Milling-Induced Esterification between Cellulose and Maleated Polypropylene

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ABSTRACT: The ball milling of cellulose and maleic anhydride grafted polypropylene (MAPP) induced the formation of ester bonds between OH groups of cellulose and maleic anhydride groups of MAPP, in marked contrast to the melt mixing of the original cellulose and MAPP, through which the esterification was hardly observed. This esterification was hardly dependent on the chemical structure of MAPP. In agreement with the enhanced interfacial adhesion due to the formation of ester bonds, a composite prepared via ball milling revealed an improvement in the tensile strength with respect to a melt-mixed composite. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1703–1709, 2004

Key words: poly(propylene) (PP); polysaccharides; esterification; FT-IR; compatibility

INTRODUCTION

Cellulose, one of the most abundant renewable natural resources, has great potential for the preparation of novel composite materials with thermoplastic polymers, exhibiting a number of well-known advantages, such as low cost, biodegradability, high stiffness, and good mechanical properties. However, the hydrophilic and aggregating nature of cellulose causes poor processability and inherent incompatibility with most hydrophobic polymers, such as polypropylene (PP). Physical and chemical methods have been developed to enhance the interfacial interactions between cellulose and a PP matrix.[1–5] Among these methods, coupling by maleic anhydride grafted polypropylene (MAPP) has received much attention because it effectively improves the mechanical properties of cellulosic materials. The improvement caused by the use of MAPP is thought to be due to esterification between anhydride groups of MAPP and hydroxy groups of cellulose.[6,7]

The esterification between MAPP and cellulosic materials has been extensively investigated in solutions in the presence of a catalyst and has been confirmed by the appearance of a new IR band, usually at 1729–1750 cm^{-1}.[2,6–9] However, no direct evidence of esterification has been reported from the melt mixing of MAPP with cellulose under a solid phase, although cellulosic-material-reinforced PP composites are generally prepared through melt mixing. This is probably due not only to the much lower mobility of MAPP in the melting state but also to the limited reactivity of the OH groups of highly crystalline cellulose. In this article, we report the ball milling of cellulose with MAPP in a solid phase, using Fourier transform infrared (FTIR) spectroscopy. The esterification causes a good dispersion of the cellulose particles, and the resultant composite accordingly exhibits tensile properties different from those of the composite obtained through melt mixing.

EXPERIMENTAL

Materials

The fibrous cellulose (CF11; prepared from high-purity cotton, with a 99% cellulose content and a length of 50–350 μm, as reported by the supplier) was a commercial product of Whatman International, Ltd. (Maidstone, England). MAPP1 pellets with a melt-flow index (MFI) of 1.3 g/10 min (as reported by the supplier) was purchased from Mitsubishi Chemical Corp. (Tokyo, Japan). MAPP2 (weight-average molecular weight ~ 9100; emulsifiable wax) was obtained commercially from Aldrich Chemical Co., Inc. (Milwaukee, WI). PP powder (MFI = 1.0 g/10 min, as reported by the supplier) was purchased also from Mitsubishi Chemical. Dehydrated acetone and dehydrated xylene were purchased from Wako Chemicals (Osaka, Japan).

Pretreatment of the materials

The PP powder was dried *in vacuo* at 60°C for 12 h in advance. Cellulose was dried *in vacuo* at 60°C for 3 days before the preparation of the composites or before milling. MAPP1 and MAPP2 were purified by complete resolution in refluxing xylene, precipitation

with acetone, and filtration. After the purification was performed two times, two MAPP samples were dried *in vacuo* at 120°C for 24 h for the complete cyclization of the dicarboxylic acids into a carboxylic anhydride form before the characterization and preparation of the composites. MAPP1 was white before and after purification, whereas MAPP2 changed from a deep brown to white; this indicated the impurity of the original MAPP2. The purified MAPPs were used to prepare composites for an analysis of the esterification.

The original MAPP1 was pulverized and then dried under the aforementioned conditions for the preparation of the composites for the testing of the mechanical properties (composites with MAPP2 were not suitable for measuring the mechanical properties because MAPP2 was an emulsifiable wax with a very low molecular weight).

Preparation of the composites

The preparation of the composites by ball milling was performed in a Planetary ball mill (Pulverisette 5, Fritsch, Frankfurt, Germany) equipped with four jars, each of which was 500 cm³ in volume and was loaded with 25 balls (diameter = 1.5 cm). A sample (40 g) in each jar was milled at a rotational speed of 200 rpm for 10 h, with a cyclic mode of 20 min of milling followed by a 10-min pause. The weight ratio of purified MAPP to cellulose was 70/30. For comparison, a composite of cellulose with PP was also prepared under the same conditions.

A mixture of 40 g of purified MAPP (70 wt %) and cellulose (30 wt %) was added into a preheated Rheomix with a chamber volume of 60 cm³ (30C150 Labo Plastomill, Toyo Seiki, Tokyo, Japan) and melt-mixed at 190°C at a mixing rate of 55 rpm for 15 min. Two kinds of cellulose were used: vacuum-dried and originally crystalline CF11 and newly milled and amorphous CF11 (milled under the aforementioned conditions). Similar composites with PP were also prepared with the same method.

To study the effect of the ball-milling-induced esterification on the mechanical properties, we prepared composites of unpurified MAPP1 with CF11 contents of 30 or 50 wt % with two methods: (1) melt mixing and (2) ball milling followed by melt mixing, as described previously. The composites were thermally pressed at 200°C and 3 MPa for 6 min to yield plates 1 mm thick for the measurement of the tensile properties, as described elsewhere.[10]

Removal of nonbound matrices from the composites

The composite was extracted in refluxing xylene for 48 h. The cellulosic residue was washed with acetone and then dried *in vacuo* at 120°C for 12 h.
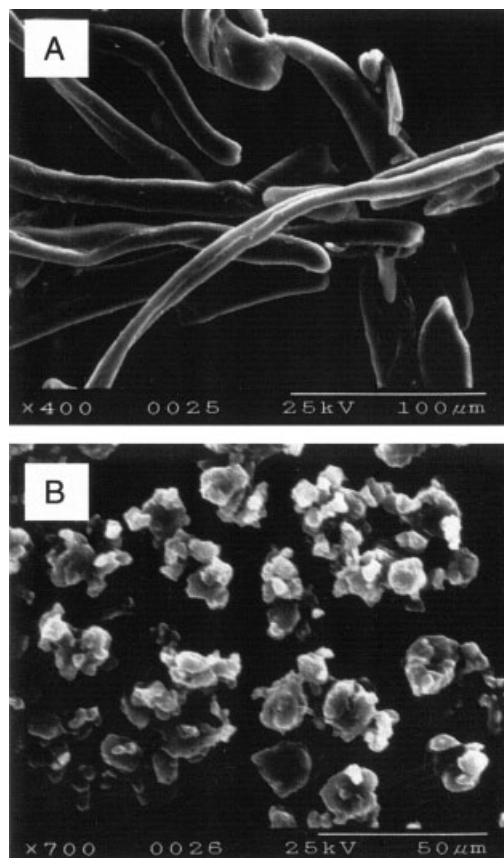
**Figure 1** Scanning electron micrographs of (A) original and (B) milled CF11.

Characterization

The grafting degree of the purified MAPP samples was measured by chemical titration.[11] Wide-angle X-ray diffraction (WAXD) measurements were carried out with a Rigaku RINT-2100 X-ray diffractometer (Tokyo, Japan) with Cu Kα radiation (40 kV, 24 mA). The morphology of the fractures of the composites was observed with a Hitachi S-2460N scanning electron microscope (Tokyo, Japan) at 25 kV after sputter coating with gold and palladium. FTIR spectra were recorded by a KBr technique on a PerkinElmer 2000 spectrometer (Tokyo, Japan) at a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1} with 300 scans.

RESULTS AND DISCUSSION

Characterization of cellulose

We chose CF11, a cellulose sample with a very high purity and a very high crystallinity of 93%,[12] because we thought it would be very useful for considering the activation of OH groups as a result of milling. Through ball milling, the CF11 fibers changed into microparticles (Fig. 1), the increased surface area of which was favorable for interfacial chemical reactions between the cellu-
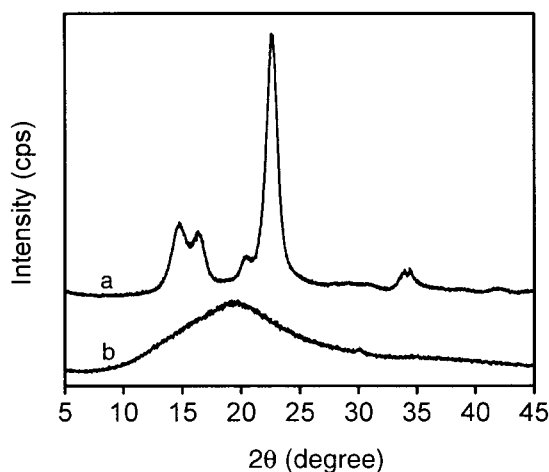
Figure 2 WAXD profiles of (a) original and (b) milled CF11.

lose and MAPP. As shown in Figure 2(a), CF11 is I-type cellulose with reflections at 2θ: (101) at 14.7°, (101) at 16.3°, (021) at 20.4°, and (002) at 22.7°.[13] The milling caused a marked decrease in the crystallinity, making the cellulose highly amorphous [Fig. 2(b)].

Figure 3 shows FTIR spectra of CF11 before and after ball milling. The ball milling caused broadening of the bands, except for a band at 898 cm^{-1}. The sharp band at 1431 cm^{-1} became broad and weak with ball milling, whereas the shoulder at 898 cm^{-1} became sharp and strong. The band at 1431 cm^{-1} was assigned to CH$_2$ symmetrical bending; the band at 898 cm^{-1} resulted from the motions of atoms attached to C$_1$, which reflected changes in the molecular conformation due to rotation about the glucosidic C$_1$—O—C$_4'$ linkage.[14] Accordingly, these bands depended strongly on the crystallinity of cellulose.[14] Furthermore, the OH stretching band shifted from 3340 to 3400 cm^{-1} because of ball milling. This indicated that a network of hydrogen bonds in the original CF11 collapsed mechanochemically to yield free OH groups in the amorphous cellulose.

In the original cellulose, almost all the OH groups were bound to one another through intramolecular and intermolecular hydrogen bonds; accordingly, only a small number of the OH groups on the surface could react with other substances. The milling of CF11 caused the collapse of the inherent hydrogen bonds, yielding a great number of free OH groups on the resultant microparticles, which may have enhanced interfacial chemical reactions.

Characterization of MAPP

We selected two samples, MAPP1 and MAPP2, to examine the reactivity of MAPP toward cellulose. The molecular weight of MAPP1 (MFI = 1.3 g/10 min)

was probably much greater than that of the MAPP2 wax (weight-average molecular weight ~ 9100). A titration analysis of the purified samples showed that MAPP1 had a very small grafted maleic anhydride content of 0.22 wt %, in comparison with 3.86 wt % for MAPP2.

The FTIR spectra of both the original and purified MAPP1 exhibited a very weak characteristic band due to grafted succinic anhydride (SA) rings [ν_s (C=O stretching)] at 1787 cm^{-1} [Fig. 4(A)]. The magnified spectra showed that a negligible peak at 1745 cm^{-1} [line a in Fig. 4(A)], which may have been due to a processing additive of PP, disappeared after purification [line b in Fig. 4(A)]. However, the spectrum of purified MAPP2 exhibited a strong band at 1784 cm^{-1} due to ν_s (C=O), accompanied by a weak band due to grafted SA rings [ν_{as} (C=O)] at 1862 cm^{-1} [Fig. 4(B)]. Accordingly, we expected MAPP1 and MAPP2 to have oligomeric grafts. The average length of the grafts in MAPP2 was probably greater than that in MAPP1 because of the lower shift of ν_s (C=O) for MAPP2 than for MAPP1.[15]
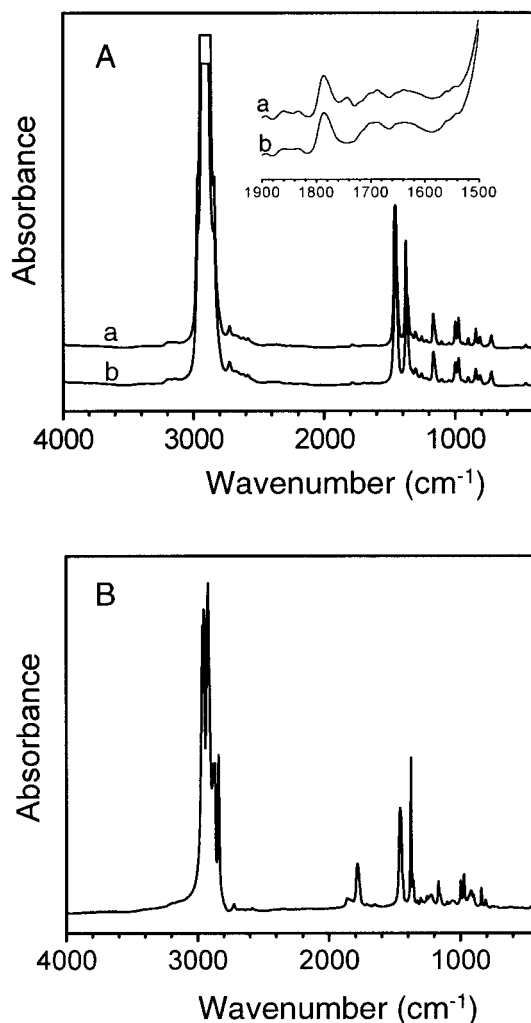
Characterization of the interfacial esterification

The residual celluloses derived from melt-mixed composites of the original CF11 with PP and MAPP exhibited almost the same IR spectra as the original CF11, as shown in Figure 5. This means that the melt mixing of original CF11 with MAPP did not cause any observable formation of ester bonds between the original CF11 and MAPP, regardless of the grafting degree and the molecular weight of MAPP.

Interestingly, IR spectra of the residual cellulose from the ball-milled composites depended on the matrix, as shown in Figure 6. Thus, the residual celluloses from the composites with MAPP1 and MAPP2 had a new absorption band around 1730 cm^{-1}, which was
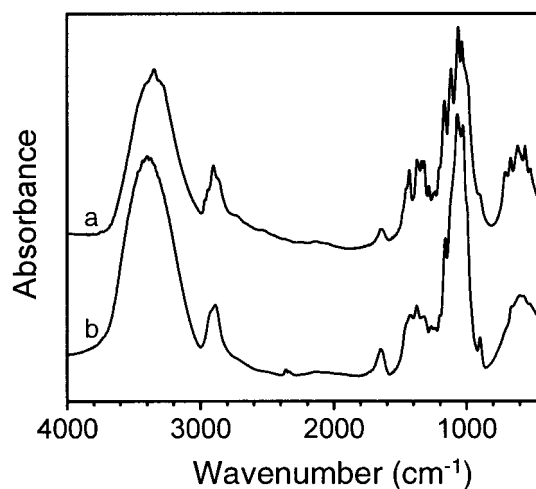
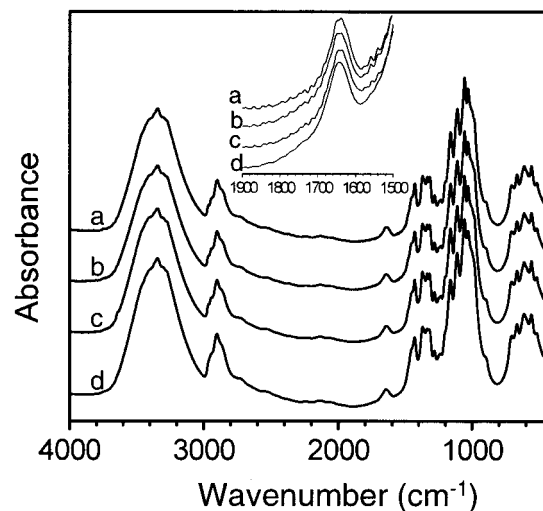**Figure 3** FTIR spectra of (a) original and (b) milled CF11.

Figure 4 FTIR spectra of (A-a) original and (A-b) purified MAPP1 and (B) purified MAPP2.

Figure 5 FTIR spectra of (a) original CF11 and (b–d) residual cellulose specimens derived from composites via the melt mixing of original CF11 with PP, MAPP1, and MAPP2, respectively.

obtained by ball milling were 0.061 with MAPP1 and 0.058 with MAPP2, whereas those for the melt-mixed composites of the milled CF11 were 0.070 with MAPP1 and 0.074 with MAPP2, comparable to the results from ball milling. Thus, the esterification degree was strongly determined by the milling of crystalline cellulose. The small effect of the graft content on the extent of esterification was probably due to the reduction in the reactivity toward cellulose of graft groups in MAPP2 on account of steric hindrance. As described earlier, MAPP2 had a greater graft content

undoubtedly assigned to ν(C=O) of ester bonds [Fig. 6(c,d)], in marked contrast to no absorption at 1730 cm^{-1} for the composite with PP [Fig. 6(b)]. This clearly indicated that esterification between cellulose and MAPP occurred mechanochemically during the ball milling. The absorption band at 1784 cm^{-1} in Figure 6(d) suggests the existence of unreacted SA groups in the MAPP2 matrix.
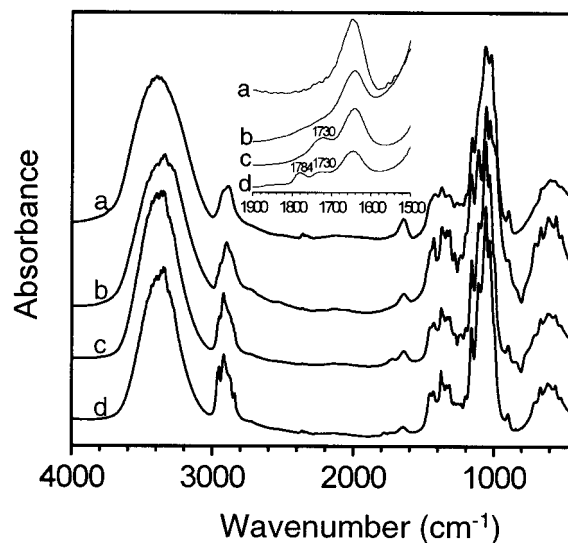
When only highly crystalline CF11 was milled in advance, the newly milled CF11 could form ester bonds with MAPP even via melt mixing, as clearly shown in Figure 7. This suggests strongly that the mechanochemical activation of crystalline CF11 was a primary factor for the formation of ester bonds through the ball milling of CF11 and MAPP.

To estimate the extent of esterification between cellulose and MAPP in the composites, we calculated the intensity ratio (I_1/I_2) of the band of ester bonds (I_1) to the band due to the C—O stretching of cellulose at 1060 cm^{-1} (I_2).[9] The I_1/I_2 values for the composites

Figure 6 FTIR spectra of (a) milled CF11 and (b–d) residual cellulose specimens derived from composites obtained via the ball milling of original CF11 with PP, MAPP1, and MAPP2, respectively.
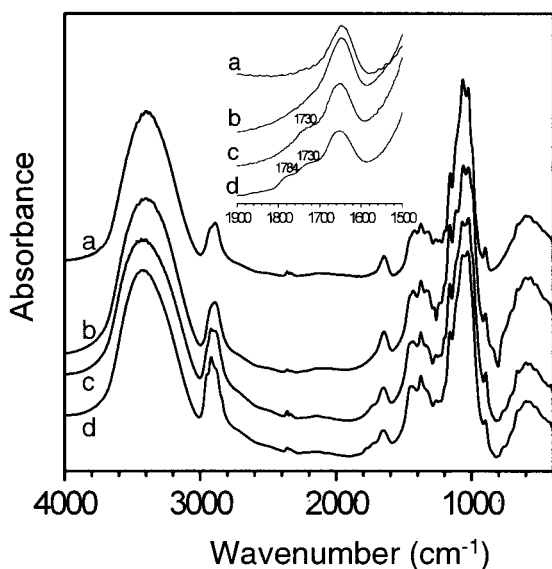
Figure 7 FTIR spectra of (a) milled CF11 and (b–d) residual cellulose specimens derived from composites obtained by the melt mixing of newly milled CF11 with PP, MAPP1, and MAPP2, respectively.

than MAPP1. The esterification of cellulose with some preferred grafts in MAPP2 caused the other grafts to remain unreacted because of the restricted proximity to OH groups of the cellulose. The bands at 1784 cm^{-1} in Figures 6(d) and 7(d) indicate the existence of unreacted SA rings in the composites with MAPP2. Accordingly, the effect of the chemical structure of MAPP on the esterification was secondary, although more detailed examinations are necessary.

These results reveal that the formation of ester bonds between crystalline cellulose and MAPP in a solid state is primarily due to the mechanochemical activation of cellulose through milling, being only slightly dependent on the chemical structure of MAPP. The milling of CF11 brings microparticles of amorphous cellulose, on the surface of which a great number of free OH groups are generated by the collapse of a network of hydrogen bonds. The free OH groups can form ester bonds with MAPP, even in a solid state.

**Tensile properties of the composites**

Composites of MAPP1 with CF11 contents of 30 or 50 wt % were prepared by the normal melt-mixing method as well as ball milling followed by melt mixing, as described previously. Their tensile strength–strain behaviors are shown in Figure 8. The tensile strength and Young's modulus increased with an increase in the cellulose content for each preparation method. The tensile strength increased more through ball milling than through normal melt mixing, with little change in Young's modulus.

Fracture surfaces of the composites are shown in Figure 9. The surface of the composite prepared with the ball-milling method [Fig. 9(C)] was smoother than that obtained through the normal melt-mixing method [Fig. 9(A)]. For the composite obtained by the melt-mixing method, the cellulose fibers were partly connected with the matrix, still leaving large naked surfaces with no interaction with the matrix [Fig. 9(B)]. This was probably due to the difficulty in the formation of ester bonds between MAPP and crystalline cellulose. By contrast, for the composite obtained by ball milling, the cellulose particles were covered and tightly connected to the MAPP matrix [Fig. 9(D)]. This may have resulted from the formation of a large number of ester bonds between MAPP and the free OH groups on activated cellulose particles. The morphologies of the composites were consistent with the interfacial adhesion caused by the formation of ester bonds.

The ball milling of cellulose fibers certainly causes a decrease in the fiber aspect ratio (Fig. 1), and this may be unfavorable for the mechanical properties of the resultant composite with MAPP. However, in the process of ball-milling cellulose fibers and MAPP, the resultant cellulose particles are so activated that they can form ester bonds with MAPP to yield strong adhesion between the two phases. Such strong adhesion may improve the mechanical properties of the composite to compensate for the reduction caused by the decrease in the fiber aspect ratio. This explains the stronger tensile strength of the ball-milled composite in comparison with the melt-mixed one in Figure 8.

Mechanism of milling-induced esterification

A mechanism of milling-induced esterification between highly crystalline cellulose and MAPP is illus-
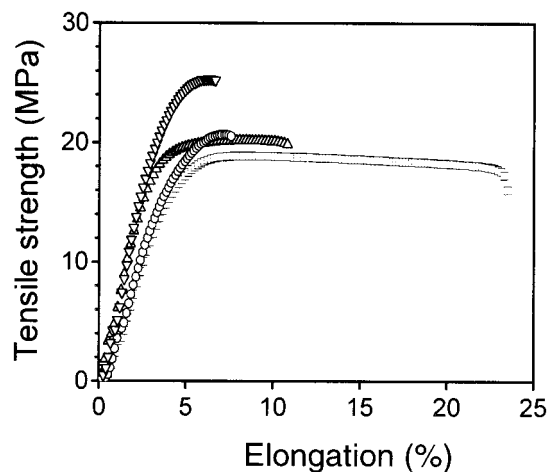
Figure 8 Strength–strain curves of the MAPP1 composites: melt-mixed with CF11 = (□) 30 or (△) 50 wt % or ball-milled and then melt-mixed with CF11 = (○) 30 or (▽) 50 wt %.
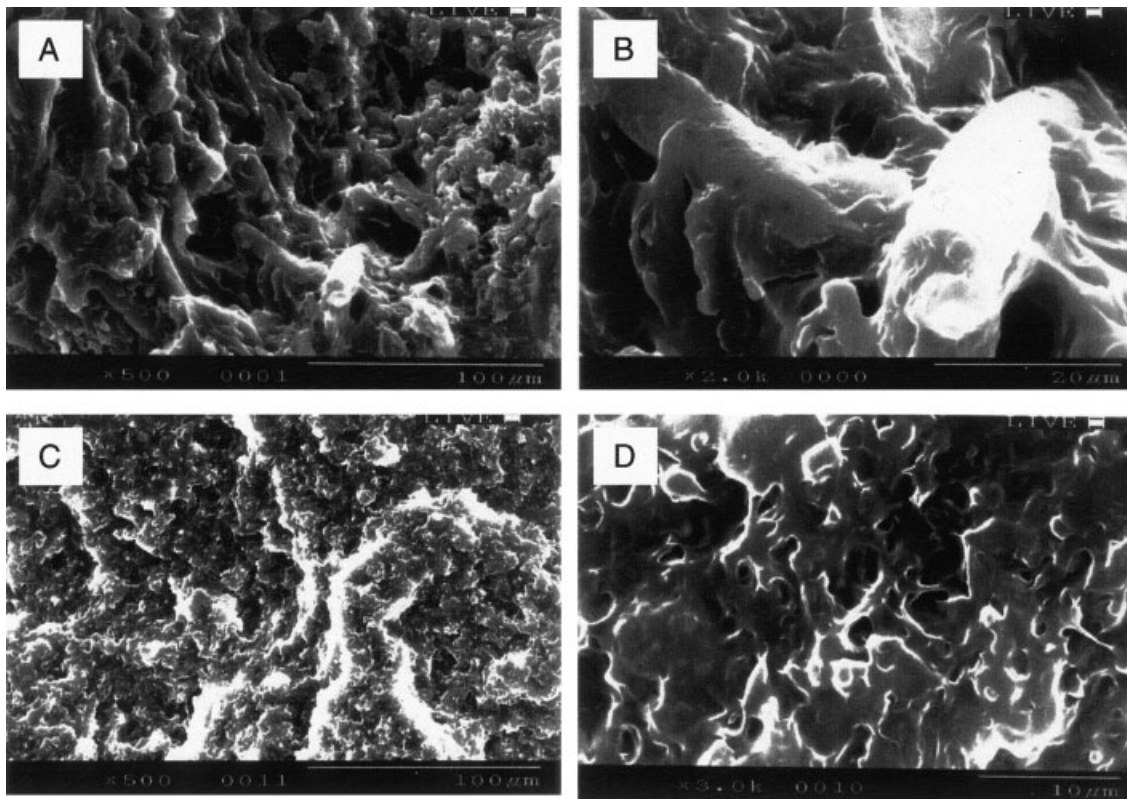
Figure 9 Scanning electron micrographs of fracture surfaces corresponding to different composites (MAPP1/CF11 = 70/30): (A,B) composites obtained by melt mixing and (C,D) composites obtained by ball milling and subsequent melt mixing. The scales were (A,C) 500×, (B) 2000×, and (D) 3000×.

trated in Figure 10. Through ball milling, the collapse of intramolecular and intermolecular hydrogen bonding generates a great number of free OH groups on the cellulose particles. The resultant OH groups on the cellulose surface are very reactive. Such activated OH groups can form ester bonds with MAPP through ball milling and through melt mixing. The MAPP chains bound onto cellulose particles through ester bonds can

exhibit good compatibility with a hydrophobic PP matrix.

CONCLUSIONS

Milling cellulose and MAPP induces the formation of ester bonds between cellulose and MAPP even in a solid phase. Such esterification is primarily due to the
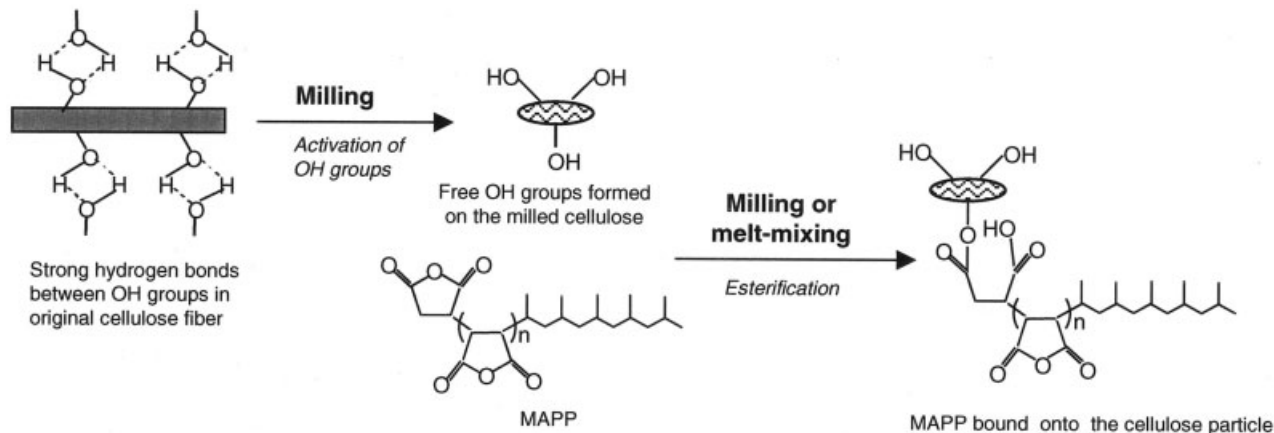
Figure 10 Proposed mechanism for milling-induced esterification between cellulose and MAPP.

mechanochemical formation of reactive OH groups on the surface of cellulose and is hardly dependent on the chemical structure of MAPP. The milling-induced esterification enhances the interfacial adhesion between the cellulose and MAPP matrix and improves the mechanical properties of the resultant composites.

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