

# Influence of Maleated Polypropylene on Mechanical Properties of Composite Made of Viscose Fiber and Polypropylene

Teemu Paunikallio, Jossi Kasanen, Mika Suvanto, Tuula T. Pakkanen

Department of Chemistry, University of Joensuu, P.O. BOX 111, FIN-80101 Joensuu, Finland

Received 29 January 2002; accepted 12 July 2002

**ABSTRACT:** The purpose of this work was to study how viscose fiber behaves in polypropylene (PP) matrix when maleated polypropylene (MAPP) is used as a coupling agent. The influences of processing conditions on composite properties was of interest. Composites were characterized by FTIR and mechanical testing. The most notable result was the effect of the MAPP concentration on the tensile strength of the composites; the tensile strength increased from 40 to

69 MPa when MAPP was added in amounts up to 6 wt % of the fiber weight. The interaction between MAPP and fiber was confirmed with FTIR. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1895–1900, 2003

**Key words:** adhesion; composites; extrusion; reinforcement; mechanical properties

## INTRODUCTION

Polypropylene is a thermoplastic polymer widely used as a matrix in wood fiber–plastic composites. Wood fibers are inexpensive fillers that reduce raw material costs while increasing the stiffness and strength of thermoplastics.<sup>1</sup> During the late 1980s, researchers began a search for coupling agents that could improve the adhesion between fiber and matrix.<sup>1</sup> Lu et al.<sup>2</sup> state in their review article that over 40 different coupling agents have been tested in wood–plastic composites. Maleic anhydride is the usual choice in modification of the polymer matrix by graft polymerization. The obtained copolymer, such as maleated polypropylene, is applied as a coupling agent.<sup>2</sup> Other widely used coupling agents are silanes and isocyanates.<sup>3</sup> The basic forms of the wood materials for wood–plastic composites are flour, chips, and fibers. Fibers can be obtained from chips by pulping techniques: mechanical, thermomechanical, chemical, and chemothermomechanical.<sup>3</sup> Also, plant fibers such as flax, sisal, and cotton can be incorporated as fillers and reinforcement materials.<sup>4</sup> The esterification reaction between different wood fibers and maleated polypropylene has been under investigation for several years now. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy

(FTIR) are the methods most often used to confirm the esterification reaction.<sup>5–9</sup>

Much of the research on wood–plastic composites has focused on natural and pulped fibers. Regenerated celluloses such as viscose fiber and other semisynthetic fibers have not been studied extensively. The purpose of this study was to find out how viscose fiber behaves in polypropylene matrix and learn more about reinforcement in thermoplastic-discontinuous wood fiber composites, especially about the effect of the coupling agent on the reinforcement. Maleated polypropylene was used as a coupling agent. Chemical behavior of the starting materials and the processing conditions were also investigated. Possible applications for tested composite materials can be found in the automobile and packaging industries.<sup>4</sup> Materials are recyclable and demands for them are growing. Composites of this type can be used for outdoor applications because when maleated polypropylene (MAPP) is used, the fiber surface becomes hydrophobic and the water uptake decreases significantly. Examples of outdoor applications include window and door frames.

## EXPERIMENTAL

### Materials and pretreatments

The polymers polypropylene (PP) and MAPP are characterized in Table I in terms of their melt flow rates, crystallinities, and densities. The manufacturer of the viscose fiber was Säteri OY and its commercial name was Viscose (Br). The staple length was 6 mm.

Correspondence to: T. T. Pakkanen (tuula.pakkanen@joensuu.fi).

**TABLE I**  
Description of the Polymers

Polymer	Commercial name	Manufacturer	Melt flow rate (g/10 min)	Crystallinity (%)	Density (kg/m <sup>3</sup> )
PP	HD120MO	Borealis	8 (230°C)	43.4	908
MAPP	EXXELOR PO 1015	ExxonMobil	150 (230°C)	23.4	900

The fiber was oven-dried at 60°C for 24 h before handling and was used without further purification. PP and MAPP were ground, after liquid nitrogen treatment, with an IKA A10 laboratory mill.

### Preparation of composites

PP, MAPP, and the fiber were preextruded under a nitrogen gas flow using a DSM twin-screw midiextruder. The parameters are listed in Table II. After preextrusion, the composite material was pelletized. Pellets were extruded and injection-moulded using a DSM microinjection moulding device. The dimensions of the tension specimen moulds used in injection moulding were thickness 1.5 mm, width 4.97 mm, and gauge length 35 mm. It has been shown that fibers degrade more easily in oxygen atmosphere.<sup>10</sup>

### Mechanical testing

Mechanical tests were carried out with material testing equipment ZWICK Z010/TH2A model 2001. Calculations were carried out with TestXpert version 8.1 software. Cross-head speed was 50 mm/min. Six standard tensile specimens were tested for each series. Specimens were stored at ambient room temperature (22–23°C) and humidity for at least 2 days before testing. Tensile strength, tensile modulus (tensile modulus was taken at a strain value of 0.1%), and elongation at fracture were measured.

### Powder X-ray diffraction

A Bruker AXS D8 advance powder X-ray diffractometer was used to determine the crystallinity of PP and MAPP. Scanned  $2\theta$  range was (3–40°).

**TABLE II**  
Parameters for the Preextrusion

Program number	Temperature (°C)	Rotation speed of the screws (rpm)	Time (min)
PE1	190	60	4
PE2	192	80	4

### Fourier transform infrared spectroscopy

A Nicolet Magna-IR spectrometer 750 FTIR was used to obtain the spectra. Scanned range was 600–4,000 cm<sup>-1</sup>. Both DRIFT technique and KBr tablet techniques were applied.

### Extraction studies on MAPP-treated fibers

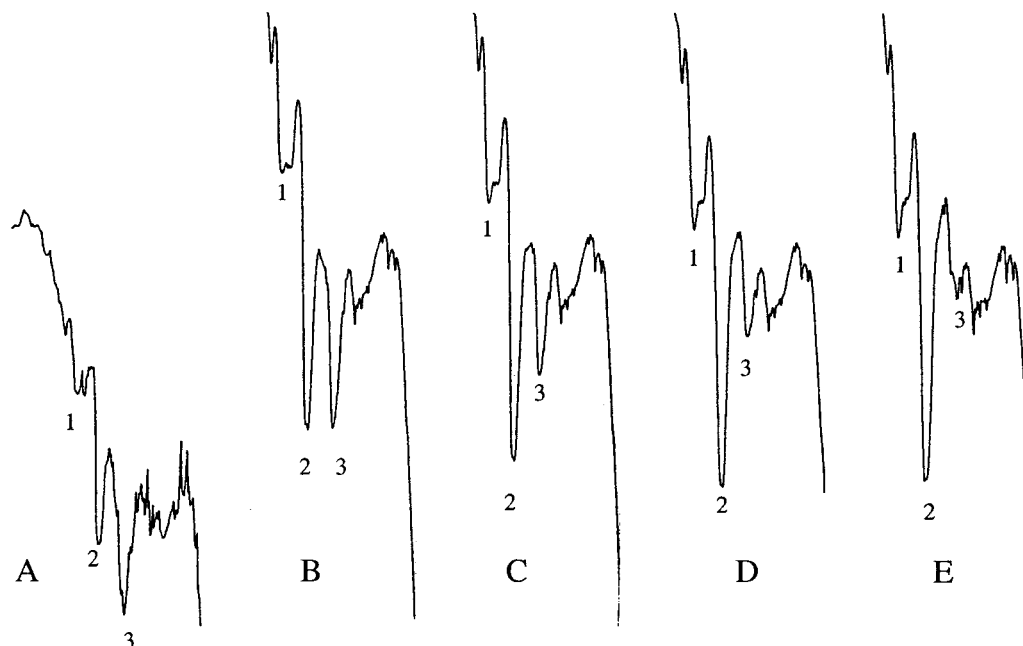
After extrusion, fibers were extracted with xylene in a Büchi 811 extraction device with the following parameters: extraction time 4.5 h and rinse time 5 min. After extraction, fibers were oven-dried for 22 h before the FTIR measurements.

## RESULTS AND DISCUSSION

### Interaction of MAPP with viscous fiber

The esterification interaction between viscose fiber and MAPP was studied by FTIR. The temperature behavior of MAPP was also investigated as this has considerable effect on the esterification reaction. The DRIFT technique was used to study the thermal behavior. The MAPP powder was placed on the surface of the KBr powder in a DRIFT cup equipped with a heating resistor to heat the KBr and the sample. The KBr and sample were then heated to the test temperature, which was held constant for 10 min. After heating, the sample was allowed to cool down to room temperature and an FTIR spectrum was measured.

The FTIR spectra of MAPP at different temperatures (25–160°C) are shown in Figure 1. The most notable feature is the change in the relative intensities of the bands. Band 2 clearly increases in intensity when the temperature is increased. Band 1 also increases in intensity from spectrum A to spectrum E. Band 3, however, decreases in intensity. The exact wave numbers of bands 1–3 are listed in Table III, along with the wave numbers reported by Felix and Gatenholm.<sup>7</sup> The changes in the spectrum are due to the reaction illustrated in Scheme 1. Bands 1 and 2 at 1,857 and 1,783 cm<sup>-1</sup> are due to the symmetric and asymmetric stretching of anhydride carbonyl, respectively,<sup>9</sup> whereas band 3 at 1,703 cm<sup>-1</sup> is due to the carbonyl stretching of carboxyl groups present in MAPP. Thus,



**Figure 1** The spectra of maleated polypropylene at 25°C (A), 130°C (B), 140°C (C), 150°C (D), and 160°C (E). The wave number range is from 1,600 to 2,100  $\text{cm}^{-1}$ .

when heated, the carboxyl groups present in MAPP change to more reactive anhydride groups.

The anhydride groups react more easily with hydroxyl groups than do the corresponding carboxyl groups. The esterification reaction between fiber and MAPP is then in accordance with Scheme 2. For study of the esterification reaction between viscose fiber and MAPP, the two components (30 wt % of the viscose fiber and 70 wt % MAPP) were extruded for 5 and 10 min at 190°C. After extrusion, the fibers were extracted with xylene. The spectra of untreated (A) and MAPP-treated fibers (B and C) with different extrusion times are shown in Figure 2. A new band at 1,740  $\text{cm}^{-1}$  is observed in the IR spectra (B and C) of the MAPP-treated fibers and is due to the interaction between the maleic anhydride and the cellulose (Scheme 2). The strong band at 1,640  $\text{cm}^{-1}$  observed in all three IR spectra is due to carbonyl groups and water present in the fiber. In some studies,<sup>10</sup> two separate bands at 1,739 and 1,746  $\text{cm}^{-1}$  due to esterification have been reported. The first band has been attributed to hydrogen bonding between carboxyl groups and cellulose, the second band to the ester bond between anhydride

groups and cellulose. Even close examination does not reveal the existence of two separate bands in our IR spectra B and C (Fig. 2). The improved adhesion between the fibers and matrix in our composites, as evident in the observed tensile properties, may therefore be considered due to either hydrogen or ester bonding.

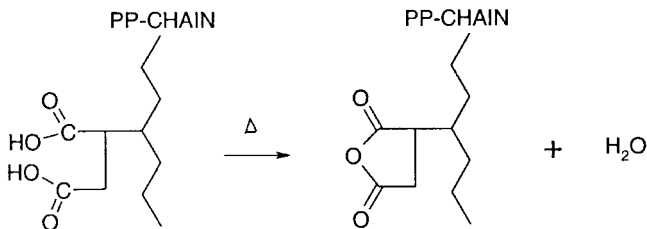
When comparing different extrusion times, even the 5-min extrusion time is long enough to cause esterification as evidenced by the absorption band at 1,740  $\text{cm}^{-1}$  (Fig. 2).

#### Optimization of processing conditions for PP-MAPP-viscous fiber composites

For preextrusion, all materials (PP and MAPP powder plus dry viscose fiber) were mixed in the hopper. To ensure the homogeneity of the final material, several batches of preextruded materials were mixed together before the second extrusion. Two different programs, PE1 and PE2, were used in the preextrusion (Table II). Parameter set PE1 was applied to study the effect of the rotation speed of the screws and to optimize the

**TABLE III**  
Wave Numbers of the Bands in Figure 1 Compared with the Wave Numbers Reported by Literature<sup>7</sup>

Band number	Wave number ( $\text{cm}^{-1}$ )	Wave number <sup>7</sup>	Source of the band
1	1,857	1,862	C=O asymmetric stretching (anhydride)
2	1,783	1,786	C=O symmetric stretching (anhydride)
3	1,703	1,717	C=O stretching (dicarboxylic acid)



**Scheme 1** Reaction of maleated polypropylene when heated.

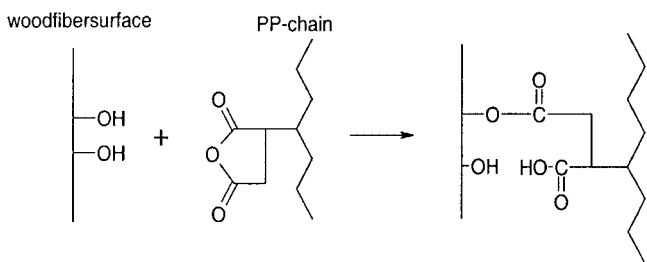
processing conditions (temperature, time, and rotation speed). With the processing conditions optimized, the set PE2 was then used in MAPP concentration studies.

Programs E1 and E2 were used in the following extrusion and injection-moulding studies (Table IV). Program E1 was used to study the effect of the rotation speed of the screws and to optimize the processing conditions.

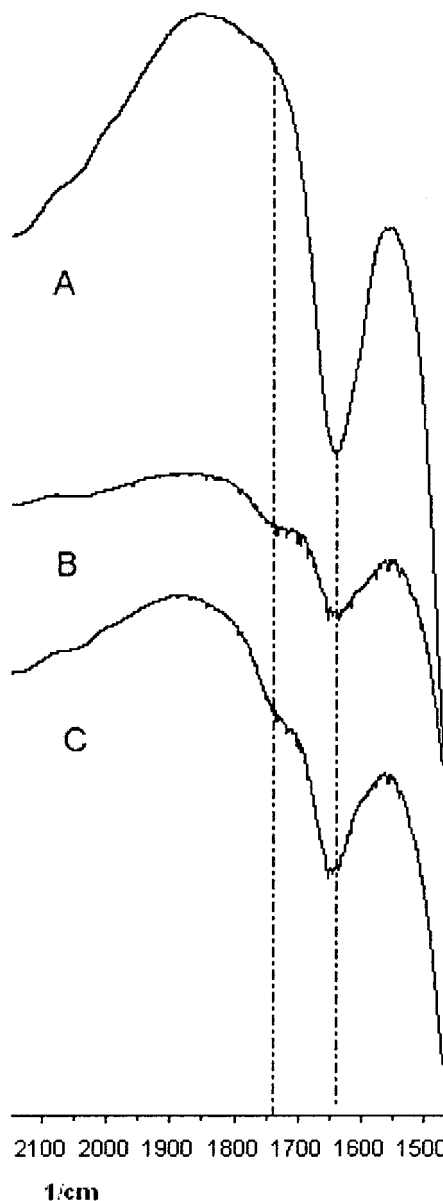
The effect of the rotation speed of the screws on tensile strength of the composites is shown in Figure 3. Composites were prepared with programs PE1 and E1. The best tensile strength result was obtained with a rotation speed of 80 rpm. It may be that dispersion is inadequate with a slower rotation speed, while a faster rotation speed causes fiber damage.

Extrusion time of 3 min was selected for the second extrusion, since earlier studies showed no significant change in tensile properties as a function of time. All extrusions were carried out under nitrogen gas flow. In earlier studies with flax fibers, we found better tensile properties when nitrogen gas was used during extrusion.<sup>11</sup> It has been shown that fibers degrade more easily in oxygen atmosphere.<sup>12</sup>

In the injection moulding, the effects of temperature of the mould and the feed opening of two different moulds were tested. Raising the temperature of the mould by 5°C from 120°C allowed the use of lower injection pressures. However, excessive increase in the temperature was found to cause a poor dispersion of fibers in the tensile specimens, which was reflected in unsatisfactory tensile properties. Large fiber agglom-



**Scheme 2** Esterification reaction between wood fiber and maleated polypropylene.



**Figure 2** The spectra of untreated and MAPP-treated fibers with different extrusion times: untreated fiber (A); viscose fibers treated with MAPP in the extruder for 5 min (B); viscose fibers treated with MAPP in the extruder for 10 min (C).

erates were visible in different sections of the specimens.

One of the most important factors in injection moulding was the feed opening of the mould. When the first mould (feed opening 1.08 mm<sup>2</sup>, mould number 9820) was replaced by one with a larger feed opening (feed opening 1.54 mm<sup>2</sup>, mould number 9814), the tensile strength increased by 9 MPa from 45 to 54 MPa. When the feed opening is larger, the fibers do not agglomerate against the mould opening and the melt flows more evenly into the mould.

**TABLE IV**  
Parameters for the Second Extrusion and Injection Moulding

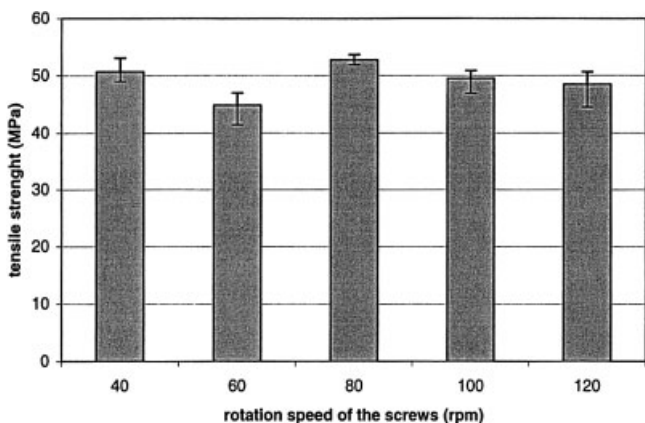
Program number	Extruder temperature (°C)	Extrusion time (min)	Screws (rpm)	Cylinder temperature (°C)	Pressure (bar)	Mould temperature (°C)	Mould number
E1	190	3	40, 60, 80, 100, and 120	190	7.25	120	9,820
E2	192	3	80	190	6.9	125	9,814

**Effect of MAPP concentration on mechanical properties of PP–MAPP–viscous fiber composites**

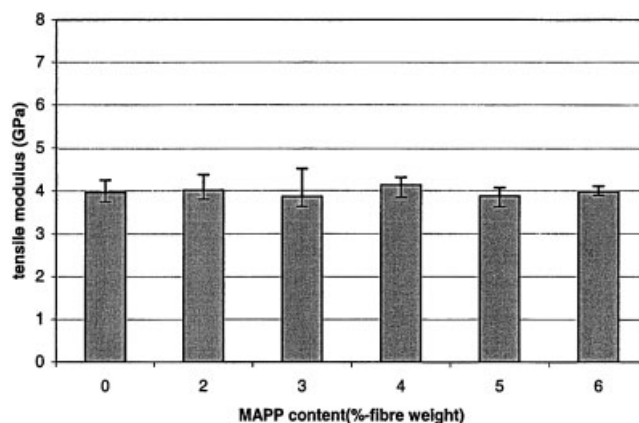
The factor with greatest influence on the mechanical properties of the composites, especially on tensile strength and elongation at fracture, was the concentration of MAPP in composites. The effect of MAPP concentration was studied using parameters of set PE2 for preextrusion and set E2 for extrusion and injection moulding. The program E2 was used in the MAPP concentration studies after the processing conditions were optimized. The extrusion temperatures in pro-

grams PE2 and E2 were 2°C higher than those in programs PE1 and E1. Even a small increase in the extruder temperature increased the melt flow and facilitated the processing.

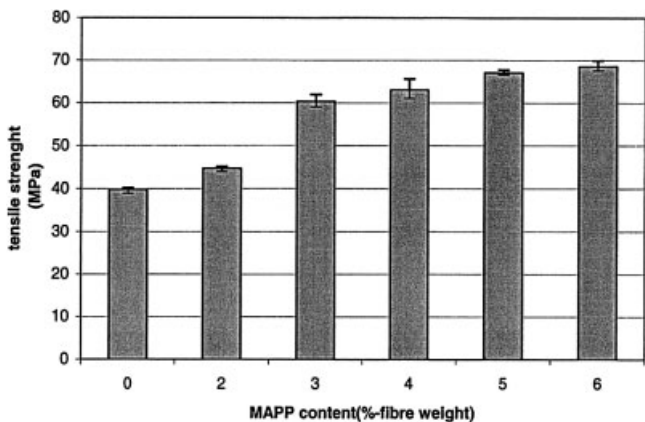
Figures 4–6 show the influence of MAPP concentration on the mechanical properties of the composites. Tensile strength increased by 28.8 MPa, from 39.8 to 68.6 MPa, between 0 and 6 wt % MAPP concentrations. This is due to the improved adhesion between fiber and PP matrix, as was shown in earlier FTIR studies. The viscose fiber is highly sensitive to MAPP



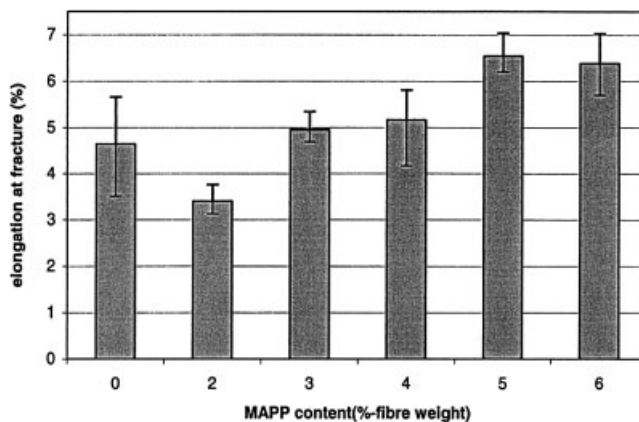
**Figure 3** Tensile strength vs. rotation speed of the screws. Fiber content is 40% and the amount of MAPP in the composite is 3% of the fiber weight. Composites prepared with programs PE1 and E1 (Tables II and IV).



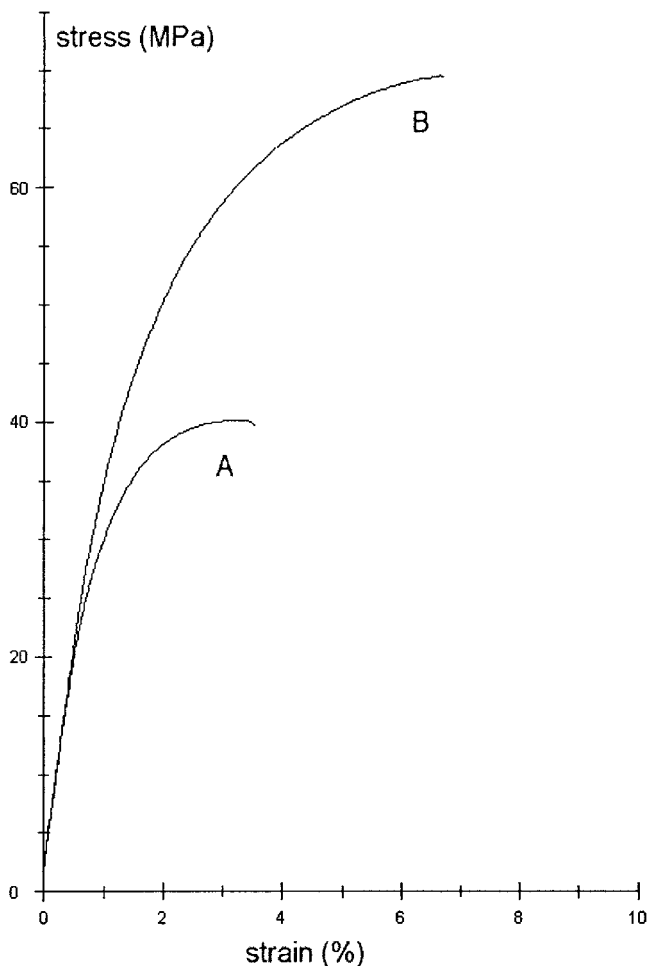
**Figure 5** Tensile modulus vs. MAPP concentration. Fiber content is 40%. Composites prepared with programs PE2 and E2 (Tables II and IV).



**Figure 4** Tensile strength vs. MAPP concentration. Fiber content is 40%. Composites prepared with programs PE2 and E2 (Tables II and IV).



**Figure 6** Elongation at fracture vs. MAPP concentration. Fiber content is 40%. Composites prepared with programs PE2 and E2 (Tables II and IV).



**Figure 7** Stress-strain curves for tensile specimens containing 6 wt % (B) and 0 wt % (A) MAPP relative to fiber weight.

concentration, probably because of the process by which it is manufactured. Depolymerization of the cellulose chains during manufacture likely gives the fibers more favorable dimensions for MAPP attachment. Furthermore, viscose fibers are drawn at the end of the manufacturing process to give them more strength. The elongation at fracture also increased with MAPP concentration. In contrast, the tensile modulus (Fig. 5) showed no correlation with MAPP concentration.

Overall, the viscose fiber-PP composites with MAPP as a coupling agent are hard and strong materials, as is evident in the tensile stress-strain curves in Figure 7. The region of plastic deformation before fracture is large with the use of MAPP (B), compared with that of the specimen prepared without MAPP

(A). The viscose fiber-PP composite prepared without MAPP is hard but more brittle than the composites containing MAPP. The changes in tensile properties when MAPP is added are due to the improved adhesion between fiber and matrix. The stress transfer from matrix to the fiber is better due to the increased adhesion.

## CONCLUSIONS

The following conclusions can be drawn from the above results and discussion. One, FTIR spectroscopy is a convenient technique for determining the active form of the coupling agent, in this case MAPP, and its interaction with viscose fiber. Transformation of the carboxylic acid form of MAPP to an anhydride form was shown to occur to a significant extent even at 150–160°C, which is much lower than the temperature used in extrusion. From the FTIR results, it can be concluded that the anhydride form of MAPP interacts with viscose fiber via hydrogen or ester bonding, leading to improved adhesion between fibers and the PP matrix.

Two, tensile strength and elongation at fracture of a composite of PP and viscose fiber increase significantly when the MAPP concentration is increased in the composite material. However, optimizing the processing parameters, especially in injection moulding (size of feed opening of the mould, temperatures of the mould and cylinder, and injection pressure), also leads to improved tensile properties.

## References

1. Wolcott, M. P.; Ennglund, K. *Comp Mater Symp* 1999, 33, 103.
2. Lu, J. Z.; Wu, Q.; McNabb, Jr., H. S.; *Wood Fiber Sci* 2000, 32 88.
3. Bledzki, A. K.; Reihmane, S.; Gassan, J.; *Polym Plast Tech Eng* 1998, 37, 451.
4. Mohanthy, A. K.; Mishra, M.; Hinrichsen, G., *Macro Mater Eng* 2000, 276/277, 1.
5. Kazayawako, M.; Balatinez, J. J.; Woodhams, R. T.; Law, S. *J Plast Comp* 1997, 16, 1383.
6. Kazayawoko, M.; Balatinez, J. J.; Sodhi, R. N. S. *Wood Sci Tech* 1999, 33, 359.
7. Felix, J. M.; Gatenholm, P. *J Appl Polym Sci* 1991, 42, 609.
8. Matias, M. C.; De La Orden, M. U.; Gonzalez, C.; Martinez Urreaga, J. *J Appl Polym Sci* 2000, 75, 256.
9. Kazayawako, M.; Balatinez, J. J.; Woodhams, R. T. *J Appl Polym Sci* 1997, 66, 1163.
10. Son, S.-J.; Lee, Y.-M.; Im, S.-S. *J Mater Sci* 2000, 35, 5767.
11. Paunikallio, T.; Suvanto, M.; Pakkanen, T. T. University of Joensuu, unpublished results.
12. Wielage, B.; Lampke, T.; Marx, G.; Nestler, K.; Starke, D. *Therm Acta* 1999, 337, 169.