

Interfacial Interaction, Morphology, and Tensile Properties of a Composite of Highly Crystalline Cellulose and Maleated Polypropylene

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ABSTRACT: A composite of highly crystalline cellulose was synthesized via a melt-mixing method with maleic anhydride (MA)-grafted polypropylene (PP), MAPP, which was prepared by melt-mixing PP with 0.25–8.0 phr (part of reagent per hundred parts of PP) of MA, and the morphology and tensile properties were examined with respect to the interfacial interactions of MAPP and cellulose. The graft degree (G_d) of MAPP increases with an increase in the initial MA amount up to 2.5 phr, beyond which it decreases because of the remaining of more free MA monomers and/or the formation of more oligomers remaining in the matrix. The morphology and tensile properties of the composite are affected strongly by G_d as well as the presence of the free MA in the matrix. For the MAPP with-

out any free MA, even the G_d value as small as 0.25–0.5 wt % yields a maximal tensile strength. The existence of free MA monomers in the MAPP decreases the tensile strength, probably because of interrupting the interactions of the grafted MA groups with the OH groups of cellulose. The tensile properties of the composite correlate with the interfacial adhesion as well as the dispersion of cellulose microfibers in the matrix, both of which are determined by the interactions of the OH groups on cellulose with the grafted MA groups. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3830–3841, 2006

Key words: composites; interface; mechanical properties; FTIR; morphology

INTRODUCTION

The extensive consumption of synthetic polymers has been causing serious environmental problems. Therefore, it is very important to develop environmentally friendly materials as substitutes for plastics from petroleum. Cellulose, one of the most abundant natural polymers, has many advantages: renewability, biodegradability, nontoxicity, high specific strength and stiffness, and low cost. However, cellulose, because of its very poor processibility, should be compounded with tractable polymers to yield composites. A variety of such composites has been developed with natural cellulosic materials.^{1–6} The typical matrices are polypropylene (PP), polyethylene (PE), polystyrene, and polyvinyl chloride. The problem to be solved in compounding cellulose with synthetic polymers is to achieve tight adhesion through strong interactions at the interfaces. Because of the incompatibility of hydrophilic cellulose fibers with

the hydrophobic polymer matrix, a lack of adhesion between cellulose fibers and PP usually results in unsatisfactory properties of the composites. Accordingly, many studies have been carried out to improve the compatibility of PP and cellulose.^{7–14} Maleic anhydride (MA)-grafted polypropylene, MAPP, is very effective for improving the interfacial adhesion of cellulosic fibers with a polypropylene matrix. The improvement by the use of MAPP is considered to be due to esterification between anhydride groups of MAPP and hydroxyl groups (OH) of cellulose. The esterification between MAPP and cellulosic materials has been confirmed in solutions in the presence of a catalyst, based on the appearance of a new IR band at 1722–1746 cm^{-1} .^{11–14} However, no direct evidence of esterification has been reported for the melt-mixing of MAPP with cellulosic materials, although melt-mixing is the most common method for preparing such composites.

Our previous research has demonstrated that MAPP is an effective compatibilizer of crystalline cellulose with PP, and that mechanical properties of the composite require an optimum MAPP content.¹⁵ Also for composites of cellulose with MA-grafted polyethylene (MAPE), we found that a very smaller amount of MA in MAPE is sufficient to yield

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satisfactory mechanical properties in the composite.¹⁶ These results suggest strongly that the reactivity of crystalline cellulose is lowered because of the formation of hydrogen bonds. In fact, the number of ester bonds formed between cellulose and MAPP is too small to be observed by FTIR in melt-mixed composites of high crystalline cellulose with MAPP, although the ball-milling intensively induces such esterification because of the elevated reactivity of cellulose with lessened crystallinity.¹⁷ Thus the natural highly crystalline cellulose as well as the large steric hindrance of MAPP determine primarily the interaction between cellulose and MAPP, and may thus determine the optimum amount of MAPP in the composites from the point of view of mechanical properties.

Considering the interactions between cellulose and MAPP, we note that unreacted free MA monomers remain in a MAPP matrix. Commercial MAPP samples contain free MA monomers and oligomers,¹⁸ and are directly used as a compatibilizer or a matrix for polymer blends and composites. Because of their higher mobility and smaller steric hindrance, the free MA monomers are probably more reactive than the grafted MA groups in MAPP. Accordingly we considered competitive interactions of free MA monomers versus grafted MA groups with the cellulose.

In this study, we prepared binary composites of MAPP and high crystalline cellulose through a melt-mixing method. The MAPP samples were prepared with different weight ratios of MA to PP. Effects of the grafted MA content in the MAPP matrix on tensile properties of the composites were investigated. We demonstrated that the free MA monomers in the MAPP matrix exhibit a strong effect on the interfacial structure between cellulose and MAPP and, accordingly, on the tensile property of the resultant composite.

EXPERIMENTAL

Materials

The isotactic polypropylene (PP) pellets used are a commercial product of Japan Polychem Corp. (Tokyo, Japan), [trade name; EA7A, melt flow index (MFI); 1.4 g/10 min at 190°C, density; 0.90–0.91 g/cm³]. The pellets were mechanically pulverized into grains of about 1 mm and dried before use. Fibrous cellulose (CF11; 50–350 μm in length, about 20 μm in diameter, I type cellulose with a crystallinity of 93%)^{19,20} was purchased from Whatman Int. Ltd. (Kent, UK). Maleic anhydride (MA) and Benzoyl peroxide (BPO) were of reagent grade, obtained commercially from Aldrich. Dehydrated acetone and dehydrated xylene were purchased from Wako Chemicals, Japan.

Preparation of MAPP and PP-MA melt-mixtures

MA and BPO (as an initiator) were dissolved in dehydrated acetone, and then mixed thoroughly with PP grains. After the acetone was evaporated completely, the mixture was put into a preheated Rheomix with a chamber volume of 60 cm³ (30C150 Labo Plastomill, Toyo Seiki, Japan). The grafting reaction was carried out in the mixer at 190°C and 75 rpm for 10 min. The initial mass ratio of PP, BPO, and MA was 100 : 1.0 : *m* (where *m* = 0, 0.25, 0.5, 1.0, 2.5, 5.0, or 8.0), and each resultant MAPP is abbreviated as MAPP-*m*. The sample was cut into small pieces and pulverized into grains (< 2 mm), then thermally treated at 125°C for 24 h to evaporate some of ungrafted MA monomers in MAPP and to perform complete cyclization of the dicarboxylic acids into an anhydride form. This crude sample was used for preparing cellulosic composites directly.

A small amount of crude MAPP was further purified by dissolving completely in refluxing xylene and then precipitating in acetone. The sample was vacuum-dried at 60°C for 24 h, and treated *in vacuo* at 125°C for 24 h to ensure complete cyclization into an anhydride form. The purified sample was used for FTIR and chemical titration.

PP-MA melt-mixtures (initial mass ratios of PP : MA = 100 : 0.5, and 100 : 5.0) were also prepared in the same conditions as above but without the initiator. The obtained mixtures are abbreviated as PP-MA0.5 and PP-MA5.0, respectively. The products were pulverized into grains for preparation of cellulosic composites. A small amount of the PP-MA mixtures was purified and thermally treated as described above.

Preparation of the cellulosic composites

Cellulosic composites were prepared by melt-mixing CF11 with MAPP in the same Rheomix as described above. The mass ratios of MAPP to cellulose were 90/10, 70/30, and 40/60. The melt-mixing was carried out at 190°C and 55 rpm for 20 min.

For comparison, corresponding composites were prepared with PP-MA under the same conditions. Composites with PP were also prepared as references.

Sheets of about 1 mm thickness were obtained by compression-molding in a Shinto press (Shinto Metal Ind. Ltd. Osaka, Japan) at 200°C, under a pressure of 4 MPa for 6 min, followed by cooling under a pressure of 9 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 sheet for measurement of tensile properties.

Analytical methods

FTIR

Compression-molded films (10–100 μm thickness) of crude and purified PP–MA mixtures, crude and purified MAPP, PP–MA/cellulose (70/30) composites, and MAPP/cellulose (70/30) composites were thermally treated *in vacuo* at 125°C for 24 h before measuring FTIR. FTIR spectra were recorded on a Perkin–Elmer 2000 spectrometer at a resolution of 4 cm^{-1} for 300 scans in the spectral range of 4000–400 cm^{-1} .

Crude MAPP-0.5 and MAPP-5.0 grains were pulverized with liquid N_2 to measure their FTIR spectra by a KBr technique.

Chemical titration

The MA content grafted on PP was analyzed by chemical titration. Purified MAPP (0.3–0.4 g) was dissolved completely in 120 mL of xylene at 120°C, and after addition of 0.2 mL of deionized water, the mixture was refluxed for 1 h. Adding dropwise 10.0 mL of a 0.1M isopropanolic KOH solution, the mixture was refluxed for another 2 h to ensure complete reaction with the MA groups. With 0.1 mL of a 1.0% phenolphthalein ethanol solution as an indicator, the hot solution was titrated with a 0.1M isopropanolic HCl solution. A blank solution also was treated under the same conditions. The grafting degree G_d (%) was calculated by the equation, $G_d = 100 \times N(V_0 - V) \times M_0 / (2 \times W \times 1000)$, where N is the acid concentration of the isopropanolic HCl solution (mol/L), W is the weight of MAPP (g), V and V_0 are the volumes (mL) of the isopropanolic HCl solution added to the MAPP and blank solutions, respectively, and M_0 is the molecular weight of MA (98.06).

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).²¹ Samples were conditioned at 20°C and 65% relative humidity in an environmental room over 24 h before measuring. The tensile properties were evaluated from the averages of at least four parallel tests.

SEM observation

The morphology of the composites was observed with a Hitachi S-2460N scanning electron microscope (SEM) at 25 kV, using fractured samples following the tensile tests. The fracture surfaces were sputter-coated with gold–palladium before viewing.

RESULTS AND DISCUSSION

Characterization of PP–MA mixtures and MAPPs

The grafting of MA onto PP chains is based on a multiple radical-reaction.^{22–26} In the melt-mixing process, an initiator is usually used to yield macro-radicals of PP. Figure 1 shows IR spectra of crude and purified PP–MA mixtures. The purified PP–MA mixtures exhibit almost the same spectral pattern as parent PP, while the crude ones have new absorptions at 1780 and 1713 cm^{-1} , which are due to monomeric²⁷ and oligomeric MA²⁸ and their hydrolysis products,²⁷ respectively. This indicates clearly that the PP–MA mixtures possess no grafted MA groups but mainly free MA monomers in the matrices, due to the absence of an initiator.

With BPO as an initiator, MA monomers are grafted on PP (Fig. 2). In Figure 2(A), new strong absorption bands at 1770–1800 cm^{-1} are assigned to

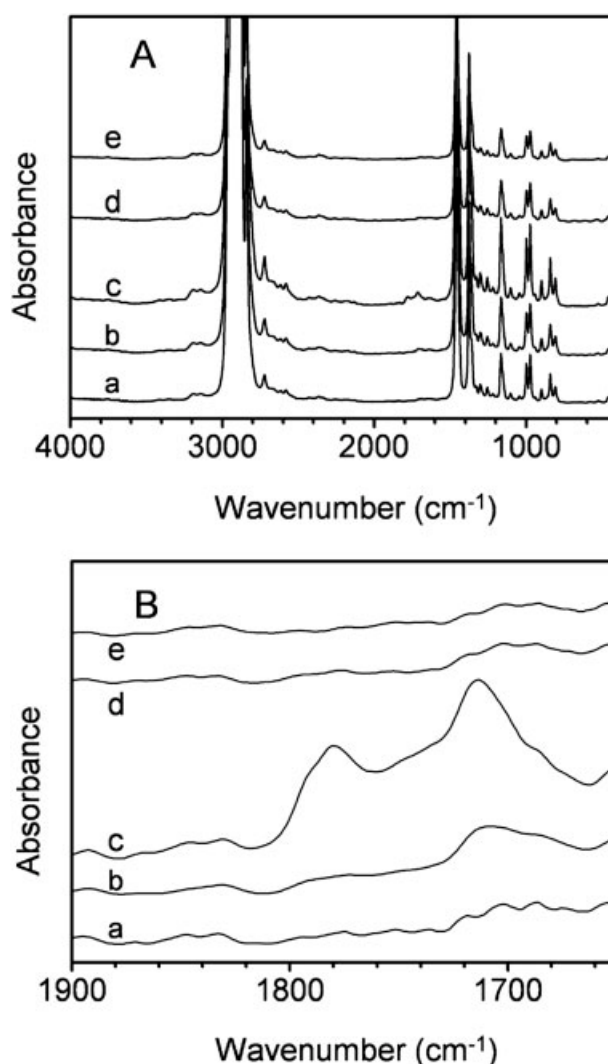


Figure 1 IR spectra of PP–MA0.5 [crude (b) and purified (d)] and PP–MA5.0 [crude (c) and purified (e)]. Curve (a) is for purified PP.

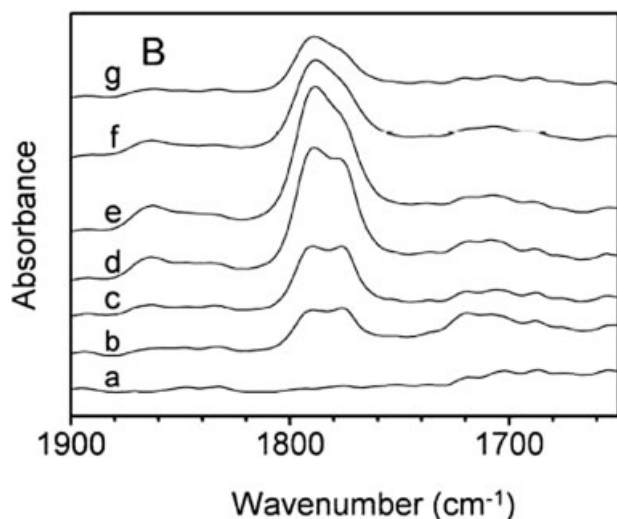
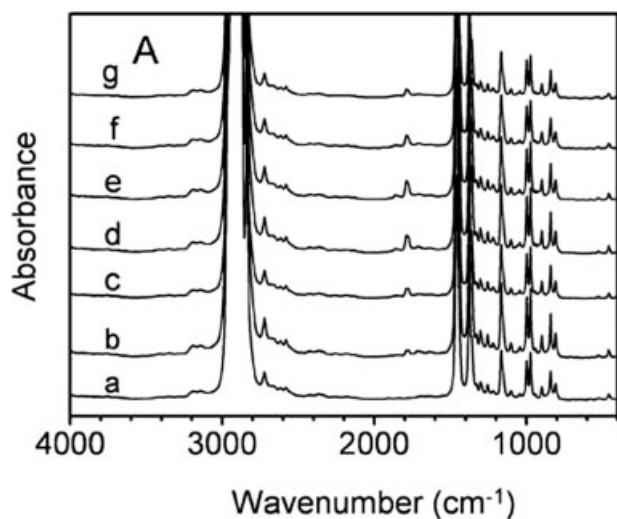


Figure 2 IR spectra of purified MAPP films: PP (a), MAPP-0.25 (b), MAPP-0.5 (c), MAPP-1.0 (d), MAPP-2.5 (e), MAPP-5.0 (f), and MAPP-8.0 (g).

the symmetric C=O stretching vibration of grafted MA, with a weak absorption band at about 1863 cm^{-1} , due to asymmetric C=O stretching.^{22,29} These bands indicate strongly that MA monomers are grafted onto polypropylene, as expected. From Figure 2(B), the symmetric stretching band with a greater wavenumber exhibits a shift from 1792 cm^{-1} to 1787 cm^{-1} with an increase in the amount of MA added, with no shift for the other band at 1774 cm^{-1} . The characteristic shift is due to the extension of the grafted chains.^{18,22,30} Thus the main structure of MAPP obtained consists of an end-grafting type ($1792\text{--}1780\text{ cm}^{-1}$) as well as a bridging type (1774 cm^{-1}), as shown in Figure 3. It is noted that the strength of the bands becomes maximal when the amount of MA added equals 2.5 phr.

Figure 4 shows IR spectra of crude MAPP films. Unlike the results of purified MAPP, the strength of

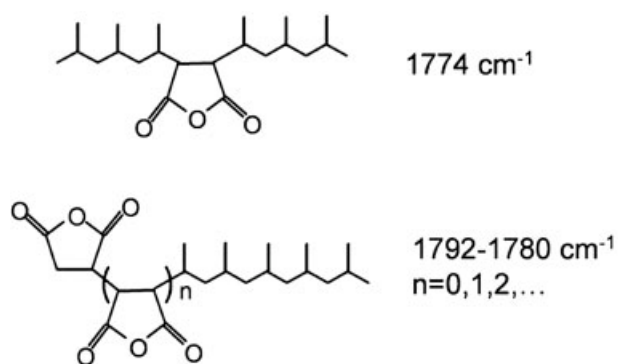


Figure 3 Main structures of MAPP and assignment of their characteristic IR absorption bands.

the bands at $1800\text{--}1770\text{ cm}^{-1}$ increases with an increase in the amount of MA added, and is almost the same as that for purified MAPP for the lower

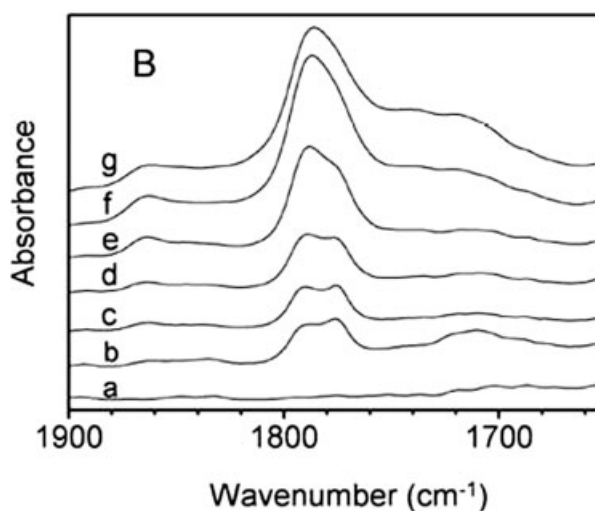
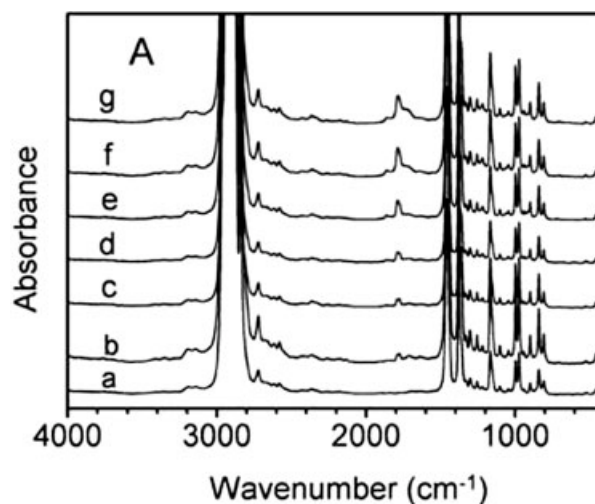


Figure 4 IR spectra of crude MAPP films: PP (a), MAPP-0.25 (b), MAPP-0.5 (c), MAPP-1.0 (d), MAPP-2.5 (e), MAPP-5.0 (f), and MAPP-8.0 (g).

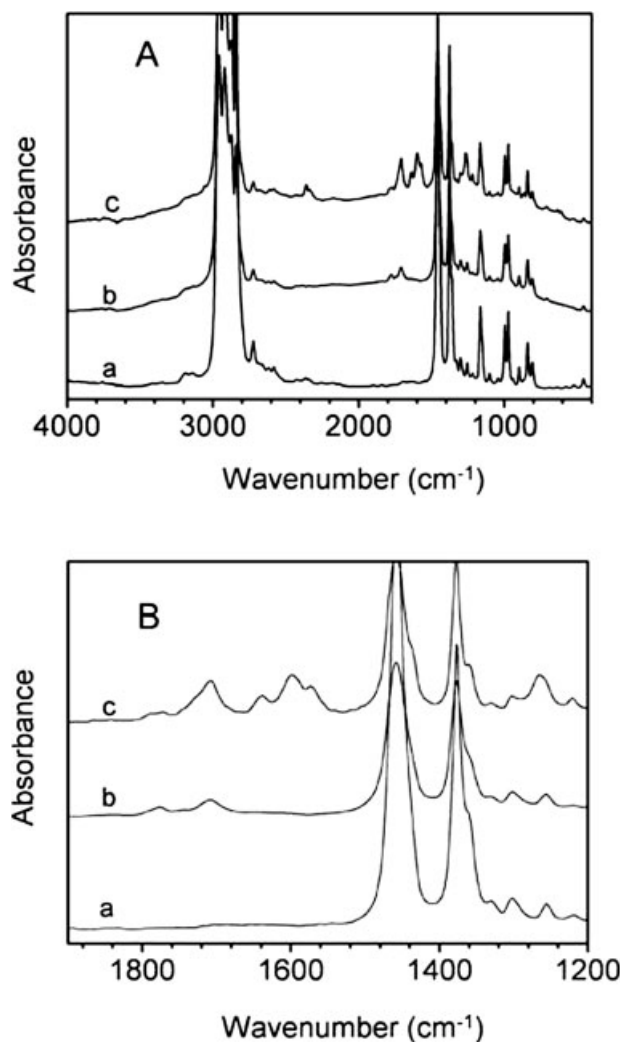


Figure 5 IR spectra of cryogenic powders of crude MAPP: PP (a), MAPP-0.5 (b), and MAPP-5.0 (c).

amount of added MA. This difference suggests that crude MAPP contains a great amount of free monomeric and oligomeric MA, both of which are removed in the process of purification with xylene. The crude MAPPs are a brown color at higher initial MA concentration, indicating the presence of MA oligomers.³¹ To prevent the free MA monomers and/or oligomers from being removed in the process of thermal preparation of the crude MAPP films, we powdered crude MAPP grains with liquid nitrogen and measured their IR spectra with a KBr technique. Figure 5 shows clearly that crude MAPP-5.0 contains a lot of free MA monomers, because peaks at 1708, 1638, 1598, 1573, and 1265 cm^{-1} are assigned to the typical absorptions of maleic acid,²⁷ a hydrolysis product of MA.

The graft degree of MAPP increases to its maximum with an increase in initial MA amount to 2.5 phr, beyond which it decreases, consistent with the monotonous decrease in the yield of grafting, as

clearly shown in Figure 6. The higher initial MA concentration increases the probability that MA monomers react with PP macroradicals to graft, but may also cause phase separation into two distinct phases—MA and PP phases, which are disadvantageous to the grafting beyond a critical concentration of MA. The lower initial MA concentration gives MAPP with higher purity, while the higher initial MA concentration results in MAPP with a greater amount of free MA, such as MAPP-5.0 and MAPP-8.0.

The nature of interfacial adhesion and the morphology of the composites

Besides the inherent properties of a matrix and filler, the interfacial properties of the interphase have a crucial effect on the mechanical properties of the composite. Accordingly, effective wetting of cellulose fibers by the PP matrix, even dispersion of cellulose microfibrils, and strong interfacial adhesion are essential to obtain composites with satisfactory mechanical properties.

It is supposed from FTIR that esterification occurs between grafted MA groups of MAPP and OH groups of cellulose. The formation of ester bonds between cellulosic materials and MAPP has been confirmed by the appearance of a new IR band at 1722 to 1746 cm^{-1} ,¹¹⁻¹⁴ when treating them in a MAPP-containing solution in the presence of a catalyst. We also have demonstrated from FTIR such esterification occurs even in a melt state with *activated* cellulose having a large amount of free OH groups on the surface of the fine particles, which is prepared mechanochemically, but is negligible with the original highly crystalline cellulose.¹⁷ Figure 7 shows FTIR spectra of PP-MA/cellulose (30 wt % cellulose) composites, which are quite similar to those of the PP-MA mixtures in Figure 1; no evident absorption of ester bonds can be found in the composites.

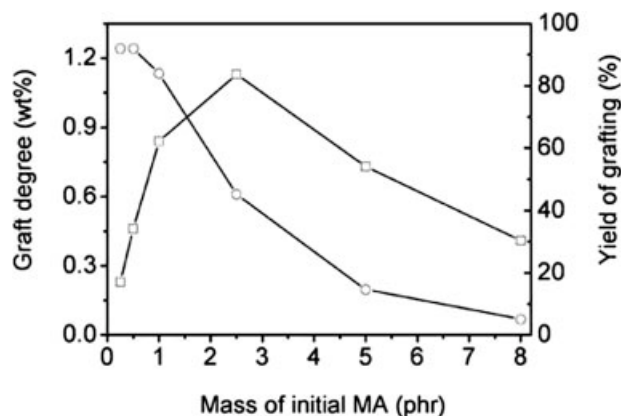


Figure 6 Changes of the graft degree (□) and the yield of grafting (○) of MAPP with an initial MA concentration.

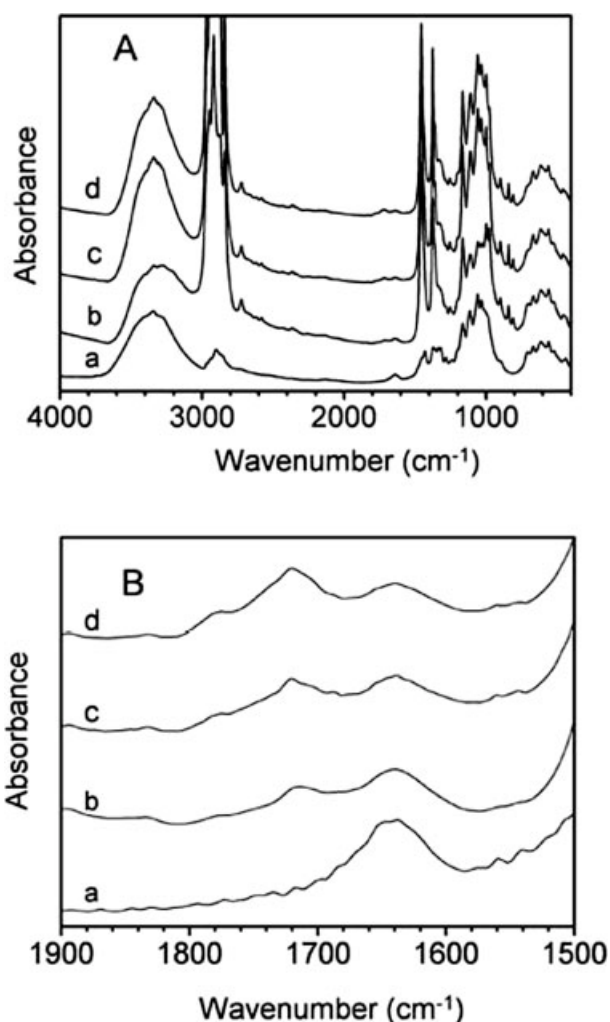


Figure 7 IR spectra of PP-MA/cellulose (70/30) composites: PP-MA0.5 (c), and PP-MA5.0 (d). The curves (a) and (b) are for cellulose and a PP/cellulose (70/30) composites, respectively.

Figure 8 gives IR spectra of MAPP composites with a cellulose content of 30 wt %. Compared with Figures 2 and 4, the strength of absorption at 1791–1770 cm^{-1} decreases, while the strength at 1720 cm^{-1} increases, particularly at a higher initial MA concentration. This suggests strongly that part of the grafted MA groups as well as free monomeric and oligomeric MA are hydrolyzed into their acids. An apparent increase in intensity of absorption at 1735 cm^{-1} is probably due to the esterification of MA monomers with cellulose, because of their higher mobility, as well as ester products of MA oligomers with benzyloxy groups at the ends. The esterification between cellulose and grafted MA is probably too little to be observed by FTIR, because of the highly crystalline cellulose used.^{17,32} Nevertheless, improved interfacial adhesion and mechanical properties of the MAPP composites (discussed below) indicate the possibility of such esterification. Figure 9

shows spectra of purified and completely cyclized MAPP-0.5 as well as its hydrolyzed sample. A marked decrease in intensity of the peak at 1792 cm^{-1} (which results accordingly in the increase in peak strength at 1715 cm^{-1}) shows clearly that the end-grafting MA undergoes hydrolysis more than does the bridge-type one. Accordingly, we presume that the OH groups of cellulose prefer to react with the end-grafting MA moieties. A similar result has been obtained in an interfacial reaction between MAPP and *Chlorella*, on the surface of which amorphous cellulose exists.³⁰

The dispersion of cellulose microfibrils in a PP matrix and the interfacial adhesion of cellulose fibers with the PP matrix were examined from SEM observations of fracture surface of the composite sheets

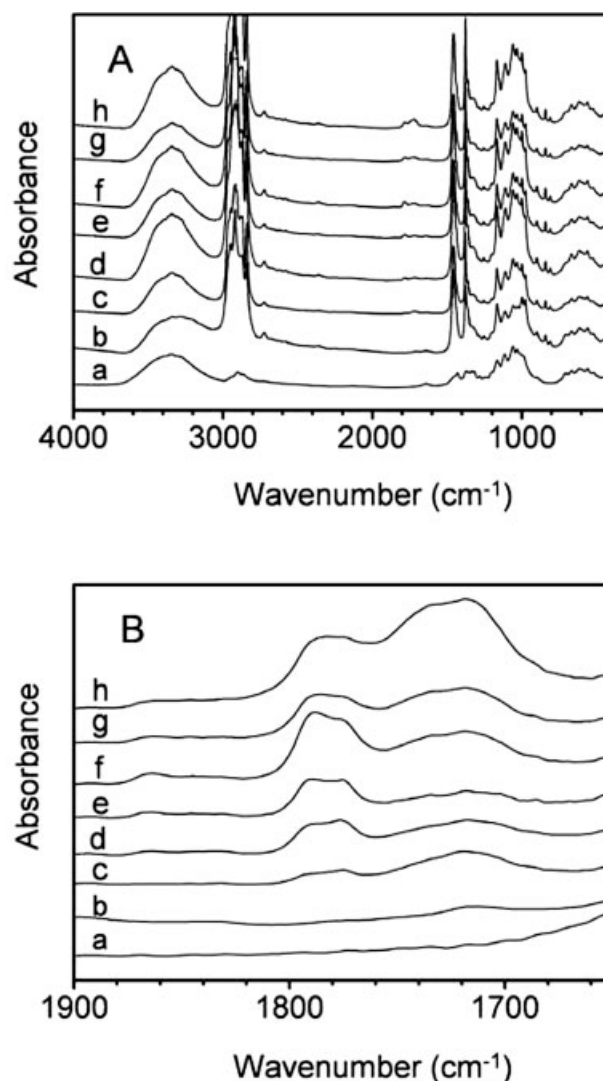


Figure 8 IR spectra of MAPP/cellulose (70/30) composites: MAPP-0.25 (c), MAPP-0.5 (d), MAPP-1.0 (e), MAPP-2.5 (f), MAPP-5.0 (g), and MAPP-8.0 (h). The curves (a) and (b) are for cellulose and a PP/cellulose (70/30) composite, respectively.

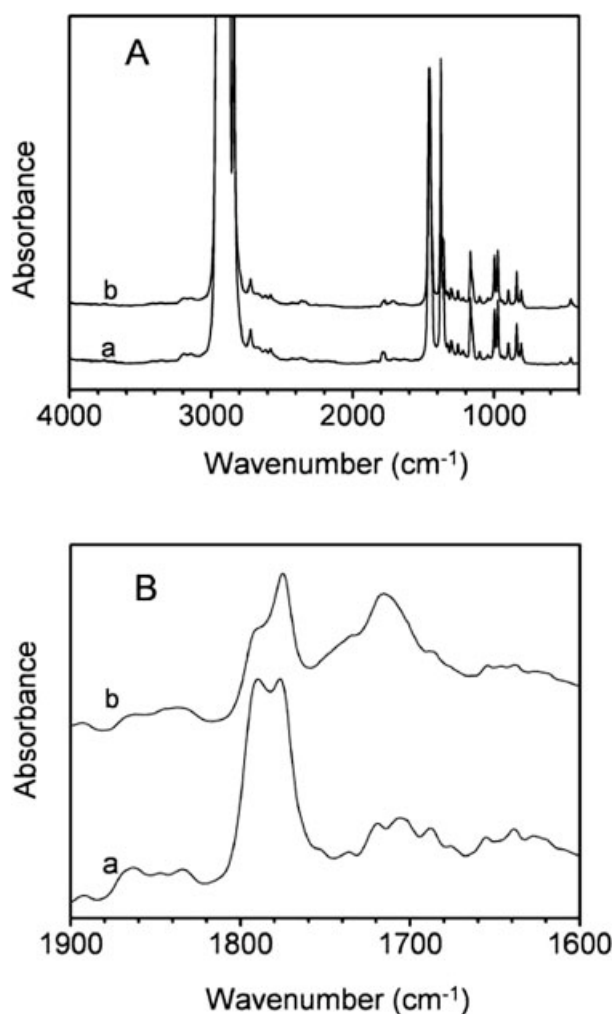


Figure 9 IR spectra of MAPP-0.5 films: purified and thermal treated (a), and further hydrolyzed samples (b).

obtained under strain. SEM micrographs of composites with a cellulose content of 30 wt % are shown in Figure 10. The SEM micrograph of a PP/cellulose composite [Fig. 10(b)] shows that poor wetting of cellulose fibers with the PP matrix, results in poor dispersion and significant coalescence of cellulose particles in the PP matrix. Cellulose fibers parallel to the strain are pulled out, while those in other directions barely maintain their positions in the original form. The extraction of undamaged long bare fibers, known as the classic pullout phenomenon, as well as the clear boundaries and gaps between the PP matrix and the cellulose fibers indicate no adhesion at the interface between PP and cellulose fibers. Thus, the lack of interfacial interactions will yield poor composite tensile strength.

The morphology of PP-MA/cellulose composites is shown in Figure 10(c and d). In spite of poor dispersion of cellulose fibers and poor adhesion of cellulose with PP, a slightly finer morphology and reduced gaps are observed, compared with the PP/

cellulose composite in Figure 10(b). This indicates that the compatibility between cellulose and the PP matrix is slightly improved by the addition of free MA monomers. The improved compatibility may be caused primarily by interactions between the MA monomers and cellulose. Such interactions of free OH groups on the surface of cellulose fibers with the MA monomers would reduce the polarity as well as the hydrophilicity of cellulose to increase the compatibility of the resulted cellulose fibers with the PP matrix.

Figure 10(e-h) give the typical morphology of MAPP/cellulose composites with different initial MA concentrations. Figure 10(e-g) reveal good wetting of cellulose fibers with MAPP and improved dispersion of cellulose fibers in MAPP, as well as strong interfacial adhesion between cellulose fibers and MAPP. This is probably caused by interfacial interactions between the cellulose fibers and the MAPP matrix. The grafted MA moieties of MAPP can react with the free OH groups on the surface of cellulose fibers in the process of melt-mixing, forming a small number of ester bonds and/or hydrogen bonds. Accordingly, cellulose fibers, connected tightly with the MAPP matrix, bring strong interfacial adhesion to the MAPP matrix, made possible by good dispersion of cellulose microfibers in the MAPP matrix. It seems that even a slight graft degree has a significant effect on the microstructure of the MAPP/cellulose composites, such as with MAPP-0.25, MAPP-0.5, and MAPP-1.0, which contain hardly any free MA monomers (Fig. 6).

On the other hand, the composites with MAPP-5.0 and MAPP-8.0 reveal poor dispersion as well as coalescence of cellulose fibers in the matrix, despite the comparatively good adhesion of cellulose fibers with the matrix [Fig. 10(h)]. This may result from a great amount of free MA monomers in the MAPP matrix. We expect that such free MA molecules are more reactive than the grafted MA groups in MAPP, due to their higher mobility and smaller steric hindrance. Thus, the free MA monomers interact with OH groups of cellulose more readily, and will interrupt the proximity of grafted MA groups to the OH groups of cellulose. The free MA-covered cellulose fibers cannot interact satisfactorily with the MAPP matrix, and are difficult to disperse evenly in the matrix. This effect may be enhanced with an increase in the cellulose content.

Typical microstructures of some composites with a cellulose content of 60 wt % are shown in Figure 11. For the PP-MA5.0/cellulose composite, significant coalescence and uneven dispersion of cellulose fibers are observed in Figure 11(a), with no interfacial adhesion in Figure 11(b). The composite with MAPP-1.0 shows an effective wetting of cellulose and good cellulose dispersion in the matrix [Fig. 11(c)], with a

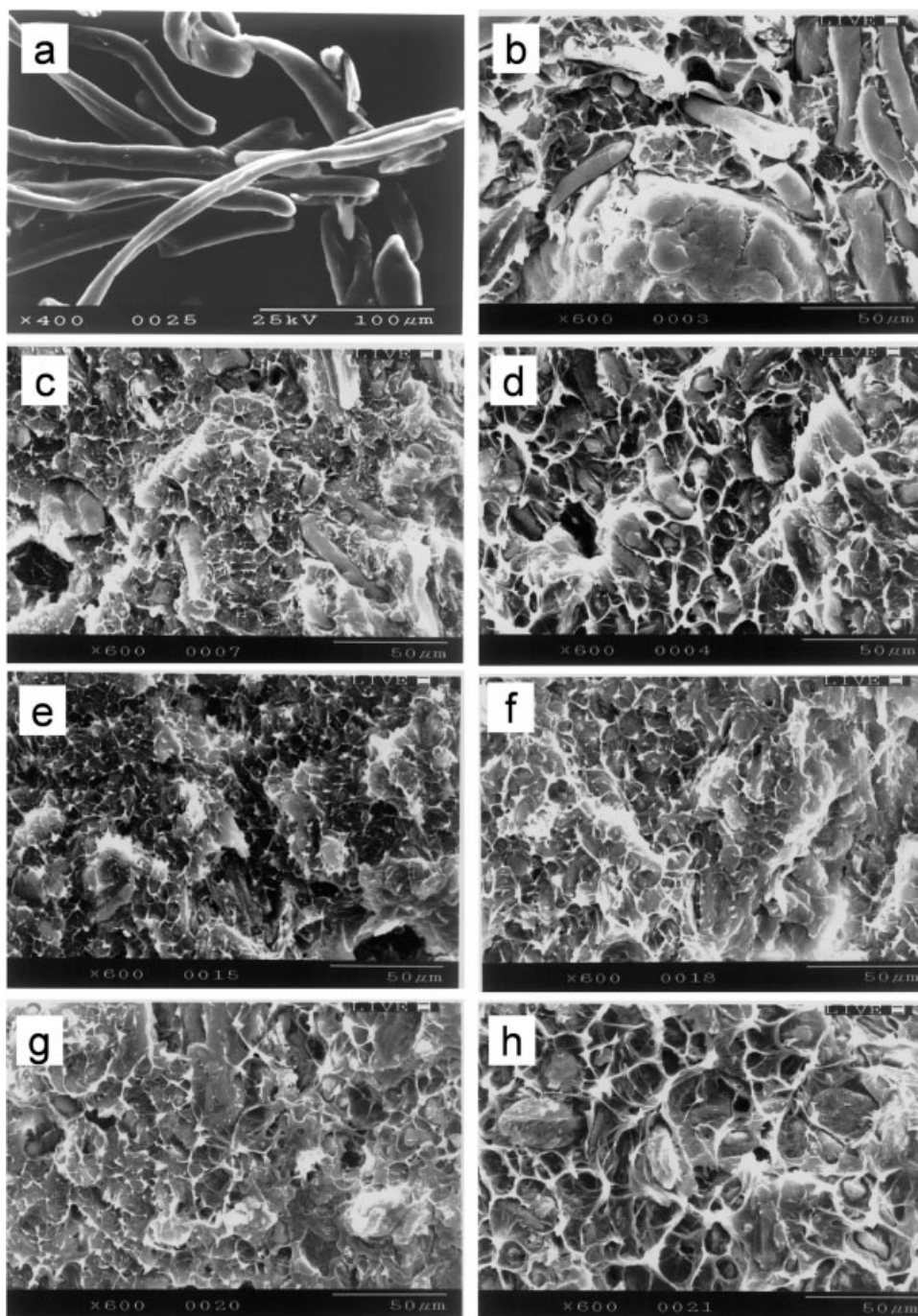


Figure 10 Morphology of cellulose (a) and cellulose composites (30 wt % cellulose): PP (b), PP-MA0.5 (c), PP-MA5.0 (d), MAPP-0.25 (e), MAPP-0.5 (f), MAPP-2.5(g), and MAPP-5.0 (h).

strong interfacial adhesion between them in Figure 11(d). No clear gaps are seen in the interfacial region between the MAPP matrix and cellulose fibers. The improved interfacial adhesion causes cellulose fibers to break and tear under strain as shown in Figure 11(d), indicating that the stress is transferred from the MAPP matrix to the cellulose fibers. However, for the composites with MAPP-5.0 and MAPP-8.0, the wetting and dispersion of cellulose particles is poorer in Figure 11(e and f). As discussed above, the

existence of free MA monomers in the matrix will decrease the possibility of interaction of grafted MA groups with OH groups of cellulose.

Tensile properties of the composites

Mechanical properties are very important composite characteristics, and the tensile properties reflect the compatibility of a reinforcement with its polymer matrix. Figure 12 shows typical stress-strain curves

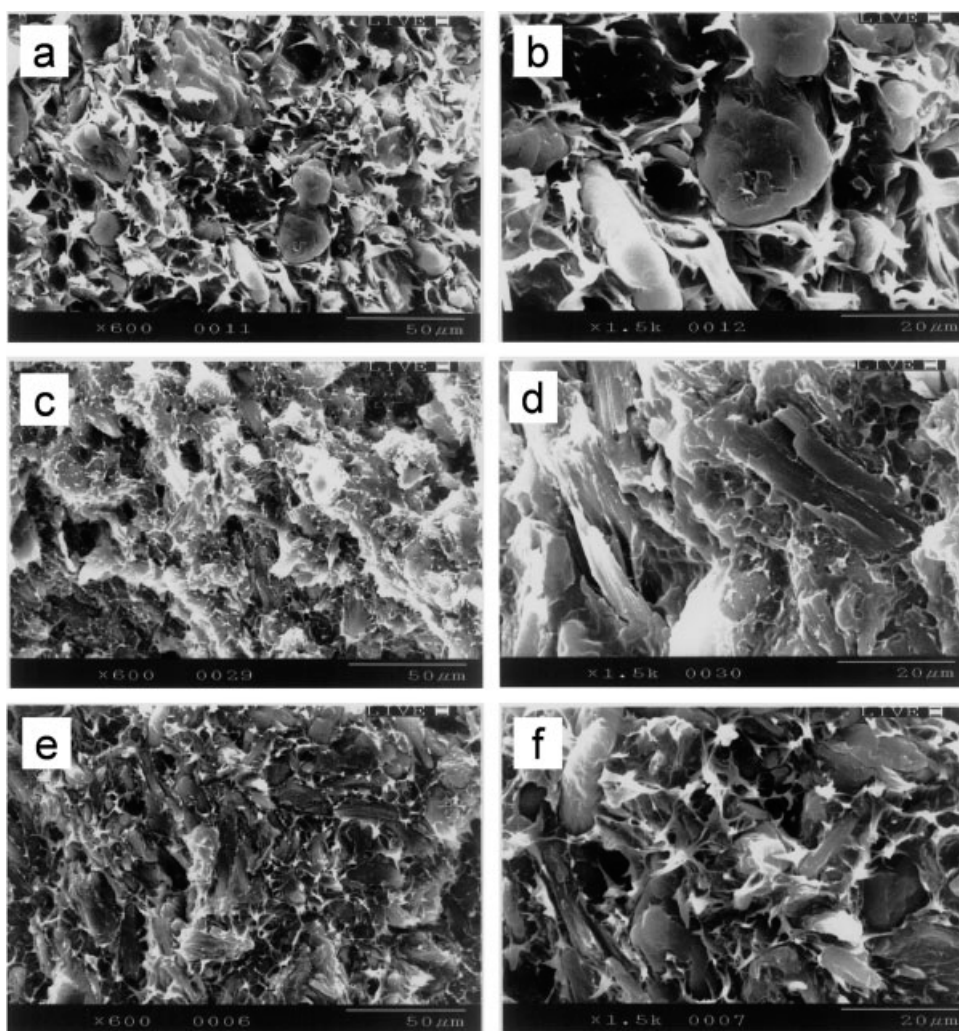


Figure 11 Morphology of cellulose composites (60 wt % cellulose): PP-MA5.0 (a and b), MAPP-1.0 (c and d), and MAPP-5.0 (e and f).

of MAPP/cellulose composites. An increase in cellulose content causes an increase in tensile strength and modulus but, meanwhile, a decrease in elongation and toughness, as may be expected from the properties of cellulose. Effects of the graft degree of MA onto PP as well as of the cellulose content on the tensile strength of the composites are shown in Figure 13. The tensile strength of the PP/Cellulose composite decreases from that of neat PP dramatically with an increase in cellulose content, because of the almost complete lack of interface interaction between PP and cellulose. Although MAPP shows a slight smaller tensile strength than the parent PP, the tensile strengths of the MAPP/Cellulose composites are much greater than that of PP, because of the strong interface interactions between MAPP and cellulose. The tensile strength of the MAPP/cellulose composite increases with an increase in cellulose content, even with a slight content of MA grafted onto PP, as shown in Figure 13. Accordingly, the composites with MAPP-0.25 to MAPP-2.5 exhibit

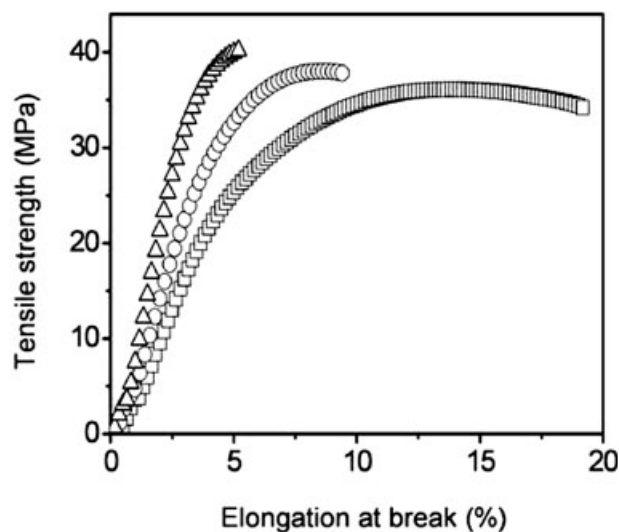


Figure 12 Tensile stress/strain curves of MAPP-1.0/cellulose composites with different cellulose contents (wt %): 10 (□), 30 (○), and 60 (△).

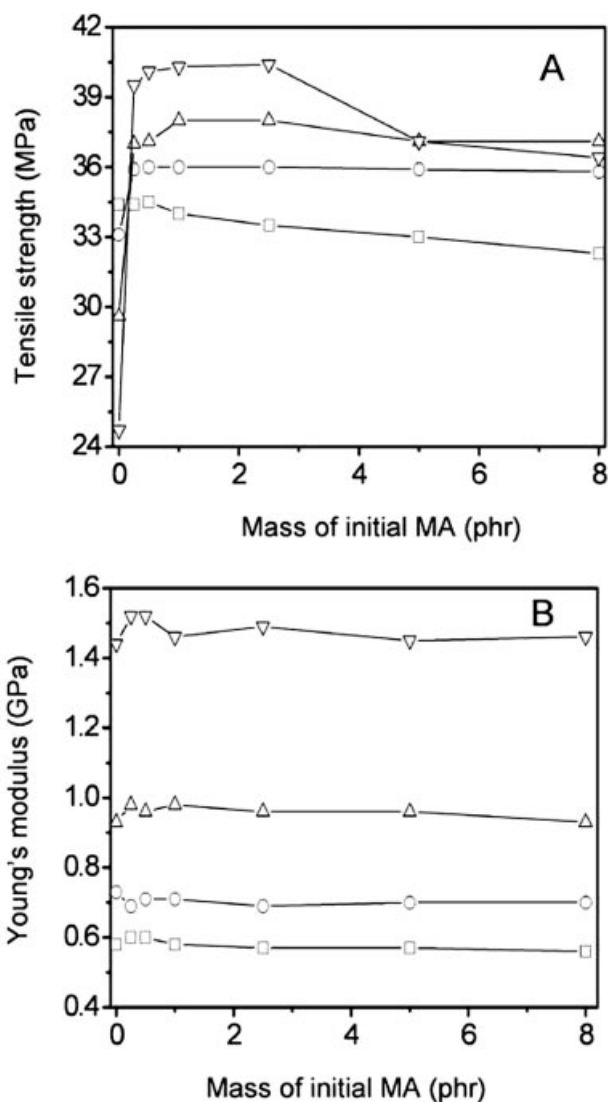


Figure 13 Effects of the initial MA concentration (m) on the tensile strength (A) and Young's modulus (B) of the MAPP-*m*/cellulose composite with cellulose contents: 0 (□), 10 (○), 30 (△), and 60 (wt %) (▽).

almost the same tensile strength in the cellulose content of 10–60 wt %. This indicates that there exists a critical graft degree of MA onto PP that yields composites with satisfactory tensile strength. In this study, the critical graft degree is as small as 0.25–0.5 wt %, because of the highly crystalline cellulose; this value may generally depend on the number of free OH groups of cellulose which is controlled by the crystallinity. In Figure 13, we also find that, with an increase in the initial MA concentration, there is a slight decrease in tensile strength for the 30 wt % cellulose composite with an initial MA concentration of 5.0–8.0 phr, and a marked drop for the 60% cellulose composite with the same MA concentrations. The graft degrees of MAPP-5.0 and MAPP-8.0 are greater than that of MAPP-0.25, as shown in Figure 6. The drop in tensile strength is probably due to the

existence of a large amount of free MA monomers in MAPP-5.0 and MAPP-8.0, as is supported by the microstructures of the composites given by SEM.

From Figure 14, free MA monomers in PP-MA certainly increase the tensile strength of the PP/cellulose composites, particularly at higher cellulose content. However, the effect imparted by free MA is much smaller than that by the grafted MA groups in MAPP. The free MA monomers, which interact strongly with cellulose fibers, further interact with the PP matrix due to molecular forces. Such molecular forces are much weaker than the interaction of the OH groups of cellulose with the grafted MA groups of MAPP, as seen when comparing the tensile strength between the composites with PP-MA and MAPP in Figure 14. The free MA molecules, with much smaller steric hindrance, can interact

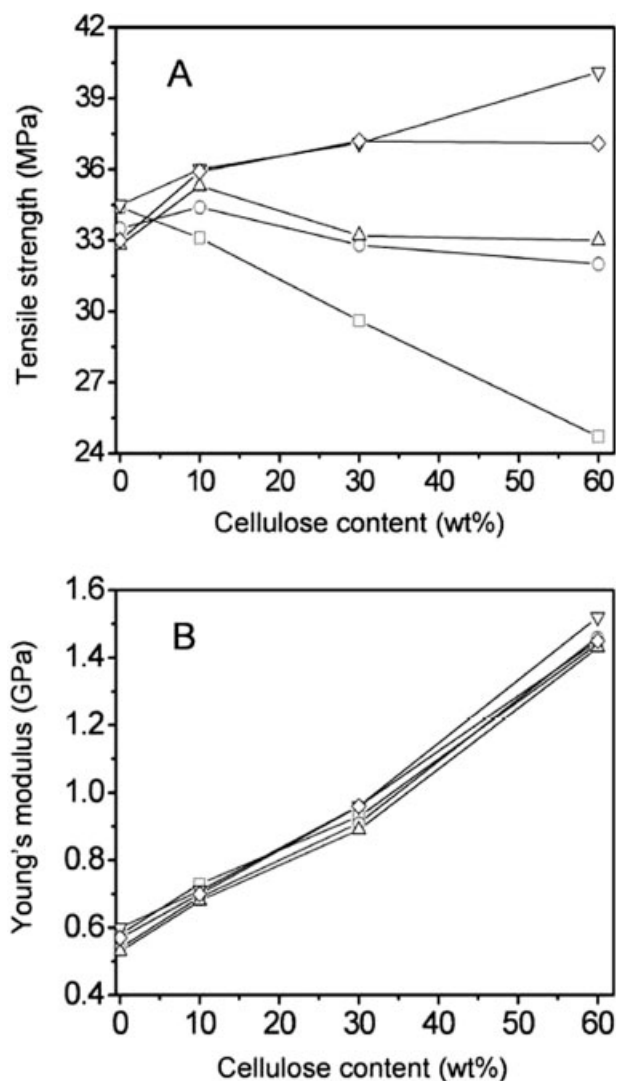


Figure 14 Effects of the free MA in MAPP and PP-MA on the tensile strength (A) and Young's modulus (B) of the composites: MAPP-0.5 (▽), MAPP-5.0 (◇), PP-MA0.5 (○), and PP-MA5.0 (△). The curves (□) are for PP composites.

more readily with cellulose fibers than the grafted MA groups and cause uneven dispersion of cellulose particles, particularly in a MAPP composite with a greater initial MA concentration of 5.0–8.0 phr.

The Young's modulus of the composite with MAPP is primarily dependent on the cellulose content [Figs. 13(B) and 14(B)], with almost no change imparted by the initial MA concentration and therefore by the free MA content, strongly reflecting the dominant contribution from cellulose.

From the above discussions, it is inferred the ultimate tensile strength of the MAPP/cellulose composite is highly dependent on the interfacial quality and the modulus is mainly a function of the moduli of the components.

A proposed model of interaction between cellulose and MAPP

We can draw an interaction model between cellulose fibers and a MAPP matrix in the composite, considering the tensile properties and the microstructures. In this study, the highly crystalline cellulose (crystallinity 93%)^{19,20} used has a very limited amount of free OH groups on the fibers because of intra- and intermolecular hydrogen bonding. It is noted that only such free OH groups can interact effectively with grafted MA groups of MAPP. Accordingly, only a very small amount of the MA groups may saturate the interface, with no interactions with most of the MA groups. Furthermore the large steric hindrance of the MA grafts will limit the proximity of the MA groups to the cellulose surface, because when a MA group interacts with a free OH group on a cellulose fiber, other MA groups cannot necessarily reach the neighboring free OH groups. Therefore, the total potential reactive sites of grafted MA groups are further reduced, and beyond a critical amount of reactive MA groups, the reactive OH groups on the cellulose surface will be saturated. The total interaction sites are too small to be observed by FTIR spectroscopy; however, even such little interaction is effective at causing good adhesion between cellulose fibers and the MAPP matrix. In accordance with the above, the interaction of cellulose with MAPP-0.25 to MAPP-2.5 is shown in Figure 15(a).

For MAPP with a higher initial MA concentration, however, we have to consider the existence of free MA in the matrix. Such free MA groups can react with the OH groups on cellulose much more readily, due to their higher mobility and smaller steric hindrance. The competitive reaction with cellulose will lessen significantly the possibility of interaction of the grafted MA groups with cellulose, which is essential for high adhesion of cellulose with the matrix, as described above. The interaction mode is

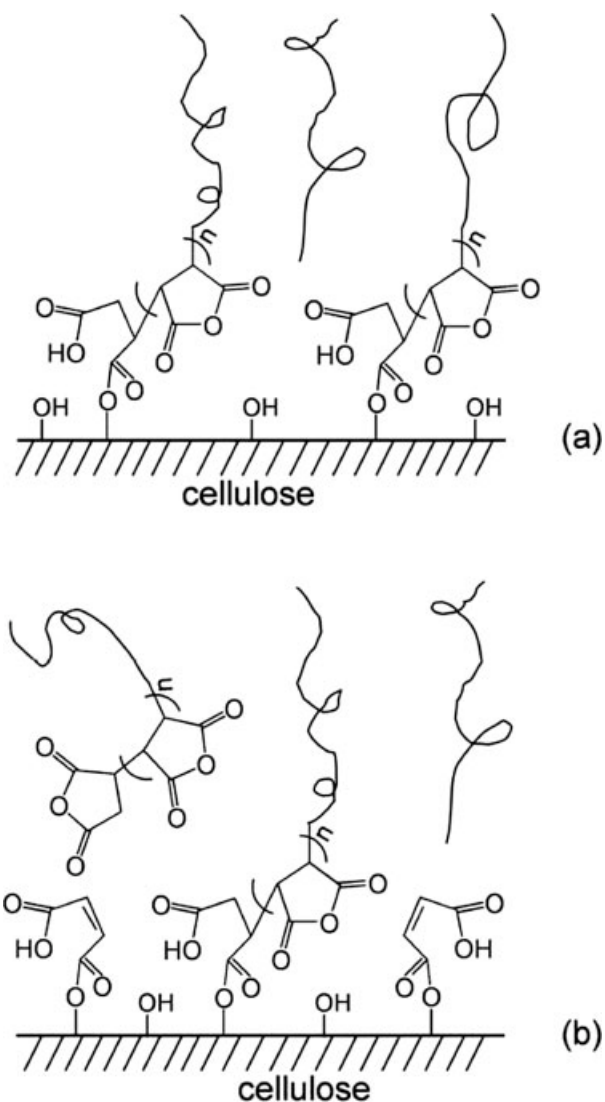


Figure 15 A model of interactions between cellulose and MAPP without (a) and with free MA monomers (b).

shown in Figure 15(b), for a composite with MAPP-5.0 or -8.0.

CONCLUSIONS

We have demonstrated that the tensile properties and morphology of a composite of MAPP and highly crystalline cellulose are affected strongly, not only by the graft degree of MA, but also by the existence of free MA monomers remaining in the MAPP matrix. If the MAPP matrix does not contain any free MA monomers, even a graft degree as small as 0.25–0.5 wt % yields a maximal tensile strength, probably because of interactions with the very small number of free OH groups on the surface of the highly crystalline cellulose. However, free MA monomers in the MAPP matrix decrease the tensile strength, probably due to their competitive interactions with the OH groups of cellulose, which will interrupt the interac-

tions of the graft groups. The tensile property of the composite depends on the adhesion of cellulose with MAPP as well as the even dispersion of cellulose micro-fibers in the matrix, both of which are determined by the interactions of the OH groups on cellulose with grafted MA groups.

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