JOURNAL OF MATERIALS SCIENCE 40 (2005) 3607 – 3614

Isocyanate as a compatibilizing agent on the properties of highly crystalline cellulose/polypropylene composites

WULIN QIU*,†, FARAO ZHANG, T. ENDO, T. HIROTSU
National Institute of Advanced Industrial Science and Technology (AIST), 2217-14
Hayashi-cho, Takamatsu 761-0395, Japan
E-mail: qiuwulin@yahoo.com

Composites of a highly crystalline cellulosic microfibres with polypropylene (PP) as well as with maleic anhydride grafted polypropylene (MAPP) were prepared by using 1,6-diisocyanatohexane (DIC) as a compatibilizing agent, their mechanical properties, morphologies, and thermal properties were investigated. Results show that the tensile strength and young's modulus of the composites improved intensively by using DIC. The enhancement is proposed to be due to stronger interfacial adhesion caused by the reduction of the polarity and hydrophilicity of cellulose fiber in PP-based composites, while much more chemically bound MAPP chains on cellulose fiber in MAPP-based composites. A maximum on tensile properties of the composite can be obtained by optimizing of the DIC content. Scanning electron microscopy (SEM) indicates that the interfacial adhesion between cellulose fibers and PP or MAPP matrix was improved in DIC coupled composites. Furthermore, DIC yields also some effects on thermal dynamic mechanical properties, as well as melting and crystallization behavior of the composites.

© *2005 Springer Science + Business Media, Inc.*

1. Introduction

Cellulose, which is the most abundant natural polymer, has gained increasing attention in novel composites [1–9]. The natural cellulose can be grouped into bast (jute, banana, flax, hemp, kenaf, mesta), leaf (pineapple, sisal, screw pine), and seed or fruit fibers (coin, cotton, oil palm) [2]. Cellulosic composites show many advantages such as low cost, low density, high stiffness, good mechanical properties as well as availability of renewable natural resources. However, the inherent incompatibility of hydrophilic cellulose with the hydrophobic thermoplastic polymers, such as polypropylene, causes unsatisfactory properties to the resultant composites. It is well known that the performance of a composite depend on the properties of the individual components as well as their interfacial adhesion. Good interfacial adhesion between the matrix and fibers is essential to transfer a stress from the matrix to the fibers and thus improve the mechanical strength of composites. To enhance the interfacial adhesion, works were carried out on modification of the fiber and/or polymer by physical and chemical methods. Physical methods, including corona or plasma discharges, are useful for polymers such as polypropylene, polyethylene and polystyrene [10–12]. Chemical methods cover pretreatment of fiber surface by coupling agent, such as silanes [13–14], and modification of the matrix by grafting polar moieties, such as acrylic acid, acrylic esters, or maleic anhydride (MA) on polymer chains [15–19].

We have been studying the composite of cellulose and polyolefin for the purpose of application as well as scientific research [20–26]. The effects of MAPP content as well as the cellulose content on the properties of the composites were investigated, results demonstrated that MAPP is an effective compatibilizer of crystalline cellulose with PP, and that mechanical properties of the composite require an optimum MAPP content [22]. We found recently that the enhanced interfacial esterification between MAPP and cellulose may be obtained by activating cellulose through ball-milling, and the resultant composites show a greater improvement in tensile strength [20, 21]. The graft degree of MAPP on the properties of cellulose composites, and the compatibility of free MA monomers in the PP or MAPP matrix were studied, too, results show that even an amount of grafted MA as small as 0.2 wt% is sufficient to impart maximum mechanical properties to the resulting composites, and the un-grafted free MA gives a slight positive effect to PP composite while a negative effect to MAPP composite [26]. We found also that such free

---

*Author to whom all correspondence should be addressed.

†*Present address*: Department of Chemistry, The University of Tennessee, Knoxville, TN 37996-1600, USA.

MA molecules are more reactive than the grafted MA groups in MAPP, due to their smaller steric hindrance and higher mobility. As a result, the free MA monomers may interact with OH groups of cellulose more readily, and interrupt the proximity of grafted MA groups to the limited superficial OH groups of cellulose.

Isocyanate, especially polymethylenepolyphenyl isocyanate, are successfully used as wood binders in wood chemistry [2, 27], and isocyanates carry an alkyl chain or a PP chain were used as a compatibilizing agent in PP/cellulosic fiber composites [2, 27–29]. It was observed that the isocyanate treatment of the cellulosic fibers enhanced the tensile strength of the composites. Through strong co-valent bonds, isocyanate is chemically linked to the cellulose matrix, both urea and biuret linkages were detected [30, 31].

By surface pre-treatment of cellulose with diisocyanate, the steric hindrance of MAPP may be reduced, and a maximum accessibility as well as reactivity to the limited superficial OH groups of cellulose may be reached. In this study, binary composites consisting of a highly crystalline cellulose fiber (30%, by weight) were prepared with PP or MAPP by using the 1,6-diisocyanatohexane as a coupling agent, and their properties were investigated.

2. Experimental

2.1. Materials

Isotactic polypropylene (PP powder, $\overline{Mw}$ ca. 250,000; density 900 kg/m^3) and polypropylene-*graft*-maleic anhydride (MAPP pellets, ca. 0.6 wt% MA; melt index 115; density 950 kg/m^3, as reported by the supplier), as well as the 1,6-diisocyanatohexane were obtained from Aldrich. Fibrous cellulose {CF11, 50–350 μm in length, about 20 μm in diameter; crystallinity 93% (cellulose I type) [32, 33]} was supplied by Whatman Int. Ltd., England.

2.2. Preparation of composites and samples

PP and CF11 were dried *in vacuo* at 60°C for 15 h, while MAPP (pulverized to a powder smaller than 1 mm) at 120°C for 15 h before using. CF11 was pretreated by the 1,6-diisocyanatohexane (DIC) and then mixed with PP or MAPP powder. Composite was prepared by melt-mixing method with a Toyoseiki Labo Plastomill 30C150 Rheomix. The mixing was carried out at 190°C at 55 rpm for 20 min. The initial mass ratio of PP or MAPP, CF11, and DIC was 70:30:n (where $n = 0$, 1, 2.5, or 5.0), and each resultant composite is abbreviated as P_n (PP matrix) or M_n (MAPP matrix).

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

2.3. 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) [34]. The composite plates were stored in a room with a constant temperature of 20°C and a constant humidity of 65% for over 48 h, before the measurement. Each result was the average taken from 6 parallel tests.

2.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) of composites was performed with a Perkin-Elmer DMA 7e using a three point bending-rectangular measuring system at a frequency of 1 Hz. The temperature was calibrated with indium and pure ice. The samples of 15×3 mm^2 area and 1 mm thickness were cooled to -30°C, maintained at the temperature for 3 min, and then heated to 130°C at 5°C/min in a flow of nitrogen. The static and dynamic forces were 330 and 300 mN, respectively. The viscoelastic parameters, i.e., the mechanical loss factor tan δ and storage modulus E' were recorded as a function of temperature.

2.5. Scanning electron microscopy (SEM)

The morphology of composites was examined using a Hitachi S-2 460N electron microscope at 25 kV, and the cryogenic fractured surfaces of composites were sputter-coated with gold-palladium alloy before viewing.

2.6. Differential scanning calorimetry (DSC)

DSC measurements were performed with a Perkin-Elmer DSC 7 instrument. Dry nitrogen gas with a flow rate of 25 mL/min was purged through the differential scanning calorimeter. The baseline for the calorimeter was run in empty cells, and the temperature and heat of fusion was calibrated with indium. Small thin piece of about 2.5 mg sample was cut from the melt-mixed composites and was used for measurement. Samples were held at 230°C for 3 min to erase the thermomechanical prehistory, then cooled to 50°C at 10°C/min and maintained for 3 min, finally reheated to 230°C at 10°C/min. Scanning of cooling and the second heating were recorded. All samples didn't show any change in weight after the DSC measurements.

3. Results and discussion

3.1. Tensile properties

The strength-strain behaviors of PP or MAPP as well as the typical composites are shown in Fig. 1. Compared with the neat PP, the elongation and the tensile strength of the composite decrease significantly, while the young's modulus increase, as shown in Fig. 1a. It is noted that the DIC reveals a compatibilizing effect on the PP/CF11 composite, causing an increase in tensile strength and the elongation of composite. Interestingly, the DIC also shows compatibilizing effect on MAPP/CF11 composite. The addition of DIC results in a further increase in tensile strength and young's modulus of MAPP/CF11 composite, and the

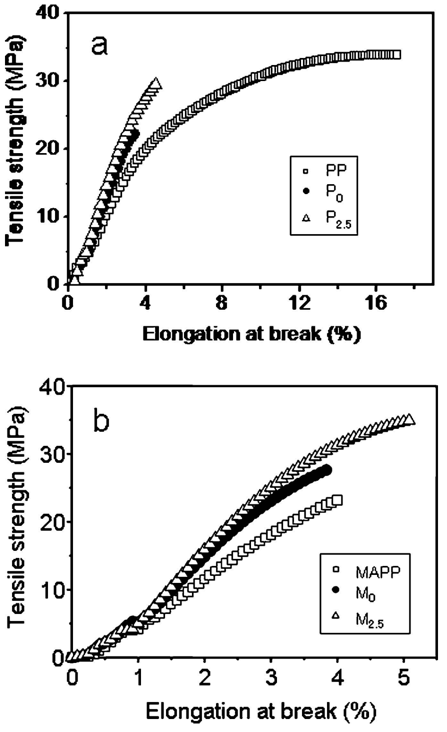


Figure 1 Strength/strain curves of (a) PP-based, and (b) MAPP-based materials.

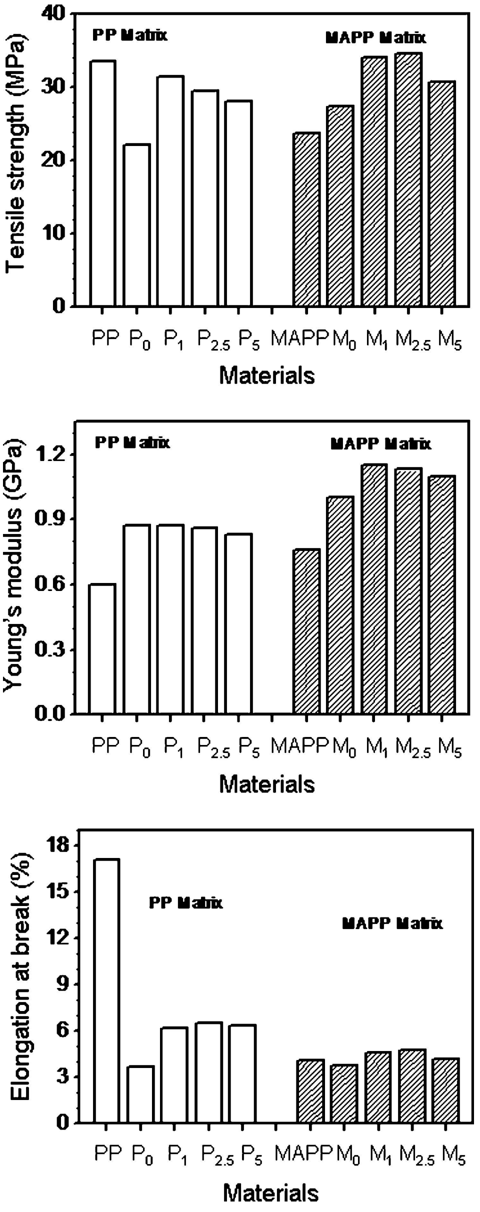


Figure 2 Tensile properties of the materials.

DIC compatibilized composite gives a larger elongation than that of neat MAPP, as can be seen in Fig. 1b.

Fig. 2 illustrates the mechanical properties of neat PP, neat MAPP, as well as their composites. The tensile strength was enhanced with the compatibilizing of DIC both in PP/CF11 (70/30) composite and in MAPP/CF11 (70/30) composite, the optimum DIC content is 1 phr (part of DIC per hundred parts of Matrix+CF11) for PP composites, and 1–2.5 phr for MAPP composites. At a DIC content of 1 phr (P_1 or M_1), the tensile strength is enhanced by 43% for PP/CF11 (70/30) composite, while 24% for MAPP/CF11 (70/30) composite. The PP composites exhibit almost the same young's modulus, while MAPP composites show a maximum at a DIC content of 1 phr (M_1). The DIC causes the elongation of PP composites to increase much more than that of MAPP composites, and the DIC content shows slight effect on elongation of the composites. By considering the tensile strength, young's modulus, and the elongation of the composites, a DIC content of 1 phr is effective enough to produce a satisfactory effect for both PP and MAPP composites. Higher DIC content may result in a slight reduction in tensile strength of both PP composite and MAPP composite, however, it is much higher than that of the un-coupled composites.

3.2. Dynamic mechanical properties

Dynamic mechanical spectra of neat PP and its composites are shown in Fig. 3. The storage modulus E' of the composites are higher than that of neat PP in all temperature domains (Fig. 3a), indicating an enhanced stiffness, which is in agreement with the results of young's modulus shown in Fig. 2. The DIC has very slight effect on storage modulus of the composites with the same CF11 content, indicating the modulus is determined mainly by the CF11 content [22]. The tan δ curves exhibit two peaks around −8°C (β) and 70°C (α), as shown in Fig. 3b. 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 [7, 35]. PP in composites shows a lower peak in tan δ curves than that of neat PP. With increasing DIC content, the intensities of both α- and β-relaxation increase, and the β-relaxation retaining almost the same peak position and shape in the composites while the α-relaxation varying. The analogous dynamic mechanical behaviors are seen MAPP-based composites, as shown in Fig. 4. This indicates that DIC has analogous effect on dynamic properties for both PP-based and MAPP-based composites. The MAPP-based composite reveals smaller tan δ values and a slightly higher storage modulus E' than the PP-based composite, however, this may be due to the higher elasticity of MAPP itself.

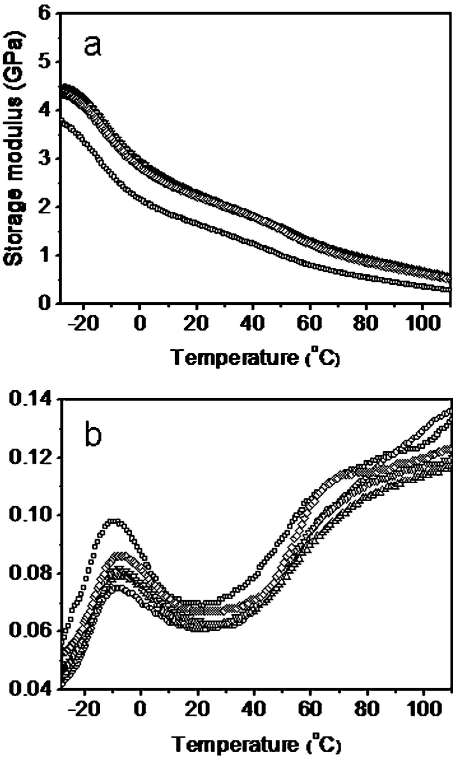


Figure 3 Dynamic mechanical spectra of PP-based composites with a cellulose content of 30 wt%. DIC content: (○) 0, (△) 1.0, (▽) 2.5, and (◇) 5.0 phr. The result of pure PP (□) is shown for comparison.

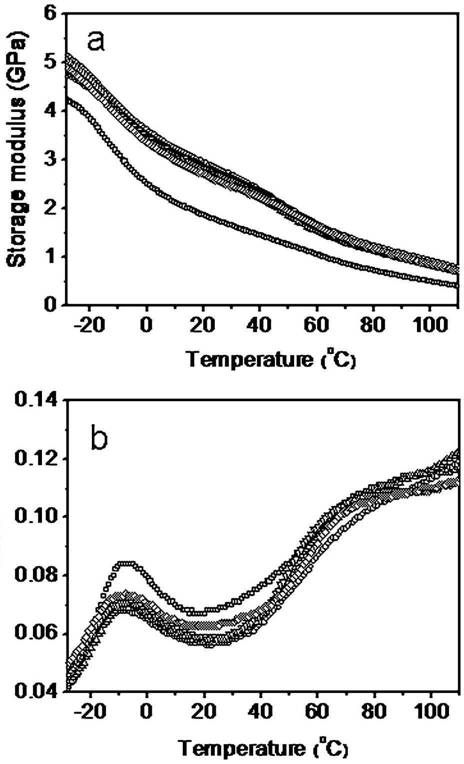


Figure 4 Dynamic mechanical spectra of MAPP-based composites with a cellulose content of 30 wt%. DIC content: (○) 0, (△) 1.0, (▽) 2.5, and (◇) 5.0 phr. The result of pure MAPP (□) is shown for comparison.

3.3. Morphology of composites

The interfacial adhesion and properties of the interphase plays a crucial role in the determination of composite properties, and the interfacial adhesion is closely related to the phase morphology [20–22, 36]. Fig. 5 shows the SEM micrographs of cryogenic fractured surfaces of the PP-based composites. The micrograph of the PP and cellulose composite shows clearly that there are large gaps and voids between PP matrix and CF11 fiber, and the surface of CF11 fiber is smooth (Fig. 5a). This indicates that there is no interfacial adhesion between CF11 fiber and the PP matrix, which is consistent with the poor tensile strength. The morphology of DIC compatibilized composites reveals good interfacial adhesion between PP and CF11 fibers (Fig. 5b–d), in which CF11 fibers are tightly connected with the PP matrix. The improved interfacial adhesion is in agreement with the enhanced tensile strength as shown in Figs 1 and 2. Fig. 6 shows that the morphology of MAPP-based composites. Although there exists strong interfacial adhesion between CF11 fibers and MAPP matrix (Fig. 6a), the addition of DIC causes further improvement in interfacial adhesion of CF11 fibers and MAPP matrix, much more torn and broken fibers were found in DIC compatibilized composites (Fig. 6b–d). The DIC caused improved interfacial interaction is in agreement with the enhanced tensile strength of the composites.

3.4. Crystallization and melting behavior

The melting and crystallization behavior of a semicrystalline polymer determines not only the processing conditions and the application areas, but also the properties of the materials. A lot of works on melting and crystallization of polymers can be found in Dr. B. Wunderlich's books [37, 38]. Table I summarizes

TABLE I DSC Data of the materials

Materials	PP /DIC/CF11 (wt%)	T_m (°C)	ΔH_m (J/g)	T_c(°C)	$-\Delta H_c$(J/g)	ΔT_α(°C)
PP	100/0/0	156.2 163.2	90.6	111.9	89.9	44.3
P_0	70/0/30	156.2 162.8	92.2	117.5	94.3	38.7
P_1	70/1.0/30	156.6 162.6	84.0	117.9	94.2	38.7
$P_{2.5}$	70/2.5/30	157.2 162.2	86.1	118.8	93.4	38.4
P_5	70/5.0/30	158.9 162.2	81.7	118.2	94.6	40.7
	MAPP/DIC/CF11 (wt%)					
MAPP	100/0/0	156.6 163.3	87.6	117.2	91.8	39.4
M_0	70/0/30	160.2	84.4	125.4	92.4	34.8
M_1	70/1.0/30	158.8	76.8	123.2	86.1	35.6
$M_{2.5}$	70/2.5/5	158.2	75.1	121.5	90.8	36.7
M_5	70/5.0/30	158.2	79.1	121.5	88.3	36.7

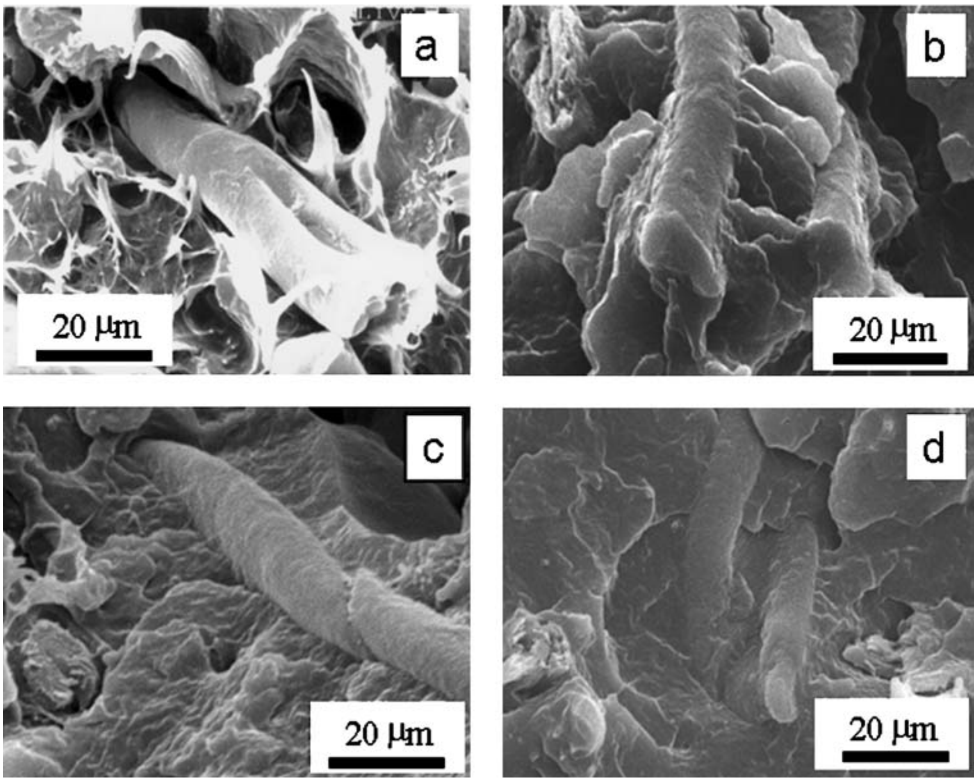


Figure 5 SEM photographs of fractured surfaces of (a) neat PP, and PP-based composites with DIC content of: (b) 1.0, (c) 2.5, and (d) 5.0 phr.

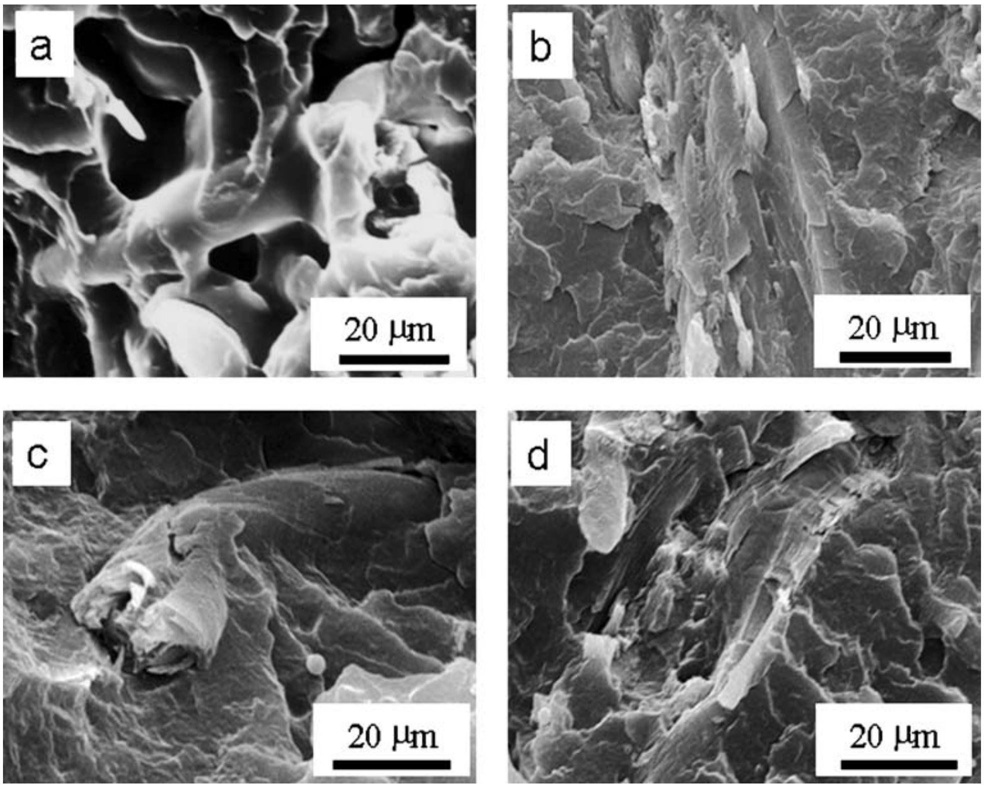


Figure 6 SEM photographs of fractured surfaces of (a) neat MAPP, and MAPP-based composites with DIC content of: (b) 1.0, (c) 2.5, and (d) 5.0 phr.

the melting and crystallization parameters of PP and MAPP. The PP reveals a main melting peak as well as a shoulder no matter in neat PP or in composites, and a higher DIC content in the composite causes the main melting peak moves to higher temperature. The higher temperature peak gets minor in the composites, and its intensity decreases with the increase of DIC content, as shown in Fig. 7A. Compared with neat PP, the crystallization peak appears at higher temperature in composites. The supercooling ($\Delta T_\alpha = T_m - T_c$) decreases in composite, and DIC shows almost no effect on supercooling at lower content, however, increase the supercooling at a DIC content of 5 phr.

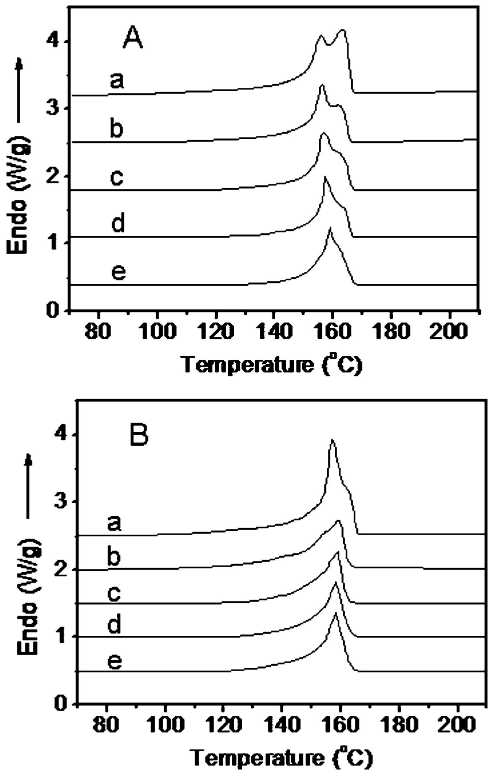


Figure 7 The effect of DIC on the melting behavior of PP (A) and MAPP (B) in the composites. DIC content: (b) 0, (c) 1.0, (d) 2.5, and (e) 5.0 phr. The result of neat matrix (a) is shown for comparison.

MAPP also shows a main melting peak and a shoulder at higher temperature. However, MAPP-based composites show a single melting peak, which appears between the main melting peak and the shoulder of the neat MAPP, as shown in Fig. 7B. MAPP in composites gives a higher crystallization temperature peak, while a smaller supercooling, compare with the neat matrix. The addition of DIC causes a decrease in melting and crystallization temperature, while an increase in supercooling, indicating a reduction of nucleating activity of CF11 by DIC.

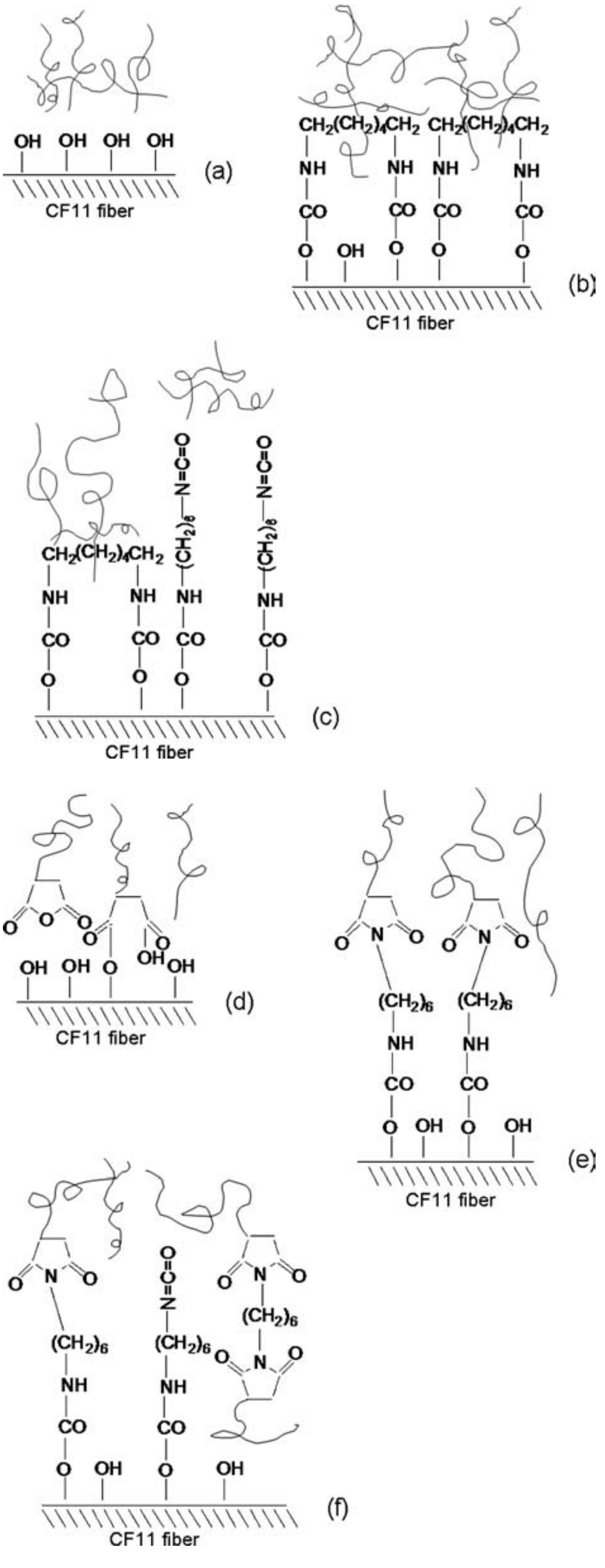
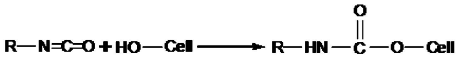


Figure 8 A proposed model of interactions between CF11 fiber and (a) neat PP, (b) PP compatibilized by lower amount of DIC, (c) PP compatibilized by higher amount of DIC, (d) neat MAPP, (e) MAPP compatibilized by lower amount of DIC, and (f) MAPP compatibilized by higher amount of DIC.

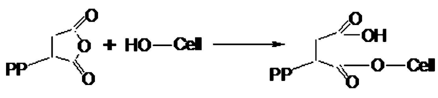
3.5. Interaction models between cellulose fiber and matrix

The CF11 used is a highly crystalline cellulose fiber that has a very limited amount of free superficial —OH groups because of intra- and intermolecular hydrogen bond [21, 22, 26]. It is noted that only such free superficial —OH groups can interact effectively with the reactive moieties such as the —NCO group or the -MA group. The —NCO group is highly reactive with the free —OH group of cellulose, yields a urethane linkage [30, 31], and therefore isocyanate is chemically linked to the cellulose matrix, as shown in Scheme I.

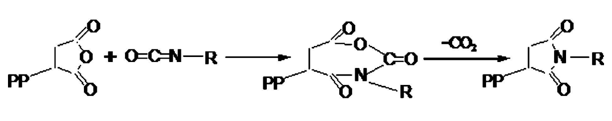


$$R{-}N{=}C{=}O + HO{-}Cell \longrightarrow R{-}HN{-}\overset{\overset{O}{\|}}{C}{-}O{-}Cell$$

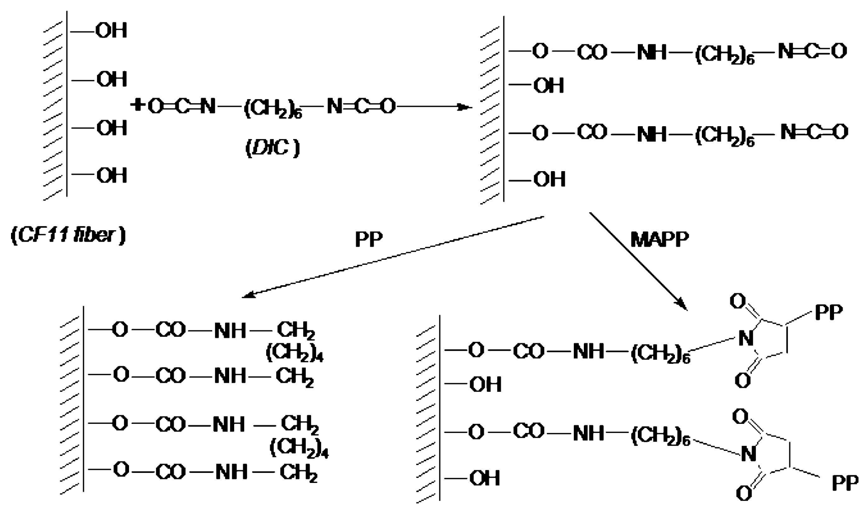
Scheme I



Scheme II



Scheme III



Scheme IV

Scheme V

The —MA group reacts with the free —OH group of cellulose, forms an ester bond (Scheme II) and therefore the MAPP matrix is chemically bonded to the cellulose fiber [15, 20, 21]. It is well known that the —NCO group reacts readily with the anhydride group, finally forming the imide linkage at higher temperature, as shown in Scheme III. When CF11 fiber is surface pre-treated with 1,6-diisocyanatohexane and compounded with PP or MAPP matrix, the main reactions are proposed as shown in Schemes IV or V. Though other reactions, such as the biuret formation and the isocyanate dimerization may also be possible.

By considering the mechanical properties and the microstructures, the interaction model between the cellulose fibers and the PP or MAPP matrix in the composites may be illustrated as shown in Fig. 8. No interaction between neat PP and CF11 fiber (Fig. 8 a), is in agreement with the morphology (Fig. 5a) and the poor tensile strength. Fig. 8 (b) gives a model of the interaction between neat PP and CF11 fiber treated by small amount of DIC, the free superficial —OH groups of CF11 reactive with —NCO groups of DIC, and such interaction would reduce the polarity as well as the hydrophilicity of CF11 fiber's surface to increase the compatibility of the resulted CF11 fibers with the PP matrix, yield the composite an enhanced tensile strength (Fig. 2) and improved interfacial adhesion (Fig. 5b). However, at higher DIC content, such reduction on polarity and hydrophilicity of CF11 fiber was lessened due to the limited amount of free -OH groups on the surface of CF11 fiber, as shown in Fig. 8c, although there exists good wetting of cellulose fibers with the PP matrix (Fig. 5c and d), the tensile strength of the composites decreases somewhat (Fig. 2).

Fig. 8d gives the model of interaction between MAPP and cellulose fiber, a good interfacial adhesion (Fig. 6a) caused by the formation of ester bonds is in accordance with the mechanical properties. However, there are still some free superficial —OH groups of CF11 fiber that was not esterified due to the large steric hindrance of the MAPP. When CF11 fiber is surface pre-treated by DIC, much more free superficial —OH groups may be reacted due to the higher mobility and smaller steric hindrance of DIC than MAPP. At lower DIC content, one —NCO of a DIC is chemically linked to the surface of CF11 fiber with another —NCO freely. The end free —NCO group with $(CH_2)_6$ chain of the DIC stretches out from the surface of CF11 fiber, forming a core-shell structure. Compared with the parents CF11 fiber, this core-shell structure yields larger reactive volume as well as much more reactive sites, while smaller steric hindrance to MAPP. Through the reaction of free —NCO group and the anhydride group of MAPP, much more MAPP chains are bound to the CF11 fiber. Fig. 8e gives the interaction at lower DIC content, which is in accordance with the tensile properties (Fig. 2) and the morphology (Fig. 6b). Because the amount of free superficial —OH groups of CF11 is limited, a very small amount of the DIC may saturate the surface of the fiber, and beyond a critical amount of DIC, the extra DIC remains freely among the CF11 fibers. At higher DIC content, the extra DIC disperses around the core-shell structure and reacts with MAPP, which may obstacle the approaching of MAPP to the core-shell structure, and therefore lessening the amount of the bound MAPP on CF11 fiber. Fig. 8f gives the possible interaction of MAPP with CF11 fiber at higher DIC content. A slight decrease in tensile strength can be found in Fig. 2, and the morphologies are shown in Fig. 6c and d.

4. Conclusions

1,6-diisocyanatohexane may be used as a compatibilizing agent for PP/cellulose composite as well as MAPP/cellulose composite. Through the reaction of the free superficial —OH groups of cellulose and the —NCO group of diisocyanate, the polarity and hydrophilicity of cellulose fiber is reduced, and therefore improves the compatibility of the cellulose fibers and PP matrix. Through the imidization reaction of —NCO group and anhydride group of MAPP, much more MAPP chains are linked on the cellulose fiber due to the much more obtainable reactive sites of cellulose. The maximum of mechanical properties of the cellulosic composite may be obtained by optimizing of the diisocyanate content.

References

1. A. K. BLEDZKI and J. GASSAN, *Prog. Polym. Sci.* **24** (1999) 221.
2. J. GEORGE, M. S. SREEKALA and S. THOMAS, *Polym. Eng. Sci.* **41** (2001) 1471.
3. P. ANNA, E. ZIMONYI, A. MARTON, A. SZEP, S. MATKO, S. KESZEI, G. BERTALAN and G. MAROSI, *Macromol. Symp.* **202** (2003) 245.
4. G. CANTERO, A. ARBELAIZ, F. MUGIKA, A. VALEA and I. MONDRAGON, *J. Reinf. Plast. Comp.* **22** (2003) 37.
5. W. G. GLASSER, R. TAIB, R. K. JAIN and R. KANDER, *J. Appl. Polym. Sci.* **73** (1999) 1329.
6. J. R. COLLIER, M. LU, M. FAHRURROZI and B. J. COLLIER, *ibid.* **61** (1996) 1423.
7. A. AMASH and P. ZUGENMAIER, *Polym. Bull.* **40** (1998) 251.
8. M. IOELOVICH and O. FIGOVSKY, *Polym. Advan. Technol.* **13** (2002) 1112.
9. G. G. ALLAN, A. P. STOYANOV, M. UEDA and A. YAHIAOUI, *Cellulose* **8** (2001) 127.
10. S. DONG, S. SAPIEHA and H. P. SCHREIBER, *Polym. Eng. Sci.* **33** (1993) 343.
11. M. N. BELGACEM, P. BATAILLE and S. SAPIEHA, *J. Appl. Polym. Sci.* **53** (1994) 379.
12. A, K. BLEDZKI, S. REIHNAME and J. GASSAN, *ibid.* **59** (1996) 1329.
13. M. H. SCHNEIDER and K. I. BREBNER, *Wood Sci. Technol.* **19** (1985) 67.
14. F. M. B. COUTINHO, T.H. S. COSTA and D. L. CARVALHO, *J. Appl. Polym. Sci.* **65** (1997) 1227.
15. J. M. FELIX and P. GATENHOLM, *ibid.* **42** (1991) 609.
16. J. M. FELIX, P. GATENHOLM and H. P. SCHREIBER, *Polym. Compos.* **14** (1993) 449.
17. I. CHUN and R. T. WOODHAMS, *ibid.* **5** (1984) 250.
18. W. CHIANG and W. YANG, *Polym. Eng. Sci.* **24** (1994) 485.
19. M. KAZAYAWOKO, J. J. BALATINECZ and R. T. WOODHAMS, *J. Appl. Polym. Sci.* **66** (1997) 1163.
20. W. L. QIU, T. ENDO and T. HIROTSU, *ibid.* **94** (2004) 1326.
21. W. L. QIU, F. R. ZHANG, T. ENDO and T. HIROTSU, *ibid.* **91** (2004) 1703.
22. *Idem.*, *ibid.* **87** (2003) 337.
23. F. R. ZHANG, W. L. QIU, L. Q. YANG, T. ENDO and T. HIROTSU, *ibid.* **89** (2003) 3293.
24. *Idem.*, *J. Mater. Chem.* **12** (2002) 24.
25. *Idem.*, *J. Apply. Polym. Sci.* **84** (2002) 1971.
26. W. L. QIU, T. ENDO and T. HIROTSU, *J. Appl. Polym. Sci.* submitted for publish.
27. A. K. BLEDZKI, S. REIHMANE and J. GASSAN, *Polym. Plast. Technol. Eng.* **37** (1998) 451.
28. C. JOLY, M. KOFMAN and R. GAUTHIER, *J. Macromol. Sci. Pure. Appl. Chem.* **A33** (1996) 1981.
29. A. VAZQUEZ, V. A. DOMINGUEZ and J. M. KENNY, *J. Thermoplast. Compos. Mate.* **12** (1999) 447.
30. S. C. BAO, W. A. DAUNCH, Y. H. SUN, P. L. RINALDI, J. J. MARCINKO and C. PHANOPOULOS, *Forest Prod. J.* **53** (2003) 63.
31. S. L. WENDLER and C. E. FRAZIER, *J. Adhesion.* **50** (1995) 135.
32. T. ENDO, R. KITAGAWA, T. HIROTSU and J. HOSOKAWA, *Kobunshi Ronbunshu* **56** (1999) 166 (in Japanese).
33. T. ENDO, F. ZHANG, R. KITAGAWA, T. HIROTSU and J. HOSOKAWA, *Polym. J.* **32** (2000) 182.
34. Japan Standard Society, "JIS K7113-1995 Testing Method for Tensile Properties of Plastics" (Japan Standard Society, Tokyo, 1995).
35. A. AMASH and P. ZUGENMAIER, *J. Appl. Polym. Sci.* **63** (1997) 1143.
36. W. L. QIU, K. C. MAI and H. M. ZENG, *ibid.* **71** (1999) 1537.
37. B. WUNDERLICH, "Macromolecular Physics, Vols. 1–3" (Academic, New York, 1973–1980).
38. B. WUNDERLICH, "Thermal Analysis" (Academic, Boston, 1990).

Received 1 December 2004
and accepted 3 March 2005