
	0	10	20	30	40	50
Fiber Treatment	Fiber (wt %)					
Untreated	36	39	43	47	51	56
MAPP-grafted fiber	36	30	31	33	33	35
MAPP-treated fiber	36	31	32	34	35	36
EPDM-treated fiber	36	38	40	44	48	51

treated conifer fiber composites, and PP/EPDM-treated conifer fiber composites are shown in Figure 6. For the pure materials, the glass-transition temperatures (T_g) were 2°C for the PP matrix (Fig. 6, plot 1) and greater than 250°C for the conifer fibers. Above this temperature the conifer fibers started to decompose. The T_g of the fiber phase above this temperature could not be determined. The T_g of the two components moves closer if the two components are partially miscible. Obviously, the T_g of the PP phase in the composites shifted from 2 to 48°C for PP/MAPP-grafted fiber composites (Fig. 6, plot 2), to 45°C for PP/MAPP-treated fiber composites (Fig. 6, plot 3), and to 37°C for PP/EPDM-treated fiber composites (Fig. 6, plot 4). This suggested that MAPP-grafting, MAPP-treating, or EPDM-treating methods can improve the compatibility of PP and conifer fibers in composites. The DSC data were consistent with substantially improved mutual partial compatibility or interpenetration.

Heat Distortion Temperature

Figure 7 shows the effect of the conifer fiber concentration on the heat distortion temperature of the composites. Clearly the heat distortion temperature of all the composites increased with increasing fiber concentration, as shown in Figure 7. At a fiber loading of 50 wt %, the heat distortion temperatures was increased by 7% for the untreated fibers, 3% for the EPDM-treated fibers, and over 10% for both MAPP-grafted fibers and MAPP-treated fibers. This established that conifer fibers can improve the thermal resistance of the composites.

Process Flowability

Table III presents torque data expressing the processing behavior of the PP/conifer fiber composites. The data in Table III show that the torque increased during mixing with increasing fiber concentration for the composites based on the untreated fibers or the EPDM-treated fibers (8 wt % EPDM). Thus, the process flowability of the raw materials with either untreated fibers or EPDM-treated fibers was poor. On the contrary, the processing of MAPP-grafted fibers and MAPP-treated fibers (6 wt % MAPP) to make composites showed a slight decrease in torque with fiber concentration. The torque of the samples containing

Table IV MFI of PP/Conifer Fiber Composites

	MFI (g/10 min)					
	0	10	20	30	40	50
Fiber Treatment	Fiber (wt %)					
Untreated	5.3	3.6	2.4	1.2	0.6	0.3
MAPP-grafted fiber	5.3	4.8	4.1	3.2	2.6	1.5
MAPP-treated fiber	5.3	4.6	3.9	3.0	2.3	1.3
EPDM-treated fiber	5.3	3.5	2.2	1.1	0.5	0.3

Measuring conditions: 230°C with a 2160-g load.

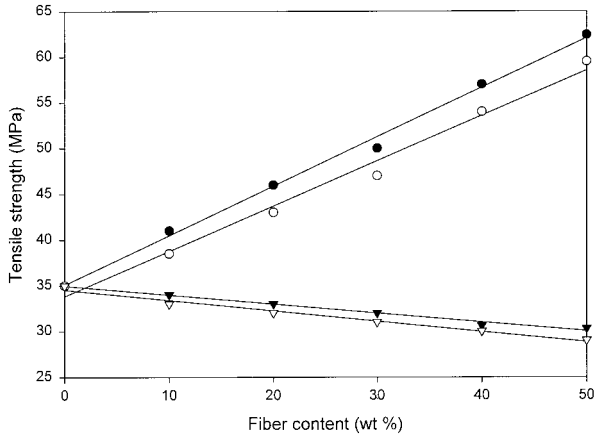


Figure 8 The tensile strength of (●) PP/MAPP-grafted fiber composites, (○) PP/MAPP-treated fiber composites, (▼) PP/untreated fiber composites, and (△) PP/EPDM-treated fiber composites.

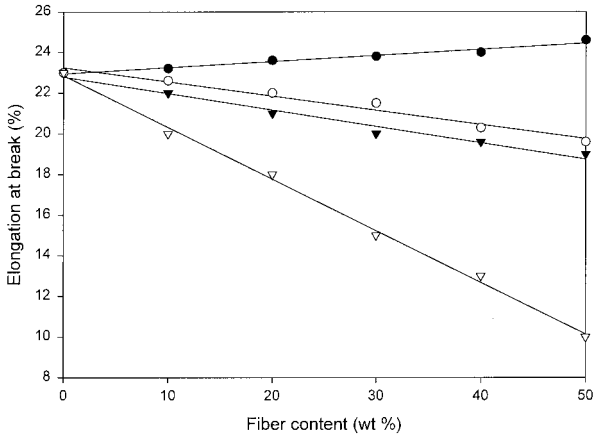


Figure 9 The elongation at break of (●) PP/EPDM-treated fiber composites, (○) PP/MAPP-grafted fiber composites, (▼) PP/MAPP-treated fiber composites, and (△) PP/untreated fiber composites.

50 wt % MAPP-grafted fibers or 50 wt % MAPP-treated fibers in the composites was comparable to that of pure PP. The MAPP-grafted and MAPP-treated fibers both substantially improved the processing flowability of the composites.

Table IV presents the MFI of PP/conifer fiber composites. The EPDM-treated fibers (8 wt % EPDM) and untreated fibers both exhibited a decrease in MFI as a function of the concentration of the fibers. This result showed that conifer fibers can increase the viscosity of the composites and that EPDM treatment does not reduce the viscosity of the PP/fiber raw materials. The comparable data for the MAPP-grafted fibers and MAPP-treated fibers showed much smaller decreases in the MFI. The decrease in MFI of the composites was mainly influenced by the amount of fiber reinforcement in the PP. This indicated that MAPP treatment or grafting of fibers also improved the composite manufacturing process through improved material flow.

Mechanical Properties

Figures 8 and 9 show the tensile strength and elongation percentage at break of PP/conifer fiber composites. Compared to the composites prepared using untreated fibers, the addition of either MAPP-grafted fibers or MAPP-treated fibers caused a significant increase in tensile strength and an expected smaller decrease in the elongation at break. At a fiber loading of 50 wt %, the tensile strength of the composites containing untreated fibers was increased by 78% for MAPP-grafted fibers and by 70% for MAPP-treated fibers. Figures 8 and 9 also show that EPDM-treated fibers caused a slight increase in elongation at break.

Figures 10 and 11 show the notched and unnotched impact strength, respectively, of the PP/fiber composites. Figure 11 shows that the unnotched impact strength of the composites with untreated fibers decreased drastically with increasing fiber concentration. In contrast, the notched impact strength of the composites with untreated fibers increased slightly with increasing fiber concentration (Fig. 10). This result indicated that conifer fibers can improve the high

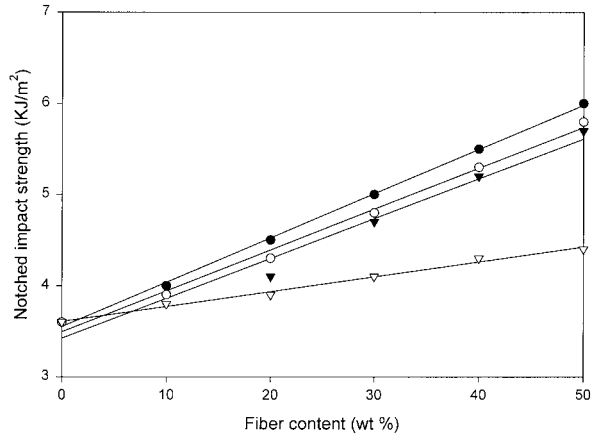


Figure 10 The notched impact strength of (●) PP/EPDM-treated fiber composites, (○) PP/MAPP-grafted fiber composites, (▼) PP/MAPP-treated fiber composites, and (△) PP/untreated fiber composites.

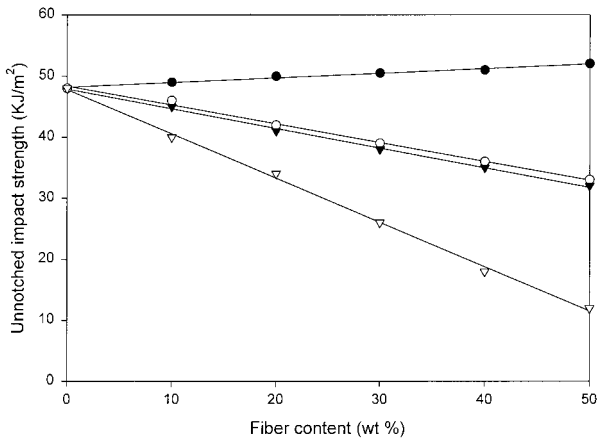


Figure 11 The unnotched impact strength of (●) PP/EPDM-treated fiber composites, (○) PP/MAPP-grafted fiber composites, (▼) PP/MAPP-treated fiber composites, and (△) PP/untreated fiber composites.

notched impact susceptibility of PP. Compared to the composites prepared using untreated fibers, the MAPP and EPDM treatments both caused a significant improvement in the notched and unnotched impact strength of the composites. At a fiber loading of 50 wt %, the notched impact strength was increased by 66% for EPDM-treated fibers, 61% for MAPP-grafted fibers, and 58% for MAPP-treated fibers. Figures 10 and 11 show that the notched and unnotched impact strengths of the composites were more significantly improved by EPDM-treated fibers than that of either MAPP-grafted fibers or MAPP-treated fibers. This result indicated that EPDM can be an effective impact modifier for PP/conifer fiber composites. MAPP treatment facilitates stress transfer from the PP matrix to the fibers and improves composite tensile strength. However, EPDM-treated fibers absorb impact and thus increase composite impact strength. The beneficial effects of MAPP and EPDM on the strength properties of PP/conifer fiber composites were attributed to an esterification reaction involving fiber hydroxyl groups and the anhydride functionality of MAPP and to fiber surface coating with EPDM.

CONCLUSIONS

The following conclusions were drawn from the above results:

1. The interfacial adhesion or the compatibility of PP with conifer fibers was improved by MAPP grafting or MAPP treating of the fibers, as shown by SEM observation and DSC measurement.
2. The high notched impact susceptibility of PP was significantly reduced by adding conifer fibers. The heat distortion temperature of PP was also enhanced by the addition of conifer fibers.
3. The composites of PP/conifer fibers with either MAPP-grafted fibers or MAPP-treated fibers produced a significant improvement in mechanical properties and processing flowability compared to untreated conifer fiber composites. The effect of EPDM-treated fibers on the composite impact strength was greater than that obtained when using either MAPP-grafted or MAPP-treated fibers.
4. MAPP grafting and MAPP treatment had similar effects on the properties of PP/conifer fiber composites.

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REFERENCES

1. Park, B. D.; Balatinecz, J. Polym Compos 1997, 18, 79.
2. Maldas, D.; Kokta, B. V. Int J Polym Mater 1990, 14, 165.
3. George, J.; Janardhan, R. J.; Anand, J. S.; Bhagawan, S. S.; Thomas, S. Polymer 1996, 37, 5421.
4. Kim, T. J.; Lee, Y. M.; Im, S. S. Polym Compos 1997, 18, 273.
5. Raj, R. G.; Kokta, B. V.; Daneault, C. Int J Polym Mater 1990, 14, 123.
6. Zadorecki, P.; Michell, A. J. Polym Compos 1990, 10, 69.
7. Brydson, J. A. Plastic Materials, 3rd ed.; Newnes Butterworths: London, 1975; Chap. 11.
8. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1992, 42, 609.
9. Kazayawoko, M.; Balatinecz, J. J.; Woodhams, R. T. J Appl Polym Sci 1997, 66, 1163.
10. Rana, A. K.; Mandal, A.; Mitra, B. C.; Jacobson, R.; Rowell, R.; Banerjee A. N. J Appl Polym Sci 1998, 69, 329.
11. Avella, M.; Casale, L.; Dell'erba, R.; Focher, B.; Martuscelli, E.; Marzetti, A. J Appl Polym Sci 1998, 68, 1077.
12. Tjiong, S. C.; Xu, Y.; Meng, Y. Z. J Appl Polym Sci 1999, 72, 1647.