Bamboo Fiber-reinforced Polypropylene Composites: Crystallization and Interfacial Morphology

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ABSTRACT: Bamboo fiber-reinforced polypropylene (PP) composites were prepared. PP and two maleated polypropylenes (s-MAPP and m-MAPP) were used as matrices. Crystallization and interfacial morphology were studied by using differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), and optical microscopy. It has been shown that the addition of bamboo fiber to any of the three polymers causes an increase in the overall crystallization rate. A considerable amount of β-form crystallinity was produced in the PP, s-MAPP, and m-MAPP by mixing with bamboo fiber; and all the bamboo fiber-filled samples contain both the α- and the β-forms. The relative amount of the β-form in the samples was calculated from WAXD data by the K value. There is no β-form observed in the pure PP, s-MAPP, and m-MAPP. Bamboo fiber acted as both a reinforcement and a β-nucleator. The nucleation density of both s-MAPP and m-MAPP at the fiber surface is remarkably higher than that of PP because an improved interfacial adhesion is reached in the case of s-MAPP and m-MAPP as matrices. The transcrystalline growth of s-MAPP and m-MAPP on the bamboo fiber surface was observed under optical microscope with crossed polars. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1267–1273, 1997

INTRODUCTION

Wood is a basic material sustaining human living. It is widely used in interior decoration and in the furniture industries. The insatiable world demand for good quality timber has led to nonrenewable logging of tropical hardwood forests in many developing countries and gave rise to serious global concern. As rain forest supplies shrink while development accelerates, it is expected to lead to a sharp rise in the cost of natural timber products in the near future. Although timber sub-

stitutes in the form of wood fiberboard are available, these products are generally of mediocre mechanical performance and cannot meet the standards required for wide application in construction and industrial processes.[1,2] Thus, there is an increasingly urgent need for developing high quality timber substitute products that can benefit the global industrial and business development, with due regard for the world environment. Recently, many works have started with bamboo fibers as naturally organic fillers of polymer composites. The reason that many studies focus on bamboo is because bamboo is an abundant natural resource in Asia, and its overall mechanical properties are comparable to those of wood.[3] Furthermore, bamboo can be renewed much more rapidly compared with wood. The time required for bamboo to reach its mature size is only six to

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eight months, less than 5% of that for wood. It has been shown that bamboo-reinforced composites have desirable mechanical properties.[4–7] However, the polymer matrices currently encountered in this field are epoxy and polyester in their solid form, which are both expensive and brittle.

In order to obtain an economical substitute having properties similar to those of wood, a project is conducted in this laboratory to develop a new type of composite materials—thermoplastic bamboo fiber-reinforced polypropylene (PP) composites. PP was chosen as matrix resin due to its low price and favorable mechanical properties. The goal of this research program is to make the composites in the form of boards, rods, and thin sheets. Bamboo fiber-reinforced PP composites are expected to have the following properties: lightweight, good weathering ability, good design and manufacture flexibility, and medium strength, which are to be used in furniture and construction industries. In this article, we present here some preliminary results of our study on the bamboo fiber-reinforced PP composites. In order to promote the interaction between matrix and bamboo fiber, maleated polypropylenes (s-MAPP and m-MAPP) were also used. Particularly, crystallization and interfacial morphology were studied by using differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), and optical microscopy. This investigation will enable us to understand better the structure–properties relationship of the composite materials and the complicated problem of interface adhesion between natural organic fillers and synthetic polymers.

EXPERIMENTAL

Materials and Preparation of Composites

The matrix materials for the preparation of the composites included PP and two types of maleated PP. The sample of PP, Profax 6201, was supplied by Himont Chemical Inc. It has an MFR = 20 and a density of 0.920 g/cm^3.

In order to promote the interaction between PP and bamboo fiber, a reactive agent maleic anhydride (MAH) was used. The reaction can be carried out either in solvent as a reaction medium or directly in a batch mixer. The first type of maleated PP used was prepared by solution surface grafting with benzoyl peroxide (BPO) as an initiator according to the method as described in Martiner et al.[8] and Sathe et al.[9] The content of MAH grafted onto the PP was ca. 1%. The sample thus obtained was designated as s-MAPP. The second type of maleated PP was prepared by directly reactive-mixing PP with MAH and a peroxide initiator according to the method as described in Lin.[10] The reaction of MAH with PP was conducted by loading PP powders into the mixing chamber of a Haake Plasticorder at 160°C while maintaining the speed of the screws at 30 rpm. After 3 min, the PP was molten, and dicumyl peroxide (DCP) was added for another 4 min. Finally, MAH was added for a further 3 min mixing. The content of MAH was 1 phr. The sample thus obtained was designated as m-MAPP.

Bamboo materials used belonged to the species *Bambusa paravariabilis,* which is grown abundantly in Asia. Bamboo clumps were chopped into small chips with a roller machine. Bamboo fiber was prepared by breaking the bamboo materials in a Toshiba MX-301 high-speed laboratory blender. The bamboo fiber thus obtained was then dried at 80°C in a vacuum oven for 48 h and was separated with a 500 μm sieve.

The composites were prepared by using a Haake Plasticorder. The polymer and the bamboo fiber were directly added into the mixing chamber, and the composite samples were prepared at 180°C and were further pressed at 180°C into sheets of various thickness. The pure polymers, PP, s-MAPP, and m-MAPP, were subject to the same treatment and were also pressed into sheets.

Measurements

A TA 2100 differential scanning calorimeter was employed to obtain the melting behavior of the samples. The sample weight used in the DSC cell was kept in the 8 to 12 mg range. The samples were first heated to 250°C and maintained at that temperature for 5 minutes. They were then cooled to 50°C at a rate of 10°C/min to trace the crystallization process, followed by heating to 250°C again to observe the melting behavior. A heating rate of 10°C/min was used in all cases. The heat of fusion was calculated from the melting peak area, and the maximum of the endotherm and the minimum of the exotherm were taken as the melting temperature (T_m) and the crystallization temperature (T_c), respectively.

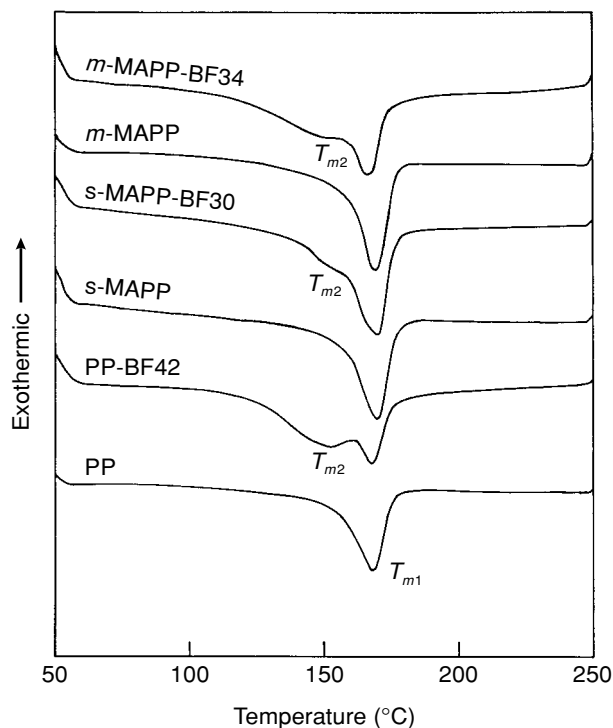The WAXD patterns were taken on a Philips

Figure 1 DSC scanning thermograms of as-prepared samples of the plain polymers and their composites. The heating rate is 10°C/min.

PW 1830 diffractometer with Cu-Kα radiation operating at 40 KV and 50 mA at room temperature. The angular scale and recorder reading (2θ) were calibrated to an accuracy of 0.01 degrees. Samples were of uniform thickness and approximately 1.5 mm thick.

Composite films containing single bamboo fiber were prepared for optical examination. An Olympus BH2-MJLT optical microscope equipped with cross-polarizers was used.

RESULTS AND DISCUSSION

Crystallization and Melting Behavior

Figure 1 shows DSC scanning curves of as-prepared samples at a heating rate of 10°C/min for PP, m-MAPP, s-MAPP, and the composites. Table I lists the melting temperatures and endothermic heats of pure polymers and the composites. For the pure PP, only a single endothermic peak occurs at $T_{m1} = 169$°C, corresponding to the melting of its α-crystalline phase. It can also be seen that both the pure m-MAPP and the s-MAPP exhibit a single melting endothermic peak at $T_{m1} = 169$°C, referred to the melting of the α-crystalline phase of their PP sequences. However, a new endothermic peak T_{m2} appears at lower temperature for all the composites. The values for T_{m2} are 152, 150, and 150°C, corresponding to the melting of the β-crystalline forms of the PP, s-MAPP, and m-MAPP in the composites, respectively. Jacoby et al.[11] and Varga[12] have measured the melting temperatures of all crystalline forms of PP. For the α-form, Tm = 168°C, whereas the value of Tm for the β-form was 152°C. It is clear that the β-phase structure was formed in all the three kinds of bamboo fiber-filled composites. The same phenomenon has been observed and studied in detail in our previous work on the PP composites filled with wollastonite[13] and with rare earth oxides.[14]

Figure 2 shows the DSC traces of PP, s-MAPP, m-MAPP, and their composites at a cooling rate of 10°C/min. The related cooling crystallization data are listed in Table II. For the pure polymers, PP, s-MAPP, and m-MAPP, an exothermic peak occurs at Tc = 107, 109, and 116°C, respectively. For their composites, these exothermic peaks shift respectively to high temperatures at Tc = 110,

Table I   Melting Behavior and β-Form Content of the As-prepared Samples of PP, s-MAPP, m-MAPP, and the Composites

Sample	Polymer/Filler (w/w)	T_{m2}/T_{m1} (°C)	$\Delta H_{f1,2}$ (J/g Compos.)	(J/g Polym.)	K Value
PP	100/0	—/169	107.1	107.1	0
PP-BF42	58/42	152/168	66.5	114.7	0.35
s-MAPP	100/0	—/169	99.2	99.2	0
s-MAPP-BF30	70/30	150/169	72.5	103.5	0.23
m-MAPP	100/0	—/169	111.6	111.6	0
m-MAPP-BF34	66/34	150/166	67.5	102.2	0.15
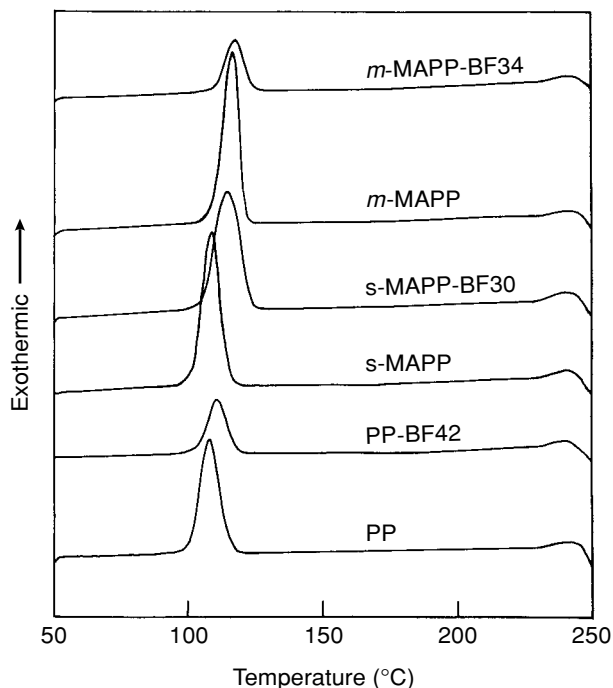
Figure 2 Cooling crystallization thermograms at $-10°C/min$ for the plain polymers and their composites.

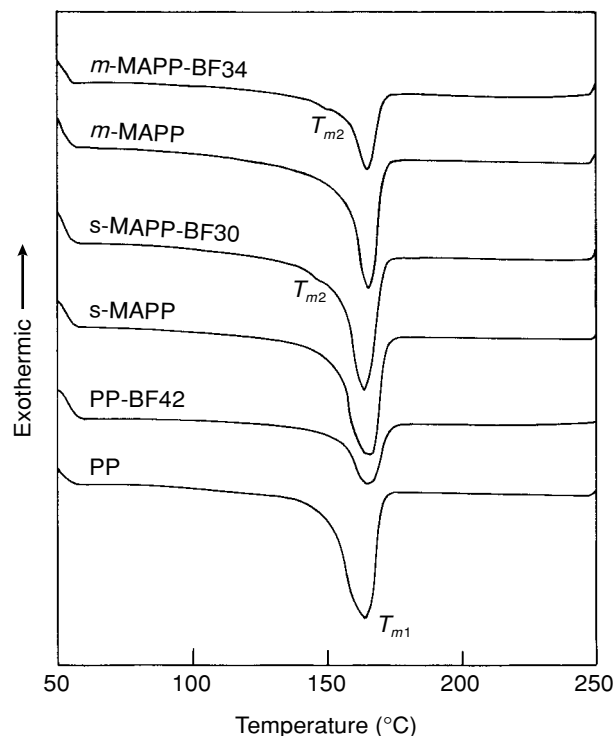**Figure 3** DSC scanning thermograms after the cooling crystallization for the plain polymers and their composites. The heating rate is $10°C/min$.

114, and 117°C. The higher Tc values of the composites than those of the pure polymers indicates that the crystallization rate of the composites becomes more rapid. The increase in Tc can be considered to be due to the nucleation effect of the bamboo fiber. Certainly, it appears that bamboo fiber can act as a nucleating agent for PP, s-MAPP, and *m*-MAPP in the composites.

The melting behavior after the cooling from the melt for PP, s-MAPP, *m*-MAPP, and their composites at a heating rate of 10°C/min is presented in Figure 3. Table III summarizes the melting

temperatures and endothermic heats of the polymers and the composites. It can be seen that all the three pure polymers exhibit a single melting endothermic peak at T_{m1} = 166°C, attributed to the melting of the α-crystalline form. It is noted that the PP/bamboo fiber composite PP-BF42 also has a single melting endothermic peak at T_{ml} = 165°C due to the melting of its α-crystalline form, implying that there is no β-crystalline phase formed during the cooling process. However, it can

Table II   Cooling Crystallization Data of PP, s-MAPP, *m*-MAPP, and the Composites

Sample	Polymer/Filler (w/w)	T_c (°C)	ΔH_c (J/g Compos.)	(J/g Polym.)
PP	100/0	107	100.4	100.4
PP-BF42	58/42	110	43.4	74.8
s-MAPP	100/0	109	99.0	99.0
s-MAPP-BF30	70/30	114	78.4	112.0
m-MAPP	100/0	116	103.4	103.4
m-MAPP-BF34	66/34	117	42.9	65.0

Table III Melting Behavior after Cooling Crystallization of PP, s-MAPP, *m*-MAPP, and the Composites

Sample	Polymer/Filler (w/w)	T_{m2}/T_{m1} (°C)	$\Delta H_{f1,2}$ (J/g Compos.)	(J/g Polym.)
PP	100/0	—/166	103.9	103.9
PP-BF42	58/42	—/165	46.1	79.5
s-MAPP	100/0	—/166	101.6	101.6
s-MAPP-BF30	70/30	148/163	85.7	122.4
m-MAPP	100/0	—/166	103.7	103.7
m-MAPP-BF34	66/34	150/166	46.3	70.2

be seen from Figure 3 that there is only a small endothermic peak that occurred at $T_{m2} = 148$ and 150°C, respectively, for the s-MAPP and *m*-MAPP composites, referred to as the melting of their β-crystalline forms. This result suggests that the content of the β-crystalline phase formed in these two bamboo fiber-filled composites during the cooling process is rather low.

The DSC results presented here clearly show that a considerable amount of the β-phase form existed in the as-prepared bamboo fiber-filled composites. Liu et al.[13,14] have found that some inorganic fillers might act as β-nucleators and formed larger amounts of the β-form; hence, the properties of the related composites should be remarkably influenced. The present work further shows that bamboo fiber can also act as a β-nucleator.

X-Ray Diffraction

The WAXD measurement shows that PP, s-MAPP, *m*-MAPP, and their composites exhibit three strong equatorial α-form peaks of PP or PP sequences, (110), (040), and (130). The WAXD patterns of the pure PP and the PP-BF42 composite are shown in Figure 4. The pattern of the composite gives a new peak located at $2\theta = 16$ degrees, which is the characteristic single β-form peak (300). Figure 4 also presents the WAXD pattern of a bamboo chop. No diffraction peak is located between $2\theta = 10$ and 20 degrees for the bamboo material. The relative amount of the β-form is usually described in terms of the K value, which is defined as follows:[15]

$$K = H_\beta/[H_\beta + (H_{\alpha1} + H_{\alpha2} + H_{\alpha3})] \qquad (1)$$

where $H_{\alpha1}$, $H_{\alpha2}$, and $H_{\alpha3}$ are the heights of the three strong equatorial α-form peaks (110), (040), and (130); and H_β is the height of the strong single β-form peak (300). The K values for all the three bamboo fiber-filled composites were calculated from their WAXD patterns by using eq. (1). Table I lists the K values thus obtained. It is interesting to notice that the K value reached as high as 0.95 for the PP samples prepared by using β-nucleators, as reported by Shi et al.[16] In the present case, the K values for these bamboo fiber-filled composites are only moderate. This can be due to the larger size of bamboo fiber and then the relatively smaller specific surface area since
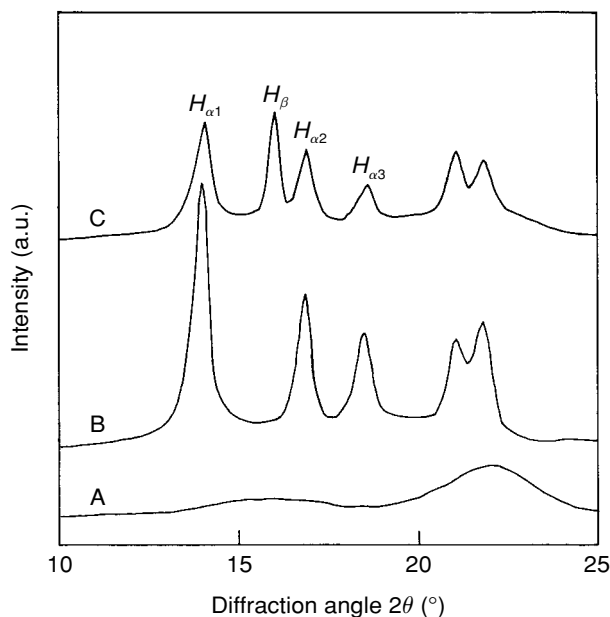

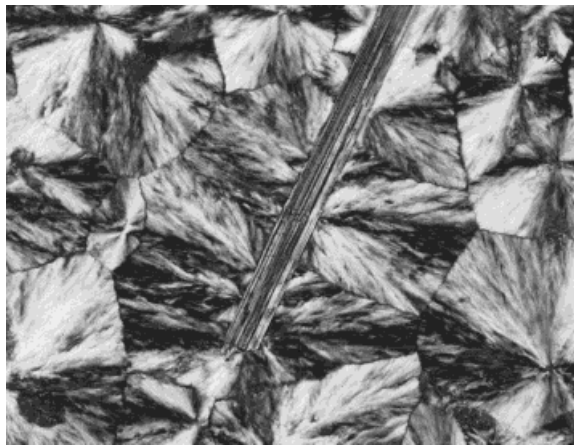**Figure 4** X-ray diffraction diagram of (A) bamboo chop, (B) pure PP, and (C) the PP-BF42 composite.

Figure 5 Optical micrographs with crossed polars of bamboo fiber in PP matrix (×100).

Figure 6 Optical micrographs with crossed polars of bamboo fiber in s-MAPP matrix, showing transcrystalline growth on the bamboo fiber surface (×100).

only the surface of the bamboo fiber can induce the formation of the β-form.

Interfacial Morphology

It has been well known that the mechanical properties of fiber-reinforced materials depend critically upon the fiber-matrix interfacial adhesion. However, the situation is rather confused as far as the properties of the interface are concerned. When using crystallizable thermoplastics, e.g., PP, as matrix, there exists a direct effect of the fibers on the processes of the crystallization; hence, it becomes possible to develop molecular orientation in the matrix. As a result, the interfacial adhesion may be additionally influenced by the morphology of the matrix close to the filler surface. For PP, heterogeneous nucleation can occur readily in the presence of certain fiber as recently reviewed by Folkes.[17] Figure 5 is an optical micrograph with crossed polars of bamboo fiber in PP matrix. It can be clearly seen that there exists nucleation phenomena on the bamboo fiber surface and isolated spherulites start to grow at several points along the bamboo fiber. However, normal three-dimensional growth is hindered, and the growth direction of the spherulites is limited. It should be pointed out that the nucleation density at the fiber surface is not sufficiently high since there is not yet transcrystalline growth around the fiber. It is noted that the spherulites of PP occur throughout the remaining matrix and have a regular shape with defined borders.
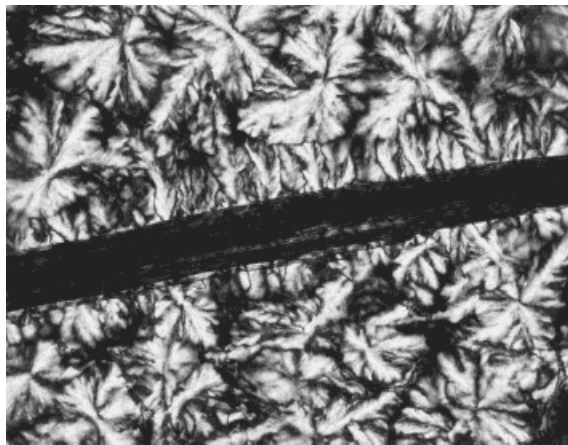
Figures 6 and 7 clearly show transcrystalline growth of s-MAPP and m-MAPP on the bamboo fiber surface, respectively. The appearance of transcrystalline growth displays that the nucleation density of both s-MAPP and m-MAPP on the bamboo fiber surface is sufficiently high. The embryonic spherulites begin to impinge greatly on each other so that normal three-dimensional growth is impossible; consequently, the spherulites grow predominantly in one direction, normal to the surface. It can also be seen from the Figures 6 and 7 that the spherulites of both s-MAPP and m-MAPP occur throughout the remaining matrices; and the spherulites of s-MAPP and m-MAPP in the composites are somewhat smaller than

Figure 7 Optical micrographs with crossed polars of bamboo fiber in m-MAPP matrix, showing transcrystalline growth on the bamboo fiber surface (×100).

those in the PP composite and display irregular shape.

It clearly appears that bamboo fiber exhibits a stronger nucleation effect to s-MAPP and *m*-MAPP than to PP. The nucleation density of both s-MAPP and *m*-MAPP at the fiber surface is remarkably higher than that of PP. This is because an improved interfacial adhesion between the filler and the matrix is reached in the case of s-MAPP and *m*-MAPP as matrices. The development of transcrystallinity around the bamboo fiber further enhance the interfacial strength.[17] Nonpolar polymer PP is fairly inert, whereas the surface of bamboo fiber is rendered hydrophilic, owing to the surface hydroxyl groups.[3] The interfacial adhesion between bamboo fiber and plain PP matrix is very weak. Thus, modification of PP by grafting MAH has been adopted to improve the interfacial adhesion between the bamboo fiber and the matrix. This results in an improved interfacial adhesion in the case of s-MAPP and *m*-MAPP and will further greatly enhance the strength of the composites, as will be discussed elsewhere.[18]

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