

Effect of Degree of Interfacial Chemical Bonds on Tensile Strength of Cellulose/Polypropylene Composites

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Abstract: we prepared cellulosic composites by melt-mixing of cellulose and polypropylene (PP), and investigated the influence of the degree of interfacial chemical bond on the tensile properties of the resultant composites. Ester bonds can be formed between cellulose and PP-*graft*-maleic anhydride (MAPP), whereas cannot with neat PP due to no reactive group in it. The degree of the interfacial ester bonds is controlled primarily by the crystallinity of cellulose; the tensile strength of the cellulose composite is in agreement with the degree of interfacial ester bonds formed during preparing. The tensile strength increases with an increase of cellulose content in the MAPP composite. However, the increase in tensile strength is limited when original cellulose (highly crystalline) is used, because the number of the interfacial ester bonds is very few. Great numbers of the interfacial ester bonds can be obtained by activation of highly crystalline cellulose through ball-milling. Accordingly, the composites prepared by ball-milling first and then melt-mixing reveals a much stronger tensile strength, due to its enhanced interfacial reaction.

Key words: Cellulose, polypropylene, ester bond, tensile strength, ball-milling

1. INTRODUCTION

With the increasing of population and the growing of resource consumption, it gets more important to minimize the environmental load, accordingly, to develop the ecomaterials and to make use of waste or by-products as far as possible. Cellulose, one of the wood-based materials, is the most abundant renewable natural polymer, and has gained increasing attention in novel composites.[1-8] The performance, such as tensile properties, of composites depends on the properties of the individual components as well as their interfacial adhesion. Cellulosic composites show 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 PP, may bring the resultant composites unsatisfactory properties. The compatibility between cellulose and a PP matrix might be improved by the interfacial chemical reaction to form chemical bonds between the OH groups of cellulose and the reactive groups of modified PP. In this study, maleic anhydride (MA) was selected as the functional group of the modified PP matrix, and the formation of ester bonds was examined. The tensile strength of the resultant

composites was investigated, considering the degree of the interfacial ester bonds.

2. EXPERIMENTAL

2.1 Materials

Cellulose (CF11, 50–350mm in length), Polypropylene (PP, M_w ca. 250,000), and PP-graft-maleic anhydride (MAPP, ca. 0.6 wt% MA, melt index 115) were obtained all commercially.

2.2 Preparation of composites

Three series cellulose composites were prepared to study the effect of degree of the interfacial ester bonds on tensile properties of the composites: (1) PP/CF11 composites were prepared by a melt-mixing method.[1] (2) MAPP/CF11 composites were prepared by the melt-mixing method. (3) MAPP/CF11 composites were prepared by ball-milling first,[2] then melt-mixing.

Composites with a cellulose content of 30wt% were treated by hot xylene to remove the un-bound PP or MAPP matrix, and the residues were used to examine the interfacial chemical reaction. Tensile strength and morphology were measured as described elsewhere.[1]

3. RESULTS AND DISCUSSION

3.1 PP/CF11 composites

PP has no reactive group, and it is undoubted that there is no interfacial chemical bond between PP and

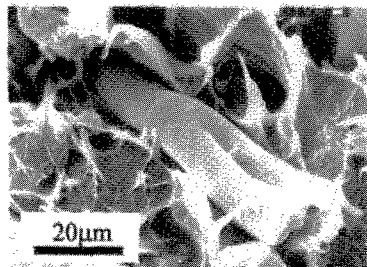


Figure 1 SEM micrograph of fracture surface of a PP/CF11 (70/30) composite

CF11 in the PP/CF11 composites. Accordingly, no interfacial adhesion will be found in the composites. As

shown in Fig.1, there are large gaps and voids between the PP matrix and the perfect cellulose fibers, demonstrating no interfacial adhesion between cellulose and the PP matrix. The fracture surfaces of the composites are consistent with their tensile strength, as

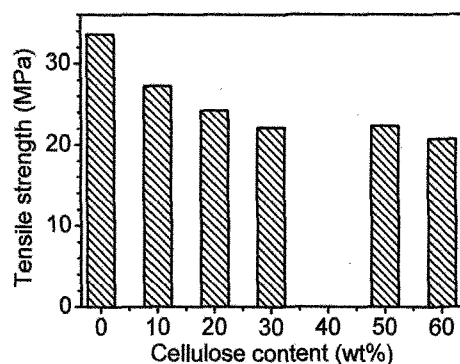


Figure 2 Tensile strength vs cellulose content of a PP/CF11 composite

shown in Fig. 2, tensile strength of the composites yield a reduction with the addition of cellulose, compared with the neat PP.

3.2 MAPP/CF11 composites by melt-mixing

MAPP has the reactive MA groups, which can react with the OH groups of cellulose to form ester bonds in

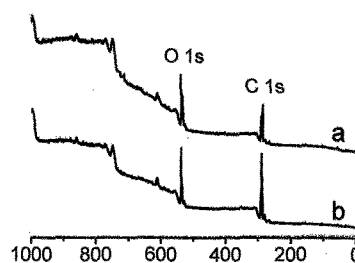


Figure 3 XPS spectra of original CF11 (a), and residual CF11 from MAPP/CF11 (70/30) composite

the interface. However, the original CF11 has a high crystallinity of 93% [9] with a very small number of free OH groups. Accordingly, for composites obtained by melt-mixing of MAPP with the original CF11, the ester bonds are so few that they cannot be measured by FT-IR

spectroscopy.[10] The XPS analysis shows that the cellulose particles derived from the MAPP-removed sample has the surface with a higher C/O ratio than that for CF11 (Fig. 3). The peak area ratio of C1s to O1s is 0.76 for the original CF11 particles, whereas 1.12 for cellulose particles derived from the composite. The results indicate that MAPP chains were chemically bound to cellulose particles in the composites. As shown

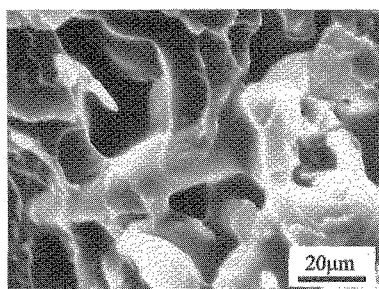


Figure 4 SEM micrograph of fracture surface of a MAPP/CF11 (70/30) composite

in Fig.4, CF11 fiber is connected tightly by the MAPP matrix, although a part of the fiber surface is still naked. This proves the existence of the interfacial adhesion between MAPP and cellulose fibers caused by the interfacial esterification, though the interfacial interaction

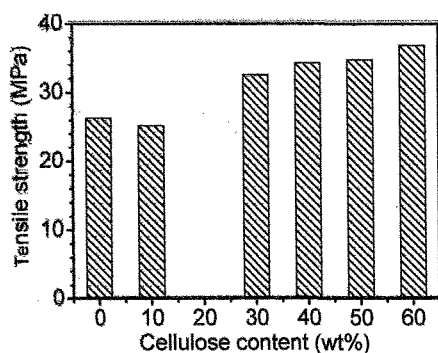


Figure 5 Tensile strength vs cellulose content of MAPP/CF11 composites

is limited. Contrast sharply with the PP/CF11 composites, the tensile strength of MAPP/CF11 composites improves with the increase of cellulose content, as can be seen in Fig.5.

3.3 MAPP/CF11 composites from ball-milling and then melt-mixing

Almost all OH groups are bound to each other through intra- and intermolecular hydrogen bonds in the original cellulose with high crystallinity. Ball-milling can cause the collapse of the inherent hydrogen bonds to yield a great number of free OH groups on the resultant cellulose particles.[9,10] Accordingly, the composites by ball-milling and then melt-mixing reveal a great number of interfacial ester bonds, which are observed by

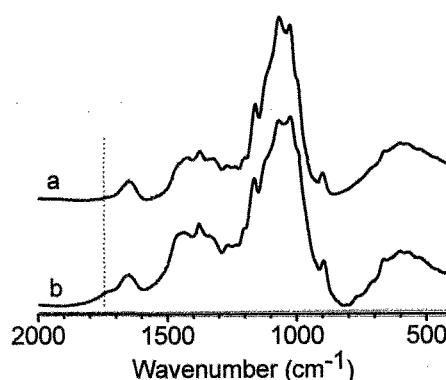


Figure 6 FT-IR spectra of ball-milled CF11 (a) and CF11 from MAPP/CF11 (70/30) composite (b).

FT-IR spectroscopy, as shown in Fig.6. The absorption of the new shoulder around 1730 cm^{-1} in Fig.6 (b) is assigned to ester bonds.[10] The enhanced interfacial esterification causes improved interfacial adhesion. As

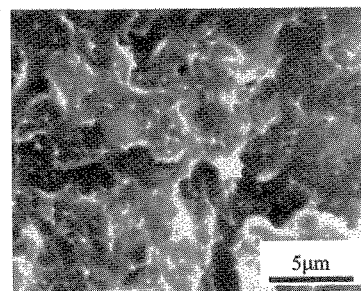


Figure 7 SEM micrograph of fracture surface of a MAPP/CF11 (70/30) composite from ball-milling and then melt-mixing

shown in Fig.7, it is difficult to differentiate cellulose particles from the MAPP matrix, as the cellulose particles are tightly covered with the MAPP matrix. The

results indicate that the ball-milling induces a great number of interfacial ester bonds occurred between the MAPP matrix and cellulose particles, and thus improves the interfacial adhesion of the composite. As a result, the composite prepared through ball-milling and then melt-mixing reveals an enhanced tensile strength, compared with the corresponding composite prepared through melt-mixing alone. Fig. 8 gives the ball-milling

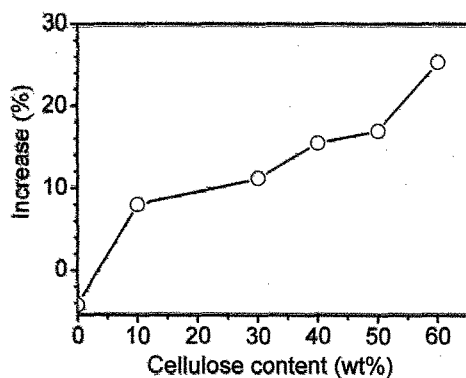


Figure 8 The increase of tensile strength of MAPP/CF11 composites caused by the ball-milling

imparted improvements of tensile strength for MAPP/CF11 composites. It is found that the improvement increases with an increase of cellulose content in the composites.

4. CONCLUSION

The tensile strength of a cellulose and PP composite is controlled by the interfacial adhesion, which results from the interfacial esterification. The tensile strength of the composite is in agreement with the degree of interfacial ester bonds formed during preparing of composites.

References

- [1] W. L. Qiu, F. R. Zhang, T. Endo, T. Hirotsu, *J. Appl. Polym. Sci.*, **87**, 337-345 (2003).
- [2] F. R. Zhang, W. L. Qiu, L. Q. Yang, T. Endo, T. Hirotsu, *J. Mater. Chem.*, **12**, 24-26 (2002).

- [3] F. R. Zhang, T. Endo, W. L. Qiu, L. Q. Yang, T. Hirotsu, *J. Apply. Polym. Sci.*, **84**, 1971-1980 (2002).
- [4] A. K. Bledzki, J. Gassan, *Prog. Polym. Sci.*, **24**, 221-274 (1999).
- [5] M. Takatani, O. Kato, T. Kitayama, T. Okamoto, M. Tanahashi, *J. Wood Sci.*, **46**, 210-214 (2000).
- [6] A. Amash, P. Zugenmaier, *Polymer*, **41**, 1589-1596 (2000).
- [7] W. G. Glasser, R. Taib, R. K. Jain, R. Kander, *J. Appl. Polym. Sci.*, **73**, 1329-1340 (1999).
- [8] J. M. Felix, P. Gatenholm, *J. Appl. Polym. Sci.*, **42**, 609-620 (1991).
- [9] T. Endo, R. Kitagawa, T. Hirotsu, J. Hosokawa, *Kobunshi Ronbunshu*, **56**, 166-173 (1999). (in Japanese)
- [10] W. L. Qiu, F. R. Zhang, T. Endo, T. Hirotsu, *J. Appl. Polym. Sci.*, in press.

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