Kudzu Fiber-Reinforced Polypropylene Composite

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ABSTRACT: Kudzu fiber-reinforced polypropylene composites were prepared, and their mechanical and thermal properties were determined. To enhance the adhesion between the kudzu fiber and the polypropylene matrix, maleic anhydride-grafted polypropylene (MAPP) was used as a compatibilizer. A continuous improvement in both tensile modulus and tensile strength was observed up to a MAPP concentration of 35 wt %. Increases of 24 and 54% were obtained for tensile modulus and tensile strength, respectively. Scanning electron microscopy (SEM) showed improved dispersion and adhesion with MAPP. Fourier transform infrared (FTIR) spectroscopy showed an increase in hydrogen bonding with an increase in MAPP content. Differential scanning calorimetry (DSC) analysis indicated little change in the melting temperature of the composites with changes in MAPP content. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1961–1969, 2002

Key words: kudzu; natural fiber; polypropylene; composites; compatibility

INTRODUCTION

Kudzu, *Pueraria thunbergiana*, is a legume that is native to Japan and China. It is a coarse-growing perennial with trifoliate leaves and coarsely lobed leaflets. Kudzu provides herbal medicines used in China and Japan. The stems yield a fiber called ko-kemp that is useful in making cloth and paper. In China, kudzu fiber is still being woven into cloth and is occasionally used to make baskets, packing materials, and suspension bridges.[1]

The noncommercial kudzu plant has been growing wild in the southeastern United States since the 1930s.[1] It is a noxious weed that grows on top of existing vegetation, thereby killing whatever it grows on. Kudzu threatens the existing ecosystem in the southeastern United States by killing the hardwood trees. It would be a significant positive contribution to the environment if we could find a value-added use for kudzu. The kudzu vine (Figure 1), which can grow as much as a foot a day under optimal growing conditions, has a fibrous structure. The composition of kudzu vine has been reported as follows:[2] cellulose 33%, hemicellulose 11.3%, lignin 14%, solubles 41.4%, ash 0.3%. The solubles are represented in part by pectin. The morphology of kudzu vines is similar to other bast fiber plants like flax and hemp.

Kudzu fibers extracted from the woody vines of the plant have a multiple cellular and unidirectional structure.[3] Kudzu fibers are classified as bast fibers (fibers extracted from the interior part of the plant sheath). When chemically treated, such fibers can be converted to long staple fibers.[2]

The harvest season and geographic location are variables that affect properties of kudzu fiber. Uludag et al.[1] found Spring to be the optimum kudzu harvest time in the southeastern United

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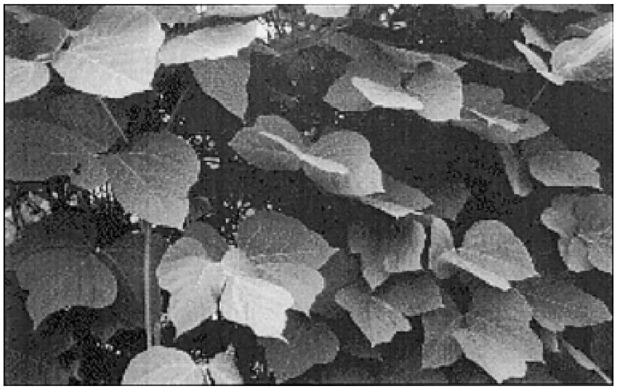


Figure 1 Kudzu plant.

States for the extraction of strong fibers. The effect of the harvest time and location on the kudzu fiber properties is summarized in Table I. The tensile strength of kudzu is compared to other natural fibers in Table II.

The objective of this study is to investigate the feasibility of using kudzu fiber as reinforcing material in a polymer composite. Kudzu fiber was chosen as the reinforcement because it is a renewable natural resource in southeastern United States and its overall mechanical properties are comparable to those of other natural fibers. Polypropylene (PP) was chosen as the matrix of the composite because it is a relatively low-cost thermoplastic with good mechanical properties. The natural fiber–PP composites have been used in marine lumber (floating and stationary docks), outdoor maintenance-free decks, and automobile parts (to reduce weight and thereby decrease fuel consumption, and increase recyclability, as required by the European Union that 50% of car parts be recyclable by 2003).

The major drawback associated with the use of natural fibers as reinforcement in the thermoplastics is the weak interfacial bonding with the polymer due to the inherently poor compatibility of the hydrophilic cellulosic fibers with hydrophobic thermoplastics. In the present work, maleic anhydride-grafted polypropylene (MAPP) is used as a compatibilizer to improve interfacial bonding. In this article we report the results of our studies on the mechanical properties of kudzu fiber-reinforced PP composites and the effect of fiber content and MAPP content. Thermal properties of the composite were characterized by differential scanning calorimetry (DSC). Scanning electron microscopy (SEM) studies were carried out to provide insight into fiber–matrix adhesion. Fourier transform infrared spectroscopy (FTIR) was used to investigate the interfacial bonding between fiber and matrix.

EXPERIMENTAL

Materials

A polypropylene resin (PP3445®) with a MFI of 35, and a maleic anhydride-grafted polypropylene (Exxelor PO-1015®) resin were supplied by Exxon Chemical Company (Baytown, TX). Kudzu vines were harvested from the Agricultural Experimental Station at The University of Tennessee in Spring 2000.

Table I Effect of Season and Location on Kudzu Fiber Properties[1]

	Season			
			Early Spring	
Property	Late Fall; Nashville, TN	Winter; Nashville, TN	Nashville, TN	Muscle Shoals, AL
Average thickness, m	0.0002	0.0001	0.000046	0.00006
Average width, m	0.002	0.002	0.002	0.002
Average length, m	0.06	0.06	0.06	0.06
Diameter of vines, m	0.00076–0.00584	0.00220–0.00767	0.00254–0.00559	0.00726–0.00779
Average linear density, g_f/m	0.128	0.182	0.075	0.145
Average tensile strength g_f/m^2	2.07×10^{10} 200 (MPa)	1.30×10^{10} 130 (MPa)	4.27×10^{10} 418 (MPa)	1.88×10^{10} 184 (MPa)
g_f/denier	2.400	0.995	4.395	2.654
g_f/tex	21.384	8.965	39.556	23.890

Preparation of Fiber

A Kraft soda pulping method (14% AA, 25% S, 0.1% AQ, 4.5 : 1 liquor: wood ratio, 1000 H-factor) of processing kudzu fiber was carried out in our laboratory.[4] The vines were chopped to 1-in. length. The chopped kudzu vines were placed into a laboratory digester, along with the solution of sodium hydroxide and sodium sulfide. The combination of heat and pressure help to force the liquor into the vine to break lignin and free fiber.

Fiber Length Determination

A light microscope Microstar IV® (Buffalo, NY) was used to determine the average length of kudzu fibers.

Preparation of Kudzu–PP Fiber Composite

The composites were prepared by weighing all components to achieve the desired composition. After drying in a vacuum oven at 80 °C for 8 h, the components of each composition were mechanically mixed in a blender. The blends were melt processed using a batch mixer (C.W. Brabender; distributed by Altran Corporation; Boston, MA) using Z-type blades at 60 rpm and 190 °C.

Tensile Test

The blended polymer mass was molded into the appropriate specimens, in accordance with ASTM D1708, with a hot press. Mechanical tensile testing was carried out according to ASTM D1708 with a tensile tester (Instron Table Model 1122®; Canton, MA).

Thermal Analysis

A Perkin-Elmer Series 7® DSC (Norwalk, CT) was used for thermal analysis of the composites and pure components. The sample weights ranged from 5 to 6 mg. All scans were performed from 40–200 °C at a rate of 10 °C/min. Melting temperatures of each composite and pure PP were measured.

Table II Tensile strength (g_f/denier) of various natural fibers and kudzu vine fiber[1]

Natural Fiber	Description	Tensile Strength, g_f/denier
Abaca	Oiled, combed	6.900
Abaca	Not twisted	6.710
Sisal	Oiled, combed	4.400
Kudzu	Wet	4.395
Cotton	Oiled, combed	3.3–6.4
Henequen	Wet	3.300
Wool		0.76–1.6

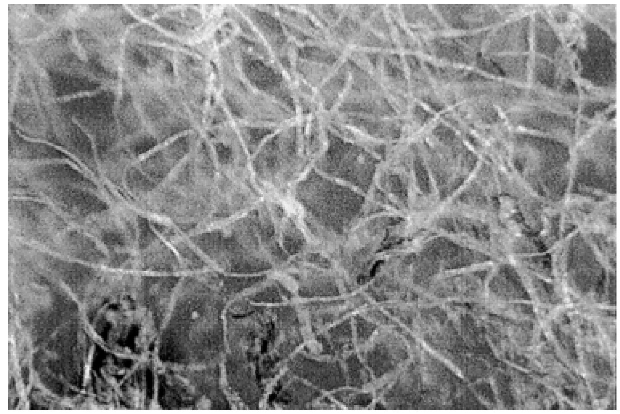


Figure 2 Kudzu fibers.

Scanning Electron Microscopy (SEM)

The macroscopic effect of maleic anhydride on the interfacial adhesion was evaluated by SEM. SEM micrographs of gold-coated fracture surfaces were obtained in a Cambridge STEREOSCAN 360® microscope (Leo Electron Microscopy Inc., Thornwood, NY).

Fourier Transform Infrared Spectroscopy (FTIR)

A Bio-Rad FTS-6000e® Fourier transform infrared spectrometer (Cambridge, MA) equipped with an UMA-500® FTIR microscope was used to collect FTIR spectra of the samples. A micro-ATR (attenuated total reflectance) technique was used to explore the nature of the interactions between the MAPP and kudzu fiber.

RESULTS AND DISCUSSION

Fiber Characterization

A light micrograph of kudzu fibers is presented in Figure 2. The average fiber length and diameter were determined to be 2.25 ± 0.01 and 0.02 ± 0.002 mm, respectively. The distribution of the fiber is shown in Figure 3. The aspect ratio was > 100. These values were based on measurement made on 100 single fibers.

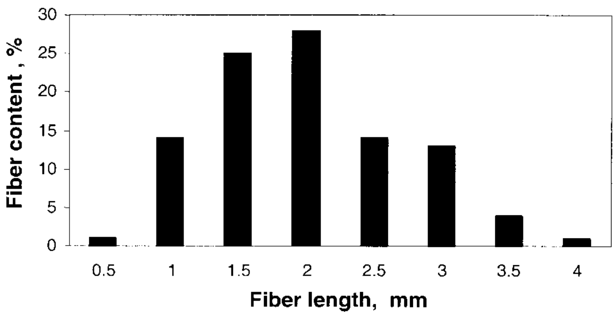


Figure 3 Fiber length distribution of kudzu fiber.

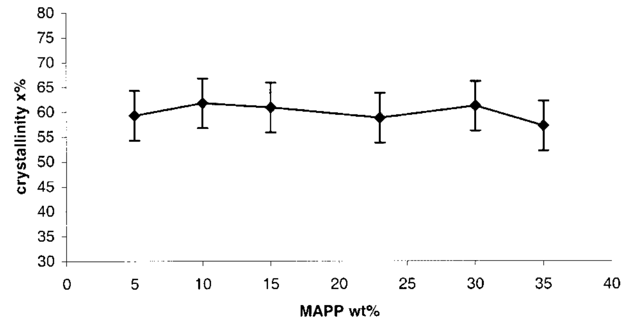


Figure 4 Effect of MAPP on the crystallinity.

Thermal Properties

The melting temperature of the kudzu–PP composites was independent of the MAPP content for concentration between 5 and 35 wt %. The concentration of kudzu fibers in all samples was 30 wt %. The melting temperatures for the kudzu–PP composites are given in Table III.

Degree of Crystallinity

FTIR spectra were used to determine the crystallinity of kudzu–PP composites. The crystallinity of the PP can be calculated from the ratio of the bands at 998 cm^{-1} , which is associated with the structural regularity, and at 974 cm^{-1}, which is associated with the molecules in the disordered arrays:[5]

$$\%X = 100 \times \left(\frac{A998}{A974}\right) - 31.4 \qquad (1)$$

where A represents the absorbance of each peak.

The influence of MAPP content on the crystallinity for the kudzu–PP composites is shown in Figure 4. No significant change was observed with increasing concentration of MAPP.

Effect of Kudzu Fraction on Mechanical Properties

The influences of fiber fraction on the tensile strength and tensile modulus are illustrated in Figures 5 and 6, respectively. The tensile strength of kudzu fiber-reinforced PP composites without MAPP does not vary significantly when the kudzu fraction is $<$ 30% and decreases when the fiber fraction exceeds 30%, as shown in Figure 5. This result can be attributed to the fact that adhesion between kudzu fibers and PP is not sufficient to develop efficient stress transfer at the interface, which is required for a composite to achieve an increase in mechanical properties. The addition of MAPP leads to increase in the tensile strength over kudzu concentration ranges from 10 to 40%. Compared with pure PP resin, there is an increase of 56% in tensile strength. The enhancement in tensile strength is attributed to improved interfacial adhesion arising from the secondary chemical bonding between hydroxyl groups of the fibers and carbonyl moieties on the MAPP. An increase in kudzu fiber content to 50% leads to decrease in the tensile strength. The reduction of the tensile strength at the higher fiber content is attributed to increase number of fiber ends in the composites, which could serve as loci for crack initiation and subsequent failure at lower stresses.[6]

The tensile modulus for both composites, with and without MAPP, increased with an increase in the kudzu fiber concentration. However, at the same fiber composition, the composites with MAPP exhibit higher modulus. Addition of kudzu fibers to a concentration of 40 wt % leads to an increase in the modulus of 93% over the pure PP.

Table III Melting Temperature of Pure PP and Composites

Parameter	Pure PP	Kudzu–PP Composites with 30% Fiber					
MAPP (wt %)	0	5	10	15	23	30	35
T_m (°C)	167	164	163	163	164	163	162

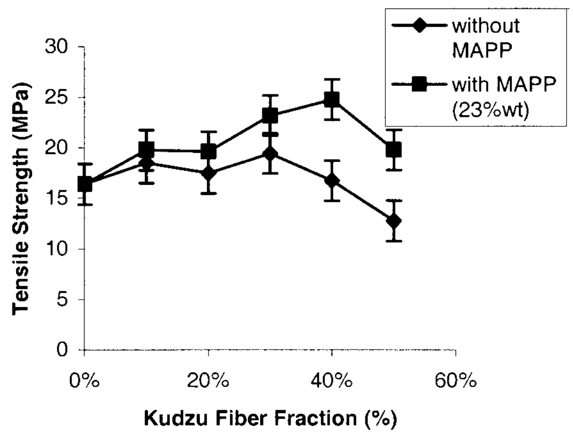


Figure 5 Effect of kudzu fiber fraction on the tensile strength.

Effect of MAPP Content on the Mechanical Properties

The adhesion between the kudzu fiber and PP is expected to be very poor because the kudzu fiber surface is characterized by the presence of polar hydroxyl groups that make it hydrophilic, whereas PP is a hydrophobic polyolefin. Maleic anhydride was used as the compatibilizer to improve the adhesion because it can interact with the hydroxyl groups on the kudzu fiber surface to form new covalent bonds and hydrogen bonds across the fiber surface. A schematic representation of the interfacial chemical reaction mechanism is illustrated in Figure 7.[7]

Considering the processing conditions and overall mechanical properties, to study the effect of MAPP content on the mechanical properties, the kudzu fraction was kept at 30 wt % and the ratio of PP to MAPP was changed. The results of the effect of MAPP on the mechanical properties are shown in Figures 8 and 9. A continuous improvement in both tensile modulus and tensile strength was observed up to concentration of 35 wt %. Increases of 24 and 54% were obtained for tensile modulus and tensile strength, respectively. Based on the results in Figure 8 and 9, the MAPP acts as a compatibilizer in this kudzu–PP system. The interfacial adhesion must have improved due to the formation of chemical bonding between kudzu and MAPP. As a result, the mechanical properties of the composites are enhanced.

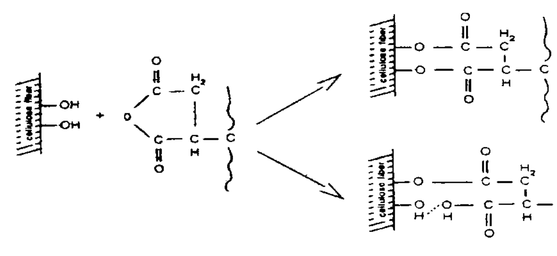


Figure 7 Scheme of the reaction between MAPP and kudzu fiber.

Theoretical Modeling of the Modulus

Many theories and equations have been developed to predict the mechanical properties of the composites. In the study described herein, the

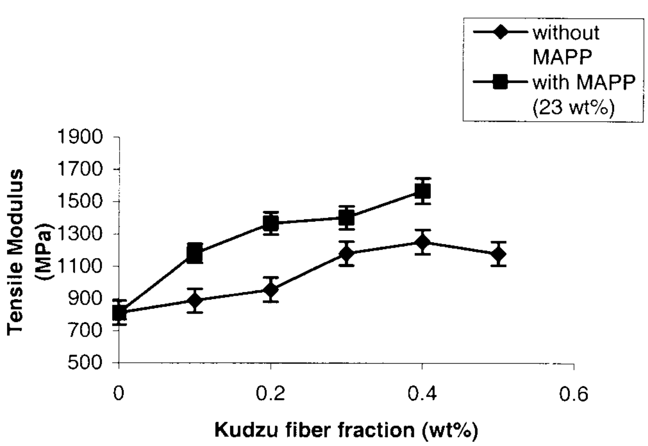


Figure 6 Effect of kudzu fiber fraction on the tensile modulus.

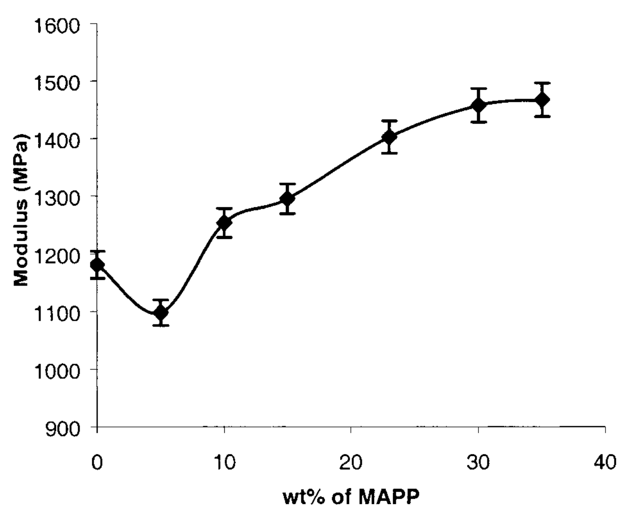


Figure 8 Effect of MAPP content on the tensile modulus.

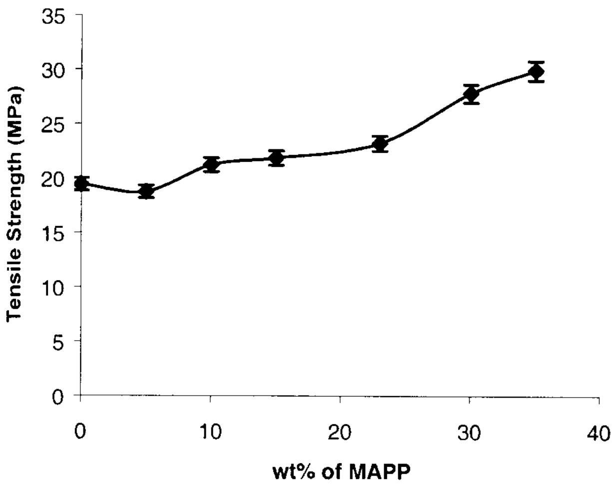


Figure 9 Effect of MAPP content on the tensile strength.

Halpin–Tsai equations[8] were used to predict the tensile modulus of PP–kudzu composites:

$$E = \frac{E_1(1 + \mathrm{AB}\phi_2)}{(1-\mathrm{B}\phi_2)} \tag{2}$$

where E and E_1 are elastic moduli of the composite and matrix, respectively, φ_2 is the volume fraction of fibers, and A and B are constants for any given composite. The constant A takes into account the effect of the fiber geometry (such as the aspect ratio), fiber distribution, and loading conditions. In this system A was chosen to be 4.93.[8] Constant B takes into account the effect of moduli of the fiber and matrix, and is defined as follows:

$$\mathrm{B} = \frac{\frac{E_1}{E_2} - 1}{\frac{E_1}{E_2} + A} \tag{3}$$

The theoretical and experimental moduli of kudzu–PP composites are shown in Figure 10. There is good agreement between the experimental and theoretical values up to 20% fiber loading for composites with MAPP. However, when the fiber loading exceeds 20% the experimental modulus values start deviating from theory. This result may be attributed to the poor distribution of the fiber in the composite at higher fiber loading. The experimentally determined moduli for the composites without MAPP show a big deviation from theory. This result indicates that without MAPP acting as a compatibilizer to improve the adhesion between fiber and matrix, there is poor transfer of stress at the interface between low strength matrix and high strength fiber.

Interfacial Properties

SEM was used to study the tensile fracture surfaces of composite samples with and without MAPP. SEM micrographs of the fracture surfaces are shown in Figure 11. SEM observations indicate considerable difference in the fiber–matrix interaction between the composite samples with and without MAPP. Because of hydrogen bonds formed between kudzu fibers and the big difference in surface character between fiber and PP, the fibers tend to agglomerate into bundles and become unevenly distributed throughout the matrix. This agglomeration is pointed out by arrows in Figure 11(a). Figure 11(c) is a SEM micrograph of the kudzu–PP composite with MAPP, which shows that with enhanced interactions between the fiber and the matrix, fiber distribution becomes more uniform in the PP matrix. The interaction between the kudzu fiber and MAPP can be attributed to the bonding formed in the interfacial region. SEM photographs of same samples taken under higher magnification are shown in Figures 11(b) and 11(d). From the micrographs, a better fiber–matrix interaction caused by MAPP is observed from the reduction of fiber pull-out. The holes and fiber ends shown in Figure 11(b) indicate that most of the fibers have come out without breaking during the fracture. This result suggests poor adhesion between the matrix and fiber. Fiber breakage rather than pull-out, which indicates a

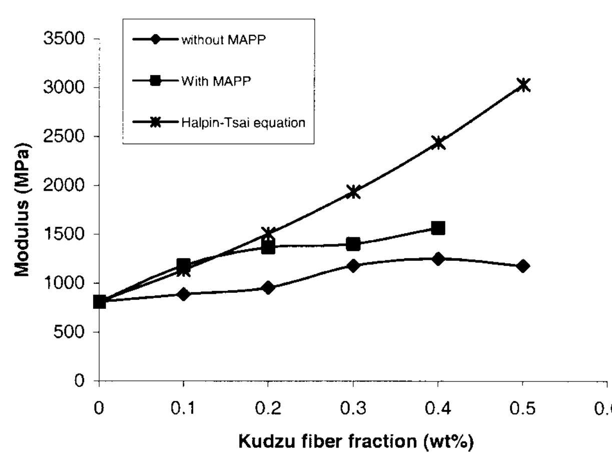
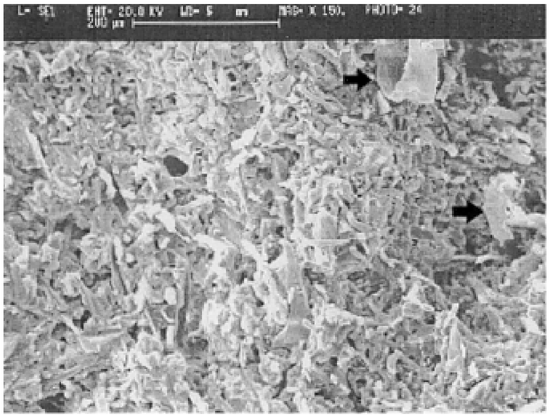
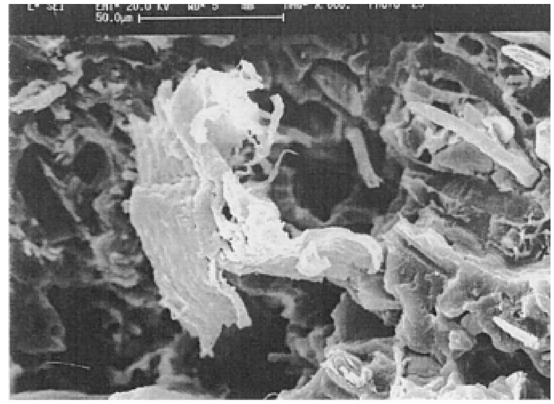


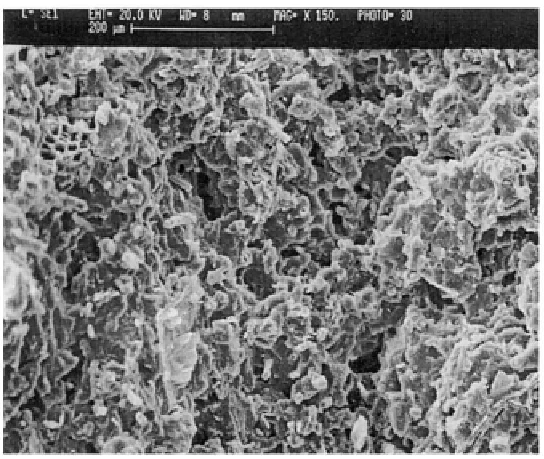
Figure 10 Comparison of the experimental moduli and theoretical moduli of PP–kudzu fiber composites.



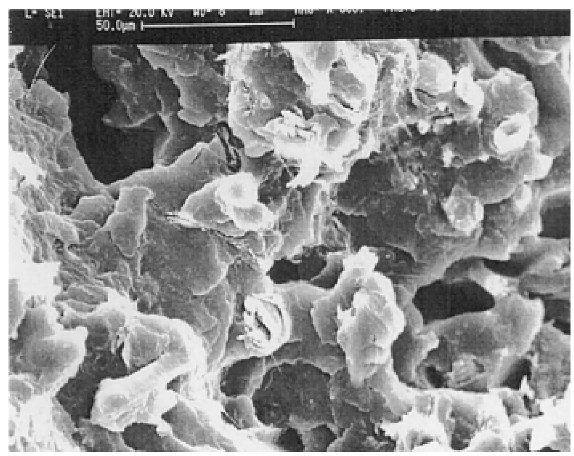
(a) SEM photograph of the fracture surface of kudzu-PP composite without MAPP (x150) (30wt% fiber)



(b) SEM photograph of the fracture surface of kudzu-PP composite without MAPP (x600) (30wt% fiber)



(c) SEM photograph of fracture surface of kudzu-PP composite with MAPP (x150) (23wt% MAPP 30wt% fiber)



(d) SEM photograph of fracture surface of kudzu-PP composite with MAPP (x600) (23wt% MAPP 30wt% fiber)

Figure 11 (a) SEM photograph (×150) of the fracture surface of kudzu–PP composite without MAPP (30 wt % fiber).(b) SEM photograph (×600) of the fracture surface of kudzu–PP composite without MAPP (30 wt % fiber). (c) SEM photograph (×150) of the fracture surface of kudzu–PP composite with MAPP (23 wt % MAPP; 30 wt % fiber). (d) SEM photograph (×600) of the fracture surface of kudzu–PP composite with MAPP (23 wt % MAPP; 30 wt % fiber).

better interfacial strength, is shown in Figure 11(d). From SEM micrographs and mechanical properties of different composites, a fairly good correlation between fiber–matrix interaction and the properties of resulting composites appears to exist.

Nature of Adhesion

MAPP can be bonded to the fibers surface by ester linkage and hydrogen bonds. FTIR was used to investigate the nature of adhesion. The IR absorption peak of free hydroxyl groups is at 3650–

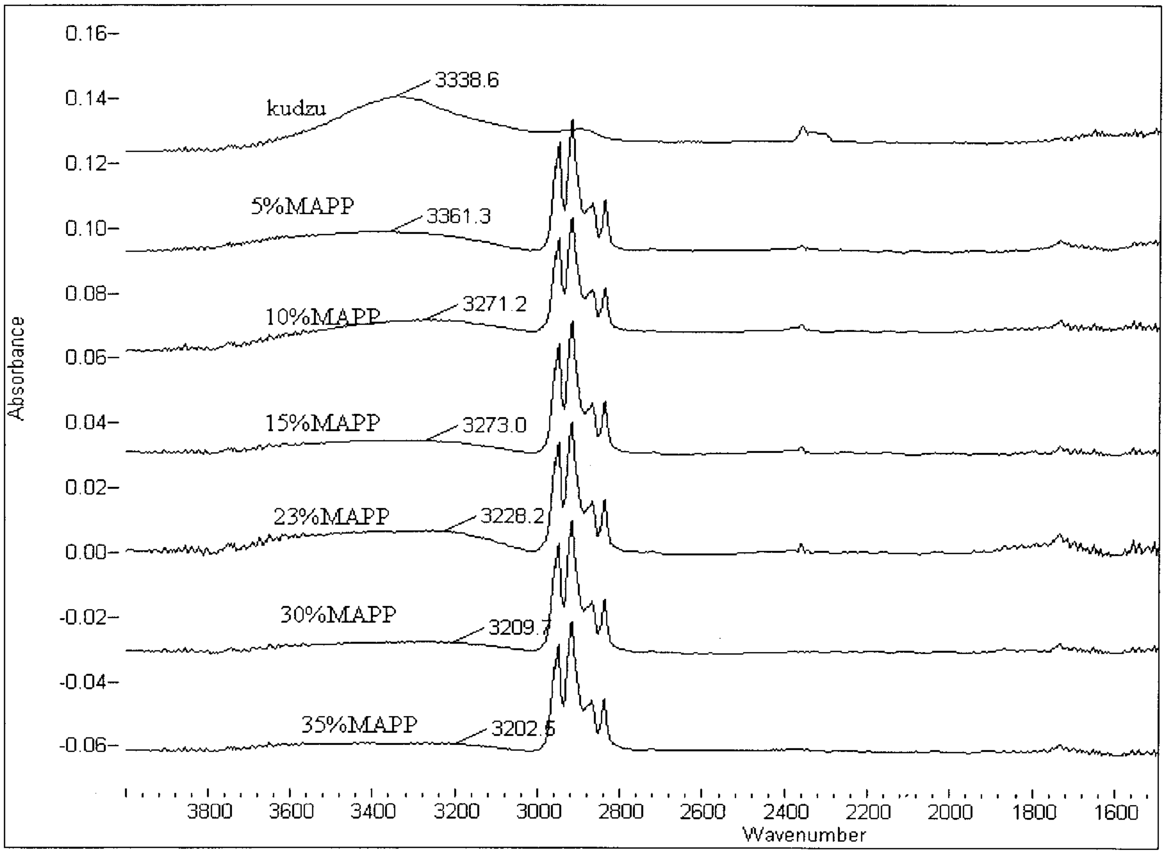


Figure 12 FTIR spectra of pure kudzu fiber and composites (each sample has 30 wt % kudzu fiber).

3590 cm^{-1}. If MAPP reacts with the cellulose hydroxyl groups of kudzu fiber to form hydrogen bonds, the hydroxyl absorption peak will shift to lower wave numbers (3500–3200 cm^{-1}). If MAPP reacts with the hydroxyl groups to form ester linkage, a new peak due to the ester group stretch will appear near 1740 cm^{-1}. The spectrum of pure kudzu fiber and spectra of composites with different MAPP content subtracted by the spectrum of pure kudzu fiber are shown in Figure 12. The shift of hydroxyl absorption was observed. The greater the spectral shift, the more hydrogen bonding formed. The relation between MAPP content and hydroxyl absorption peak shift was investigated. The larger spectral shift correlates with the high MAPP content.

The degree to which the fiber and matrix are linked by chemical bonds has a strong effect on the adhesion between fiber and matrix, and, hence, the mechanical properties of the composites. The FTIR studies support the tensile testing results discussed in the previous section. The correlation is shown in Figure 13. The tensile strength increases with content of MAPP because interfacial adhesion is improved due to more hydrogen bonds formed across the fiber surface. However, a decrease in both tensile strength and hydroxyl peak shift is observed for sample containing 5 wt % MAPP. The reason for the decrease needs to be investigated in future studies.

CONCLUSIONS

Kudzu fiber with sufficient mechanical properties was made by the Kraft soda pulping process. The

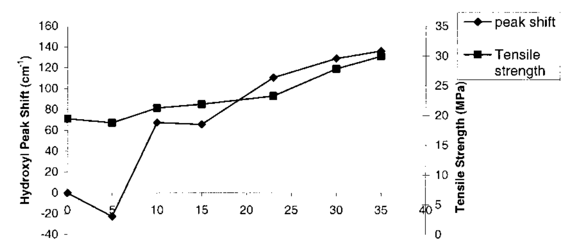


Figure 13 Hydroxyl peak shift and tensile strength versus MAPP content.

inclusion of MAPP in the composite increased the tensile modulus and tensile strength by 24 and 54%, respectively. The Halpin–Tsai equation was used to predict the modulus of the composite. The predicted values show a good agreement with the experimental values up to the 20% kudzu fiber loading. SEM and FTIR studies show that interfacial adhesion between the fiber and PP matrix is improved when MAPP is introduced.

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