

Preparation and Characteristics of Composites of High-Crystalline Cellulose with Polypropylene: Effects of Maleated Polypropylene and Cellulose Content

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ABSTRACT: Binary composites of high-crystalline fibrous cellulose with polypropylene (PP) or maleic anhydride-grafted polypropylene (MAPP) were prepared by melt-mixing with different contents of cellulose from 0 to 60 wt %. Ternary composites of cellulose with PP and MAPP were also prepared to investigate the effects of MAPP as a compatibilizer between cellulose and PP. Scanning electron microscopy revealed that the addition of MAPP generates strong interactions between a PP matrix and cellulose fibers: All cellulose fibers are encapsulated by layers of the matrix and connected tightly within the matrix. Thus, the tensile strength and Young's modulus of MAPP-containing composites increase with an increase in MAPP and cellulose content, in contrast to the decrease in tensile strength of a PP-based binary composite with an increase in cellulose.

Cellulose fibers act as a nucleating agent for the crystallization of PP, which is promoted by the addition of MAPP through an increase of the crystallization temperature of PP in the composite. Accordingly, both cellulose and MAPP facilitate the thermooxidative stability of PP composites in the following order: MAPP/cellulose > PP/MAPP/cellulose > PP/cellulose > PP. Relative water absorption increases with an increase in cellulose content, decreasing with the addition of MAPP. MAPP-containing cellulose composites have high potential for applications as environmentally friendly materials. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 337–345, 2003

Key words: poly(propylene); polysaccharides; compatibility; composites; morphology

INTRODUCTION

Polypropylene (PP), one of the most popular thermoplastic polymers, has the advantages of low cost, recyclability, and high thermal stability and thus has yielded many kinds of composites. Among the fillers used, increasing attention has been paid to cellulose fibers in recent years.^{1–6} Cellulose-reinforced polymer composites are characterized by low cost, low density, high stiffness, biodegradability, and good mechanical properties as well as availability of renewable natural resources. However, because of the inherent incompatibility of hydrophilic cellulose fibers with hydrophobic PP, the lack of adhesion between cellulose and PP results in unsatisfactory properties of the resultant composites.

It is well known that the performance, such as mechanical properties, of composites depends not only on the properties of the individual components but also on their interfacial compatibility. The properties of the interphase play a crucial role in determining the properties of fiber-reinforced materials.^{7,8} Good interfacial adhesion between the matrix and fibers is essen-

tial to transfer stress from the matrix to the fibers and thus improve the mechanical strength of composites. Many studies have been carried out to improve the interfacial adhesion between fibers and the matrix. Much attention has been focused on modification of the fiber and/or polymer by physical and chemical methods. Physical methods, including corona or plasma discharges, are useful for polymer matrices such as PP, polyethylene, and polystyrene.^{9–11} Chemical methods cover the pretreatment of fiber surfaces by coupling agents, such as silanes^{12–14} and isocyanates,^{15,16} and modification of the matrix by grafting different chemical moieties on polymer chains. Non-polar PP is usually grafted with polar acrylic acid, acrylic esters, maleic anhydride, etc.^{17–19} Among these methods, maleic anhydride-grafted PP (MAPP) has been found to be most efficient in improving interfacial adhesion of fibers and a PP matrix.^{1–3,5,6,19–22}

Although many studies have been made on PP and cellulose fiber composites in recent years, there still exist many outstanding problems in this field. Our ultimate aim is to make clear the possibility of the preparation of composites with a very high cellulose content. In this study, we describe some preliminary results involving composites of PP with fibrous cellulose with a high crystallinity. Binary composites of cellulose with PP or MAPP were prepared by melt-

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mixing with different cellulose contents from 0 to 60 wt %. Also, ternary composites from PP, MAPP, and cellulose were prepared by using MAPP as a compatibilizer to optimize the MAPP content. Effects of the cellulose content and MAPP content on properties of the composites were examined.

EXPERIMENTAL

Materials

Isotactic PP (PP powder, \bar{M}_w ca. 250,000; density 0.900 g/cm³) and PP-*graft*-maleic anhydride (MAPP pellets, ca. 0.6 wt % MA; melt index 115; density 0.950 g/cm³, as reported by the manufacturer) were obtained from Aldrich (Milwaukee, WI). Fibrous cellulose [CF11, 50–350 μ m in length, about 20 μ m in diameter; crystallinity 93% (cellulose I type)^{23,24}] was supplied by Whatman Int. Ltd. (Maidstone, England).

Preparation of composites and samples

PP and CF11 were dried *in vacuo* at 60°C for 15 h, and MAPP was pretreated *in vacuo* at 120°C for 15 h before mixing. Composites with different constituent ratios were prepared by a melt-mixing method with a Toyoseiki Labo Plastomill 30C150 Rheomix (the volume of the mixing chamber: 60 cm³). The mixing was carried out at 190°C; at 55 rpm for 20 min.

Sheets of about 1-mm thickness were obtained by compression molding in a Shinto press (Shinto Metal Ind. Ltd.) at 200°C, under the pressure of 3 MPa for 6 min, followed by cooling under the pressure of 8 MPa to room temperature at a fixed cooling speed. Teflon films were used to avoid the adhesion of MAPP to the stainless surface of the mold. Standard specimens were cut from the pressured sheets.

Tensile tests

Tensile properties were measured with a Shimadzu AGS-5kNG universal testing machine in accordance with the testing method for tensile properties of plastics (at a strain speed of 5 mm/min).²⁵ Samples were stored in a room with a constant temperature of 20°C and a constant humidity of 65% over 24 h before the measurement. The results were obtained from six parallel tests.

Dynamic mechanical analysis (DMA)

DMA of the composites was performed with a Perkin-Elmer DMA 7e using a three-point bending rectangular measuring system at a frequency of 1 Hz. The samples of a 15 \times 3-mm² area and 1-mm thickness were cooled to –30°C, maintained at the temperature for 3 min, and then heated to 130°C at a heating rate of

5°C/min in a flow of nitrogen. The static and dynamic forces were 330 and 300 mN, respectively. The viscoelastic parameters, that is, the mechanical loss factor (damping) $\tan \delta = E''/E'$ (E'' and E' are loss and storage moduli, respectively) and E' , were recorded as a function of temperature.

Scanning electron microscopy (SEM)

The morphology of composites was examined using a Hitachi S-2 460N electron microscope at 25 kV. Fracture surfaces of composites after tensile tests were sputter-coated with a gold-palladium alloy before viewing.

Differential scanning calorimetry (DSC)

DSC measurements were performed with a Perkin-Elmer DSC Pyris 1 instrument in a nitrogen atmosphere. Samples were held at 230°C for 3 min to erase the thermomechanical prehistory, then cooled to 50°C at a rate of –10°C/min, maintained at 50°C for 3 min, and then reheated to 230°C at a rate of 10°C/min. Scannings while cooling and during the second heating were recorded.

Thermooxidative property

Thermooxidative stabilities of composites were examined with a MAC Science TG-DTA 2000 instrument under a flow of air, heating from about 50 to 500°C at a rate of 10°C/min. Samples were dried at 60°C for 24 h before the measurement.

Water-absorption tests

The water absorption of the composites was examined by immersion of sheet samples of 1-mm thickness in distilled water for 1500 h, periodically measuring the increase in the weight of the samples.

RESULTS AND DISCUSSION

Tensile properties

The tensile strength, Young's modulus, and percent elongation at break of the composites are shown in Figures 1 and 2. For PP-based binary composites (Fig. 1), the tensile strength and the elongation at break exhibit sharp decreases from those of neat PP even in a cellulose content of 10 wt %, beyond which the tensile strength further decreases. The results imply that the interfacial adhesion of the cellulose fiber/matrix is very poor; in other words, there is little compatibility between the PP matrix and the cellulose fibers, which is consistent with the SEM observation described later, that is, there are voids around the

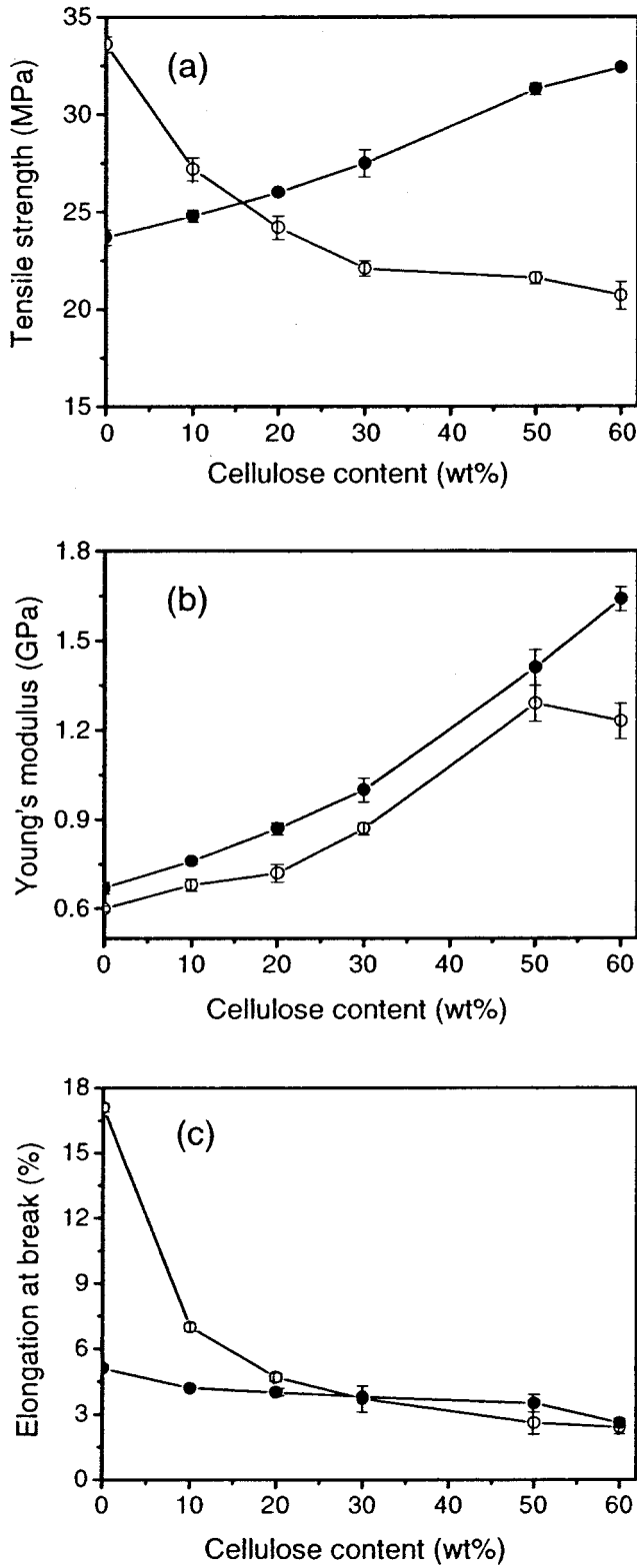


Figure 1 Mechanical properties of binary composites of cellulose with (○) PP and (●) MAPP.

cellulose fibers. The marked decrease in the elongation at break is due to the presence of the filler.²⁶ The increase in the Young's modulus was influenced

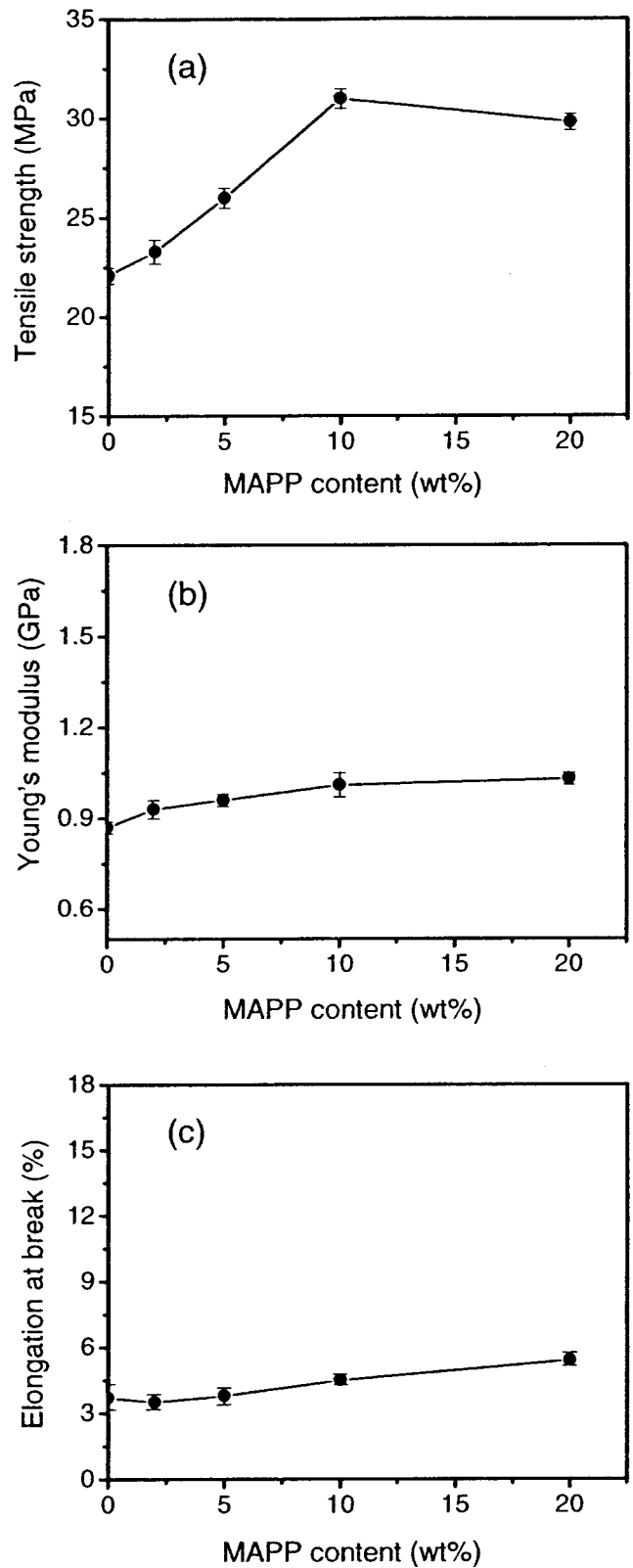


Figure 2 Effects of MAPP content on mechanical properties of ternary composites with a cellulose content of 30 wt%.

mainly by the proportion of the cellulose content in the composite, because of the high modulus of the cellulose.

Quite unlike PP-based binary systems, the MAPP-based binary exhibits a strong increase both in the tensile strength and in the Young's modulus with increasing cellulose content [Fig. 1(a,b)]. Furthermore, the elongation at break decreases only very slightly with an increase in the cellulose content [Fig. 1(c)]. These performances are probably due to the interaction between maleic anhydride groups grafted onto PP and OH groups of cellulose fibers that improve the interfacial adhesion of cellulose fibers with the matrix. The tensile properties of the MAPP-based binary composite is consistent with the SEM observation that cellulose fibers are wrapped tightly by the MAPP matrix.

In ternary composites with a cellulose content of 30 wt %, the Young's modulus of the composite increases slightly with an increase in MAPP content up to 10 wt %, beyond which it reaches a plateau. The tensile strength increases greatly with an increase in the MAPP content, showing a maximum around an MAPP content of 10 wt %. The results strongly suggest that MAPP, as a compatibilizer, improves the compatibility between hydrophilic cellulose fibers and the hydrophobic PP matrix. There exist strong interactions between cellulose fibers and maleic anhydride groups on MAPP, and, meanwhile, there is good compatibility between PP and the PP segments of MAPP. Therefore, a diffuse interlayer can be formed between the components exhibiting excellent adhesion to each other. Figure 2(a) suggests that there is a critical amount of MAPP at which MAPP exhibits the strongest interactions with cellulose fibers as well as the PP matrix. Thus, beyond an MAPP content of 10 wt %, the tensile property of the ternary composite decreases due to the lower compatibility between maleic anhydride groups of MAPP and the PP matrix, as well as to the lower tensile strength of MAPP. A slight increase in elongation at break of the MAPP-containing composite [Fig. 2(c)] is probably due to the improved distribution of cellulose fibers promoted by MAPP.

Dynamic mechanical properties

Dynamic mechanical spectra ($\tan \delta$ and E' as a function of temperature) of PP-based binary composites are depicted in Figure 3(a,b). The $\tan \delta$ curve of neat PP exhibits two peaks around -8°C (β) and 70°C (α). The dominant β -peak is due to the glass-rubber transition of amorphous portions in PP, while the shallow α -relaxation shoulder is attributed to a lamellar slip and rotation in the crystalline phase.^{6,27} With increasing cellulose content, $\tan \delta$ decreases gradually and E' increases because of the high elasticity of cellulose. This means that composites with a larger content of

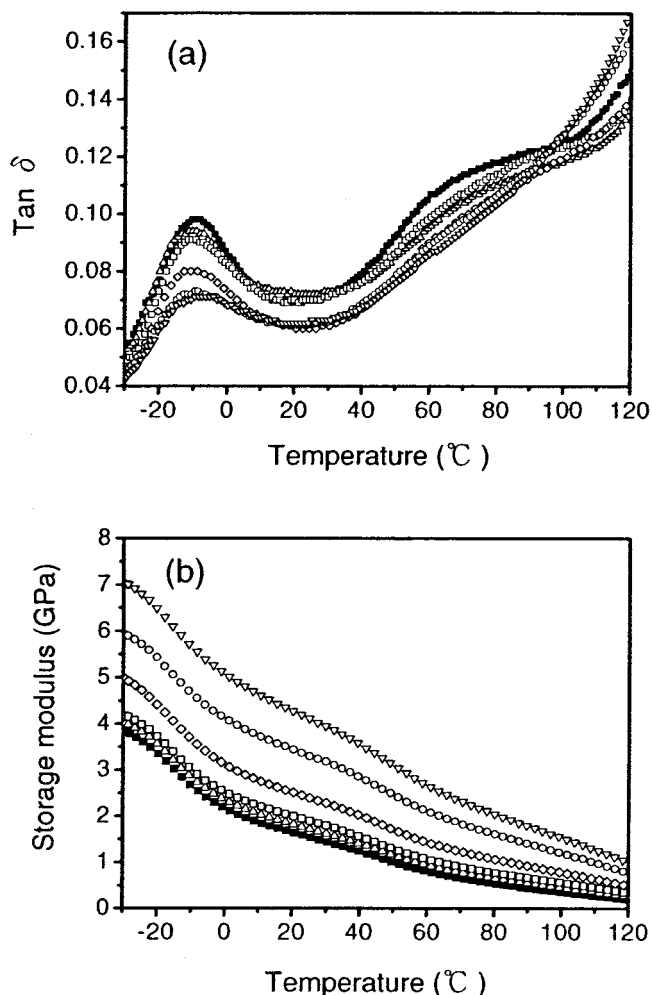


Figure 3 Dynamic mechanical spectra of PP/CE binary composites. Cellulose content: (■) 0, (Δ) 10, (\square) 20, (\diamond) 30, (\circ) 50, and (\triangle) 60 wt %.

cellulose have enhanced stiffness, in agreement with the results of the Young's modulus shown in Figure 1(b). The intensities of both the α - and β -relaxations decrease significantly with increasing cellulose content, the β -relaxation retaining the same peak position and shape, while the α -relaxation broadens. It seems that the lamellar movement in the crystalline phase is apt to be affected by the cellulose content. This may be explained as a retardation of the relative motion of lamella.²⁷

The dynamic mechanical behaviors of MAPP-based composites are analogous to those of PP-based composites. Figure 4 shows the viscoelasticity of MAPP-based binary composites, compared with PP-based composites. For the same cellulose content, the MAPP-based composite reveals smaller loss tangent ($\tan \delta$) values and a slightly higher storage modulus (E') than those of the PP-based composite. This may be due to the higher elasticity of MAPP itself.

Figure 5 shows dynamic mechanical spectra of the ternary composites with a constant cellulose content

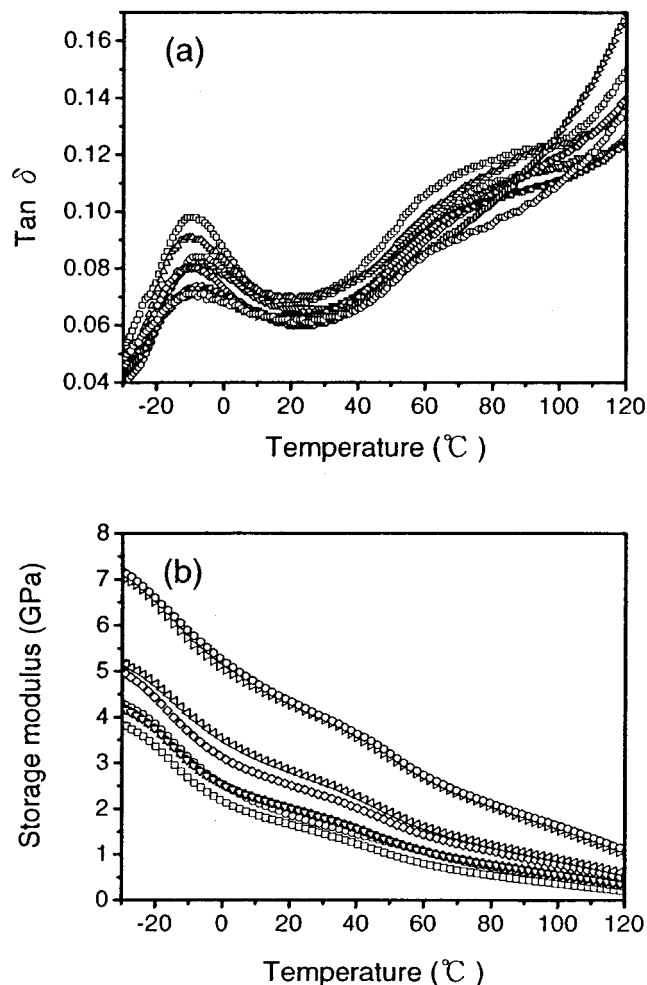


Figure 4 Comparison of dynamic mechanical spectra between PP/CE and MAPP/CE binary composites. Cellulose content in PP and MAPP: (\square , \circ) 0, (\triangle , ∇) 20, (\diamond , \blacktriangleleft) 30, and (\triangleright , \circ) 60 wt%.

of 30 wt %. Compared with the PP/CE (70/30) composite, the addition of MAPP up to 20 wt % results in little change in the $\tan \delta$ and storage modulus (E'), as expected from the results in Figure 4.

Morphology of composites

SEM micrographs of fracture surfaces of the composites are shown in Figure 6. The fracture surfaces of the composites are consistent with their mechanical properties. In Figure 6(a,b), micrographs of the PP-based binary composites clearly show that there are large gaps and voids in the PP matrices as well as along the cellulose fibers, the surfaces of which are smooth and practically intact, and that there exist some aggregates of cellulose fibers. The morphology demonstrates that the interfacial adhesion between cellulose and the PP matrix is very poor. Figure 6(c,d) represents the morphology for MAPP-based binary composites, while Figure 6(e,f) corresponds to that for PP/MAPP/CE

ternary composites. The SEM findings provide strong evidence that interactions occur between MAPP and the cellulose fibers. For all the MAPP-containing composites, no large cellulose agglomerates are observed, and it is difficult to differentiate cellulose fibers from the matrix. All the cellulose fibers are tightly connected with the matrix, and some cellulose fibers are broken and/or torn up. The improved interfacial adhesion observed in all the MAPP-containing composites is consistent with the increased mechanical properties, indicating that MAPP acts as a compatibilizer between cellulose fibers and the PP matrix. Most MAPP is probably localized at the interfaces between cellulose fibers and the PP matrix, similar to the case of woody fillers and the PP matrix in which MAPP forms an interphase.²⁸

Crystallization and melting behavior

The results of the melting and crystallization behavior are summarized in Table I. For all the composites, only

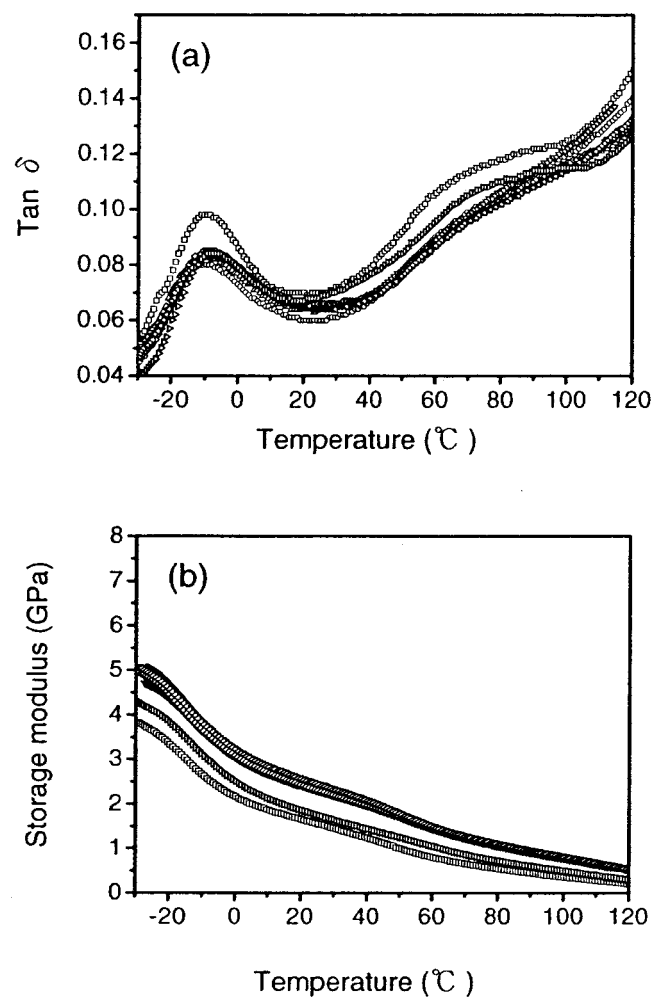


Figure 5 Dynamic mechanical spectra of PP/MAPP/CE ternary composites with a cellulose content of 30 wt %. MAPP content: (\circ) 0, (\triangle) 2, (∇) 5, (\diamond) 10, and (\blacktriangleleft) 20 wt %. The results of (\square) pure PP and (\triangleright) MAPP are shown for comparison.

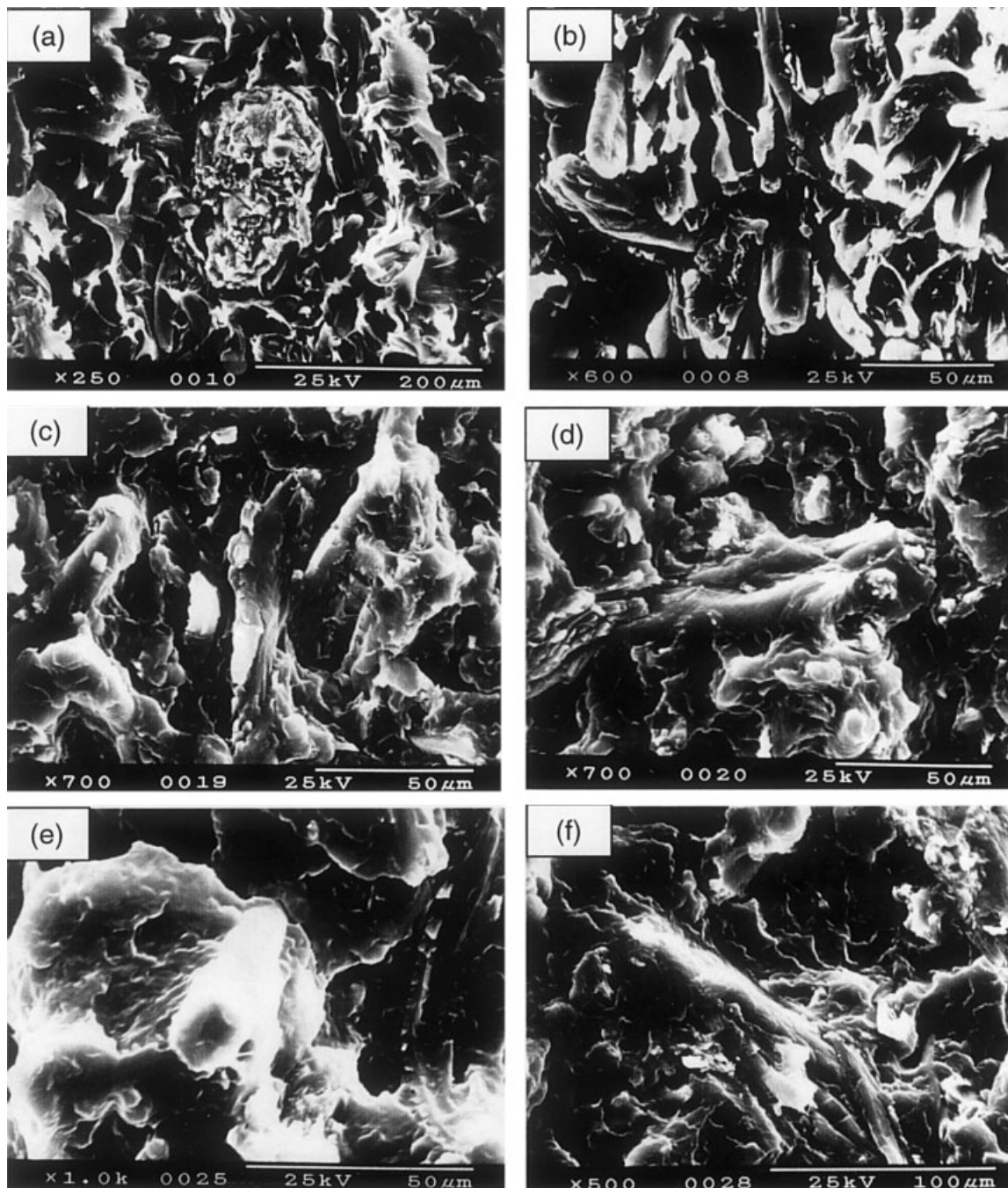


Figure 6 SEM micrographs of fracture surfaces of composites. Compositions (weight ratio): (a) PP/CE = 70/30; (b) PP/CE = 50/50; (c) MAPP/CE = 70/30; (d) MAPP/CE = 50/50; (e) PP/MAPP/CE = 65/5/30; (f) PP/MAPP/CE = 60/10/30.

a single melting endothermic peak appears. In both PP-based and MAPP-based binary composites, the addition of a slight amount of cellulose causes a remarkable increase in the crystallization temperature (T_c) and the onset temperature (T_{onset}) of the PP matrix. This is probably due to the cellulose fibers acting as an efficient nucleating agent for the crystallization of PP and, consequently, increasing the crystallization rate of PP.^{6,29} The values of T_c and T_{onset} increase [and, accordingly, the supercooling ($T_m - T_c$) decreases]

with an increase in cellulose content, almost reaching plateaus at a cellulose content greater than 30 wt %. This means that a critical cellulose content is effective for the formation of an upper-limiting concentration of crystallization nuclei. The same phenomenon was observed in PP/talc composites.³⁰

In ternary composites, addition of MAPP, as compared with the no-MAPP composite, resulted in further increases in T_c and T_{onset} and, accordingly, a further reduction of supercooling ($T_m - T_c$). This is

TABLE I
DSC Characterization of Composites

Sample (wt %)	T_m^a (°C)	ΔH_m^c (J/g)	T_c^b (°C)	T_{onset}^b (°C)	$-\Delta H_c^c$ (J/g)	$T_m - T_c$ (°C)
PP/CE						
100/0	156 163 ^d	86	113	118	93	43 ^e
90/10	158	88	120	124	95	38
80/20	158	87	121	124	97	37
70/30	158	87	120	124	98	38
50/50	160	85	126	130	97	34
40/60	159	84	126	130	97	33
MAPP/CE						
100/0	157 ^d 163	88	117	122	92	40 ^e
90/10	159	87	122	126	90	37
80/20	159	82	124	128	89	35
70/30	160	84	125	130	92	35
50/50	159	75	129	136	91	30
40/60	159	77	129	135	92	30
PP/MAPP/CE						
70/0/30	158	87	120	124	98	38
68/2/30	160	88	124	128	96	36
65/5/30	161	87	125	128	97	36
60/10/30	160	88	125	129	95	35
50/20/30	161	88	126	129	95	35

^a T_m : Melting peak temperature.

^b T_c : Crystallization peak temperature; T_{onset} : onset-temperature of dynamical crystallization.

^c ΔH_m and ΔH_c denote the enthalpies of melting and crystallization based on the matrix, respectively.

^d Corresponds to the main peak.

^e The value calculated from the peak at the lower temperature.

likely due to the stronger interaction between cellulose fibers and the PP matrix compatibilized by MAPP, which improves the nucleating activity of cellulose fibers for PP. In other words, the interaction between cellulose fibers and the PP matrix is enhanced strongly through MAPP, and, accordingly, the cellulose fibers influence the crystallization behavior of the matrix more in the composite with MAPP than in that without MAPP.

Thermooxidative property

Figure 7 shows thermogravimetric (TG) curves of some composites. The 5, 10, 25, and 50% weight-loss temperatures (T_5 , T_{10} , T_{25} , and T_{50} , respectively) for all the composites are listed in Table II. In both PP-based and MAPP-based binary composites, each weight-loss temperature, except that for T_{50} , increased with an increase in cellulose content. In MAPP-containing ternary composites with the same cellulose content of 30 wt %, each weight-loss temperature further increased with an increase in the MAPP content. From Table II, the thermooxidative stabilities of composites with the same cellulose content is in the order MAPP/CE > PP/MAPP/CE > PP/CE, and all the composites have higher thermooxidative stabilities than those of neat PP. One reason is that cellulose has higher thermal stability than has a PP matrix; another may be

attributed to the strong interaction between cellulose and the matrix caused by MAPP. It can be concluded that both cellulose and MAPP enhance the thermooxidative stability of the PP composites. This will prove useful for application to eco-friendly materials with a higher cellulose content.

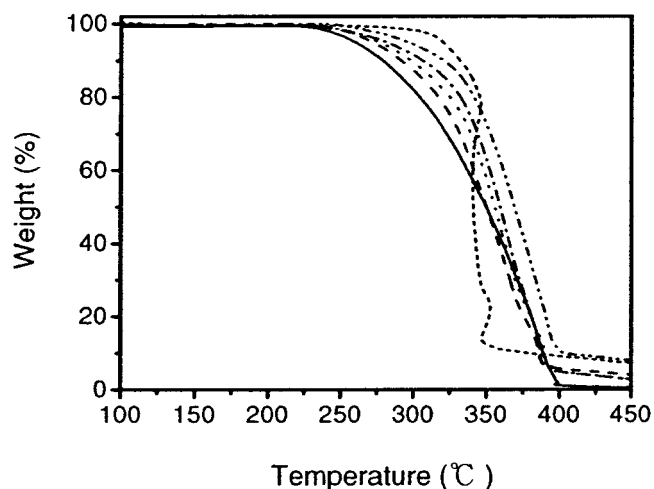


Figure 7 Thermogravimetric analysis of composites. Compositions (weight ratio): (—) PP; (----) PP/CE = 70/30; (····) PP/MAPP/CE = 68/2/30; (-·-·-) PP/MAPP/CE = 60/10/30; (-·-·-·) MAPP/CE = 70/30; (----) CF11.

Water absorption

It is important to examine the water-absorption behaviors of the composites, because the dimensional stability of the final products deteriorates as a result of moisture absorption. Figure 8 shows the water-absorption results, which are given as a percent weight increase as a function of the immersion time. The PP-based binary composites exhibit higher rates of water absorption than those of the MAPP-containing composites, as is especially demonstrated by a comparison of the binary composites with a cellulose content of 60 wt %. As expected, neat PP and MAPP show the lowest levels of water absorption. Saturated water absorption increases with the content of hygroscopic cellulose. Fortunately, however, saturated water absorption decreases with an increase of the MAPP content, as shown from the results of the composites with a cellulose content of 30 wt %. These behaviors are probably due to the different interfacial structures seen in the SEM observation. For the PP-based binary composites, because the adhesion between cellulose fibers and the PP matrix is very poor, water molecules are readily adsorbed on cellulose fibers and/or microcavities in the interfaces. For MAPP-containing composites, however, there exists strong adhesion between cellulose fibers and the matrix, and, accordingly, the cellulose fibers are encapsulated within the MAPP matrix, preventing water molecules from penetrating into the composites. The results of water ab-

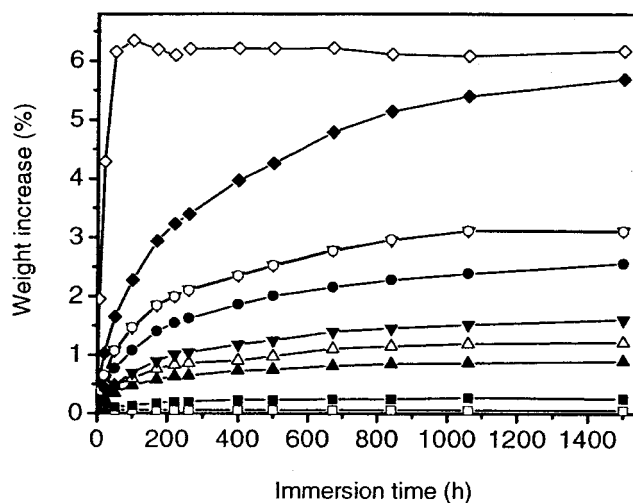


Figure 8 Water absorption of composites. Compositions (weight ratio): (□) PP; (■) MAPP; (△) PP/CE = 90/10; (▲) MAPP/CE = 90/10; (▽) PP/CE = 70/30; (▼) MAPP/CE = 70/30; (○) PP/MAPP/CE = 68/2/30; (●) PP/MAPP/CE = 60/10/30; (◇) PP/CE = 40/60; (◆) MAPP/CE = 40/60.

sorption are also in agreement with the results of the mechanical properties and thermooxidative stability.

CONCLUSIONS

Composites with high crystalline cellulose were prepared through melt-mixing with PP and/or MAPP. A strong interfacial adhesion exists at the cellulose fiber/matrix interface in MAPP-containing composites, in contrast to very poor adhesion in PP-based binary composites. The mechanical properties (such as tensile strength, Young's modulus, and storage modulus) of the MAPP-containing composites increase with an increase in the cellulose content, indicating that MAPP acts as an efficient compatibilizer in preparing PP/cellulose composites, while the tensile strength of the PP-based binary composite decreases with increasing cellulose content. Cellulose fibers act as a nucleating agent for the crystallization of PP, which is further promoted by the addition of MAPP, to increase the crystallization temperature of PP in the composite. Both cellulose and MAPP facilitate the thermooxidative stability of PP composites. The thermooxidative stabilities of the composites are in the following order: MAPP/CE > PP/MAPP/CE > PP/CE > PP. Relative water absorption increases with an increase in the cellulose content, but decreases with the addition of MAPP. Accordingly, MAPP-containing cellulose composites have much potential for application as environmentally friendly materials.

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TABLE II
TG Characterization of Composites

Samples (wt %)	T_5	T_{10}	T_{25}	T_{50}
	(°C)			
PP/CE				
100/0	260	279	314	350
90/10	263	283	316	348
80/20	267	288	323	347
70/30	275	293	324	351
50/50	278	306	333	352
40/60	286	310	332	350
0/100	316	329	346	341
MAPP/CE				
100/0	268	287	326	358
90/10	277	302	341	368
80/20	297	325	350	370
70/30	298	321	348	369
50/50	304	324	346	364
40/60	306	326	346	364
PP/MAPP/CE				
70/0/30	275	293	324	351
68/2/30	276	298	334	356
65/5/30	276	297	332	356
60/10/30	281	306	339	359
50/20/30	283	312	342	362
0/70/30	298	321	348	369

T_5 , T_{10} , T_{25} , and T_{50} are decomposition temperatures at which the weight losses are 5, 10, 25, and 50%, respectively.

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