

Mechanochemical preparation and properties of a cellulose–polyethylene composite

Farao Zhang, Wulin Qiu, Liqun Yang, Takashi Endo and Takahiro Hirotsu*

Institute for Marine Resources and Environment Research, National Institute of Advanced Industrial Science and Technology (AIST), 2217-14 Hayashi-cho, Takamatsu 761-0395, Japan. E-mail: takahiro-hirotsu@aist.go.jp

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Ball milling of crystalline cellulose with maleated polyethylene (MPE) yields a novel composite with ester bonds formed by reaction of the hydroxy groups of the cellulose with the maleic anhydride groups of MPE; the composite exhibits much improved toughness and ductility compared with the product formed by melt-mixing, probably because of the formation of an interphase of MPE chains bonded on cellulose particles.

The utilization of biomass for novel composites has attracted growing interest because of its eco-friendly and renewable nature.^{1–3} Cellulose, the most plentiful biopolymer on earth, has been extensively studied for potential application to thermoplastic composites.¹ A cellulose–polyethylene composite is expected to be a particularly promising candidate, because polyethylene (PE) is a widely used polymer with excellent thermoplasticity that may compensate for the poor processability of cellulose. Recently many efforts have been made to enhance the mechanical properties of cellulosic composites through improved compatibility between hydrophilic cellulose and hydrophobic thermoplastic materials.^{4–9} However, the marked decrease in toughness and fluidity of cellulosic composites with an increase in cellulose content has stood in the way of the development of novel composites.

Formation of an interphase between the cellulose phase and the PE phase, with PE chains bonded on to cellulose particles, is probably a solution to the problem. A previous study showed that the usual melt-mixing of crystalline cellulose with maleated polyethylene (MPE) does not cause the formation of chemical bonds.¹⁰ This implies that activation of crystalline cellulose is essential for the formation of such chemical bonds. Accordingly, we have explored a mechanochemical preparation of composites of crystalline cellulose with MPE through ball milling. In this study we demonstrate that ball milling intensively induces the bonding of MPE on to cellulose.

Fibrous cellulose¹¹ was purchased from Whatman International Co., Ltd. (UK), and MPE with a maleic anhydride (MA) content of *ca.* 0.8 wt% from Mitsubishi Chemical Co., Ltd. (Japan). The cellulose was vacuum-dried at 50 °C for 7 days, and the MPE was mechanically sieved into spherical grains with sizes below 1 mm. Cellulose (13.5 g) and MPE (31.5 g) were added together in a Pulverisette 5 ball mill (FRITSCH, Germany), and milled at 250 rpm for 24 h to obtain a mechanochemically milled mixture (MC mixture); the mixture (37.5 g) was then melt-mixed in an R60 mixer (Toyo Seiki Seisakusho, Japan) at 180 °C for 30 min to obtain a mechanochemically prepared composite (MC composite). A composite (UM composite) with the same composition was prepared only by the melt-mixing as mentioned above, for comparison. The extent of MPE bonded on to cellulose in the mixture or the

composites was examined by removing free MPE from the crushed sample (2 g) with xylene (400 ml) in a Soxhlet extractor (125 °C, 72 h). The bonding of MPE on to cellulose was characterized using a Spectrum 2000 FTIR spectrometer (Perkin-Elmer Co., Ltd.) at a resolution of 2 cm⁻¹. The crystallinity of test samples was measured by X-ray diffraction (XRD) with a Rigaku RINT2000 diffractometer (Cu K $\alpha_{1,2}$ at 40 kV and 40 mA).

From the solvent extraction of free MPE, the weight losses of the UM composite, the MC mixture, and the MC composite were 67.8%, 56.5%, and 54.4%, respectively, falling between the extreme cases of pure MPE (100%) and pure cellulose (0%). The results indicate that because pure MPE does not contain cross-linked gels, MPE that is not bonded to cellulose in the mixture and the composites can be removed completely. Accordingly, the fraction of MPE bonded to the cellulose particles may be determined from the weight loss. This bonded fraction is 3.1% for the UM composite, 19.3% for the MC mixture, and 22.3% for the MC composite. This demonstrates clearly that ball milling strongly induces the bonding of MPE on to cellulose even in the solid state, a quite different result from the case of usual melt-mixing.¹⁰

IR spectra of the UM composite, the MC mixture and the MC composite are shown in Fig. 1, and compared with those of MPE. Characteristic absorption bands of MPE appear at 1792 and 1713 cm⁻¹ due to saturated succinic anhydride groups and their hydrolysis derivatives (Fig. 1a), respectively,^{3,12} with the complete cyclization of the hydrolysis derivatives into the anhydride after vacuum-drying (in vacuum at 120 °C for 3 h) as shown in Fig. 1b. The esterification reaction between maleic anhydride groups of MPE and hydroxy groups of cellulose can be characterized by the appearance of an absorption band at around 1735 cm⁻¹.^{3,6} From Fig. 1c, the UM composite exhibits no absorption band at around 1735 cm⁻¹, with only the band at 1792 cm⁻¹ due to saturated succinic anhydride groups, suggesting little esterification between MPE and cellulose. By contrast, the MC mixture exhibits three overlapping absorption bands at 1737, 1721, and 1713 cm⁻¹ as shown in Fig. 1d. It is noted that, after vacuum-drying, the disappearance of the band at 1713 cm⁻¹ is accompanied by the appearance of the band at 1792 cm⁻¹, with a slightly lower shift of the bands at 1737 and 1721 cm⁻¹. Furthermore, the MC composite shows two distinct bands at 1733 and 1717 cm⁻¹, with the band at 1792 cm⁻¹. Comparing with the results of MPE, the bands at 1733–1735 cm⁻¹ are undoubtedly due to ester bonds, while the bands at 1717–1719 cm⁻¹ are due to monocarboxylic acid groups, to which the adjacent groups form ester bonds (Table 1), because free succinic acid groups (1713 cm⁻¹) change into their anhydride derivatives (1792 cm⁻¹). It is very interesting that such mechanochemical esterification

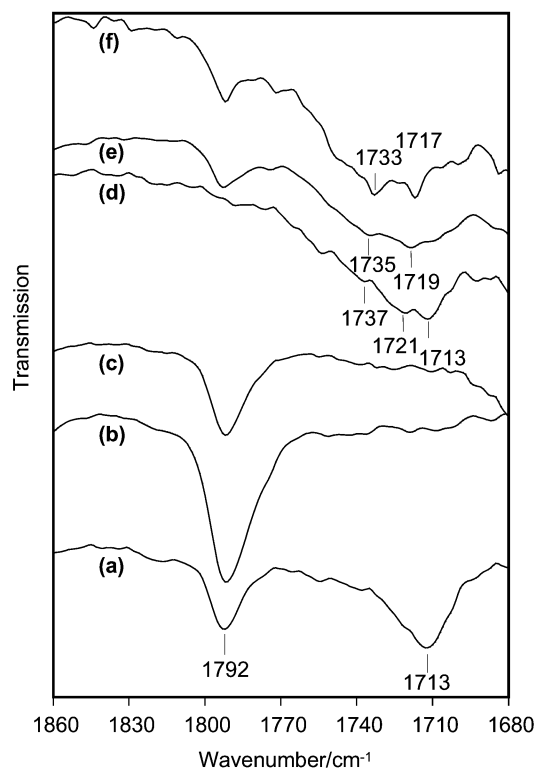
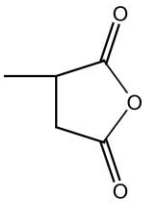
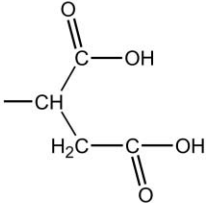
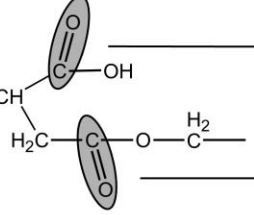


Fig. 1 IR spectra of MPE (a), dried MPE (b), UM composite (c), MC mixture (d), dried MC mixture (e), and MC composite (f).

proceeds between high-crystalline cellulose and MPE in a solid state, as clearly demonstrated by the results of the MC mixture. This suggests strongly that the activation of cellulose by milling is probably the primary cause of the formation of such reactive OH groups on cellulose, which are free from hydrogen bonding with each other, and thus can yield ester bonds with MPE.

Table 1 Assignment of IR bands

Functional group	Wavenumber/cm ⁻¹
	1792
	1713
	1717-1721 1733-1737

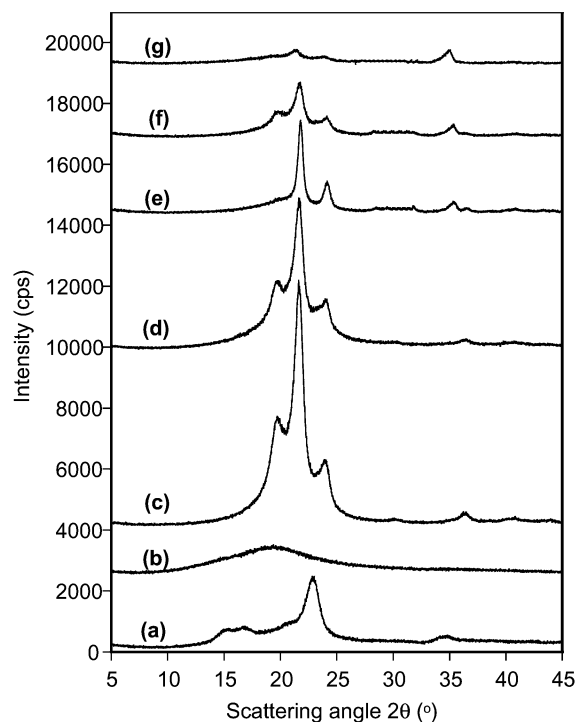


Fig. 2 X-Ray diffractograms of original cellulose (a), milled cellulose (b), MPE (c), UM composite (d), MC mixture (e), MC composite (f), and the sample after removing non-bonded MPE from the MC composite with xylene (g).

The XRD patterns of the UM composite, the MC mixture, and the MC composite are shown in Fig. 2. Milled cellulose is amorphous, completely different from the original cellulose, which has the crystalline structure of cellulose and a crystallinity of 93%.¹³ The MC composite exhibits a significant decrease in crystallinity of MPE, compared to the UM composite. Fig. 2g shows that MPE chains bonded on to cellulose particles are in an almost amorphous state, suggesting that the bonded chains are in a disordered state that prevents the crystallization of MPE.

On the basis of the aforementioned results, we can describe a mechanism for the compounding of crystalline cellulose with MPE under milling, as shown in Fig. 3: (1) activation of cellulose produces reactive OH groups, and (2) reaction of the OH groups with MPE yields ester bonds between cellulose and MPE. Therefore the activation of cellulose is essential for the compounding of crystalline cellulose with MPE through ester bonds.

Thermal and mechanical properties of the UM and MC composites are shown in Table 2. The MC composite exhibits a lower melting enthalpy and a lower thermal expansion coefficient than does the UM composite, consistent with the lower crystallinity of MPE in the MC composite than in the UM composite (Fig. 2), implying the stronger interactions between cellulose and MPE in the MC composite. The MC composite exhibits almost the same tensile strength as, but a much greater elongation than, the UM composite. The Izod impact strength of the MC composite is surprisingly enhanced by 173%. This indicates that the mechanochemical method can greatly improve the toughness¹⁴ and ductility of the MC composite, probably as a result of the formation of an interphase between cellulose particles and the MPE matrix, which can alleviate any external stress or energy.

In conclusion, the milling of crystalline cellulose with MPE yields a novel composite with ester bonds between OH groups of the cellulose and maleic anhydride groups of MPE, which exhibits much more improved toughness and ductility.

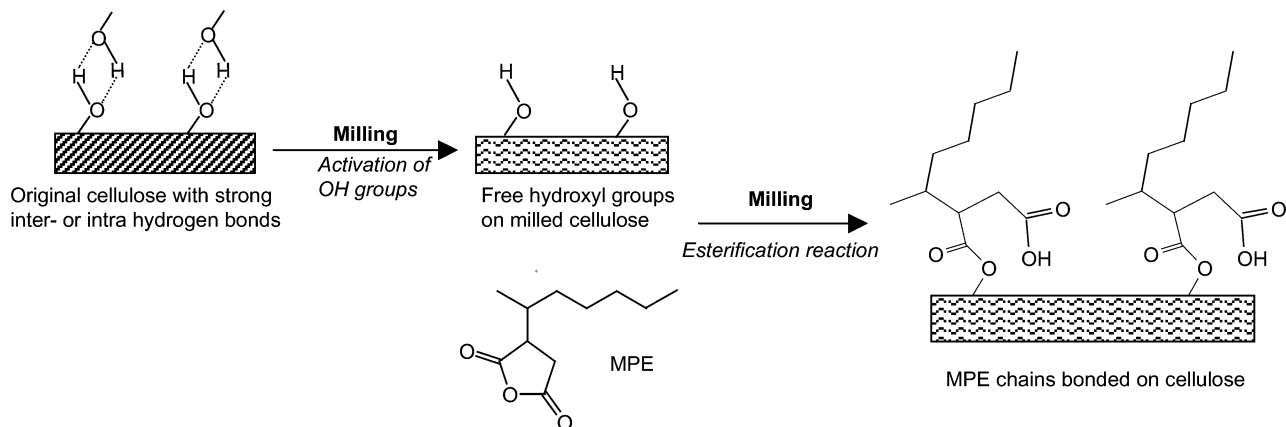


Fig. 3 A proposed mechanism for the mechanochemical formation of MPE chains bound on cellulose.

Table 2 Thermal and mechanical properties of the UM and MC composites

	Thermal properties		Mechanical properties		
	Melting enthalpy ^a /J g ⁻¹	Linear expansion coefficient ^b /mm mm ⁻¹ °C ⁻¹	Tensile strength ^c /MPa	Tensile elongation ^c (%)	Izod impact strength ^d /kJ m ⁻²
MPE	139.6	36.2×10^{-5}	19.6	>500	No break
UM composite	97.0	27.6×10^{-5}	23.9	32	9.3
MC composite	87.2	23.4×10^{-5}	24.1	73	25.4

^aThe values were determined from differential scanning calorimetry (DSC) at a heating rate of 5 °C min⁻¹ with a Perkin-Elmer Pyris 1 DSC apparatus. ^bThe values were determined from thermal mechanical analysis (TMA) at a heating rate of 2 °C min⁻¹ with a Perkin-Elmer DMA 7e. ^cThe values were determined with a Shimadzu AG-100A tensile tester at a strain speed of 50 mm min⁻¹, according to Japan Standard Society, JIS K7113-1995 Testing method for tensile properties of plastics, 1995. ^dThe values were determined with a Yasuda No.258 impact tester with a hammer of 5.5 J, according to Japan Standard Society, JIS K7110-1984 Determination of Izod impact strength, 1984.

Notes and references

- A. K. Bledzki and J. Gassan, *Prog. Polym. Sci.*, 1999, **24**, 221.
- F. Zhang, H. Kabeya, R. Kitagawa, T. Hirotsu, M. Yamashita and T. Otsuki, *Chem. Mater.*, 1999, **11**, 1952.
- F. Zhang, T. Endo, R. Kitagawa, H. Kabeya and T. Hirotsu, *J. Mater. Chem.*, 2000, **10**, 2666.
- F. M. B. Coutinho, T. H. S. Costa and D. L. Carvalho, *J. Appl. Polym. Sci.*, 1997, **65**, 1227.
- C. Joly, M. Kofman and R. Gauthier, *J. Macromol. Sci., Pure Appl. Chem.*, 1996, **A33**, 1981.
- J. M. Felix and P. Gatenholm, *J. Appl. Polym. Sci.*, 1991, **42**, 609.
- P. Bataille, L. Ricard and S. Sapieha, *Polym. Compos.*, 1989, **10**, 103.
- R. Karnani, M. Krishnan and R. Narayan, *Polym. Eng. Sci.*, 1997, **37**, 476.
- J. M. Felix and P. Gatenholm, *Polym. Compos.*, 1993, **14**, 449.
- F. Zhang, T. Endo, W. Qiu, L. Yang and T. Hirotsu, *J. Appl. Polym. Sci.*, in the press.
- A fibrous powder with an average length and width of 300 and 20 μm, and a crystallinity of 93%.
- B. De Roover, M. Sclavons, V. Carlier, J. Devaux, R. Legras and A. Momtaz, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 829.
- T. Endo, F. Zhang, R. Kitagawa, T. Hirotsu and J. Hosokawa, *Polym. J.*, 2000, **32**, 182.
- Toughness is directly proportional to the multiplication of tensile strength and elongation.