All-Wood Biocomposites by Partial Dissolution of Wood Flour in 1-Butyl-3-methylimidazolium Chloride

Mitsuhiro Shibata, Kentaro Yamazoe, Masaya Kuribayashi, Yuto Okuyama

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan
Correspondence to: M. Shibata (E-mail: shibata@sky.it-chiba.ac.jp)

ABSTRACT: After cedar-derived wood flour (WF) and bark flour (BF) were mixed with 1-butyl-3-methylimidazolium chloride (BMIC) at 100°C, the obtained compounds with BMIC content 40 wt % were compression-molded at 210°C to give WF/BMIC and BF/BMIC composites, respectively. The BMIC contained in the composites was twice extracted with ethanol at 60°C to afford WF/BMIC-E and BF/BMIC-E biocomposites, which were subsequently annealed at 200°C for 24 h to produce WF/BMIC-A and BF/BMIC-A biocomposites. The Fourier transform infrared spectroscopic analysis revealed that WF has a higher content of cellulose and a lower content of lignin than BF does, and that the BMIC content diminished by the extraction process. The scanning electron microscopy analysis showed that woody particles joined together by the compression molding of WF/BMIC and BF/BMIC compounds, and that the extraction of BMIC roughened the surface and the annealing again smoothed the surface due to the fusion of the residual BMIC and woody particles. The XRD measurements indicated that the annealing enhanced the crystallinity of cellulose component. The tensile properties and 5% weight loss temperature of the biocomposites were considerably improved by the extraction of BMIC and further by the annealing. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The efficient utilization of lignocellulosic biomass is becoming increasingly important due to restricted availability of petrochemical resources as well as global heating warnings caused by carbon dioxide emission. Wood is widely used for building materials and furniture. However, most of the waste timbers from wrecking of wooded building and forest-thinning are simply incinerated to energy. Also, a massive outbreak of damaged cedar trees infected by *Cercospora sequoiae Ellis et Everhart* ("*Sugi-Mizogusare*" disease) which cannot be used as log and lumber is becoming a serious problem in Chiba, Japan.[1] Therefore, there is an increasing demand for new processes that could provide new means to use the waste lumbers and untapped wood in a more efficient manner, not only as a fuel but also as a regenerated structural material.

The main components of wood are cellulose, hemicellulose, and lignin. Cellulose microfibrils are assembled by a large amount of intramolecular and intermolecular hydrogen bonds.[2] This makes cellulose insoluble in water and most of organic solvents.[3] Although cellulose is mainly crystalline, hemicellulose, a polymer of various sugars such as xylose, arabinose, mannose, glucose, galactose, and glucuronic acid, is completely amorphous. Lignin is an irregular polymer composed of randomly crosslinked phenylpropanoid units and forms a three-dimensional network in which cellulose and hemicellulose fibers are embedded. Especially, wooden biomass has high lignin contents.[4] Therefore, wood is practically insoluble in almost solvents and does not melt by heating. The poor processability of wood has severely hampered the uses for various applications as thermoplastic polymers are put to.

As it was reported that some imidazolium-based ionic liquids (ILs) can dissolve cellulose,[3] many ILs are known to dissolve cellulose.[5–11] Furthermore, ILs turned out to dissolve lignin and lignocellulose.[12,13] This allows homogeneous chemical modifications of dissolved lignocelluloses[14–18] and purification of cellulose.[19–21] All-cellulose biocomposites by partial dissolution of cellulose in ILs have been already reported by some groups.[22,23] The preparation of synthetic wood composites by dissolution of cellulose, hemicellulose, and lignin in IL has been also reported.[24] However, all-wood biocomposites by partial dissolution of wood flour (WF) in IL has not yet been reported to the best of our knowledge.

This study describes the preparation of all-wood biocomposites by partial dissolution of cedar-derived WF in 1-butyl-3-methyli-midazolium chloride (BMIC), subsequent extraction of the IL, and then annealing. It is known that BMIC can dissolve wood chips partially.[8,12] The mechanical and thermal properties of the obtained all-wood biocompoistes are also investigated.

EXPERIMENTAL

Materials

BMIC was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). WF and bark flour (BF) were supplied by Kowa Technos, (Sammu-shi, Chiba, Japan), which are the xylem and bark of Sanbu cedar (Chiba, Japan) crushed into particles through 3 mm screen mesh, respectively. The supplied WF and BF were further pulverized for 5 min using a coffee mill (TK-9213S, Tsann Kuen Japan, Tokyo, Japan) to produce pulverized WF and pulverized BF. Their woody flours were dried at 110°C for 24 h before use. Sanbu cedar lumber was also supplied by Kowa Technos, Microcrystalline cellulose (MCC) powder with about 20 μm, lignin with low sulfonate content (average M_n ca. 10,000; average M_w ca. 60,000, total impurities 9 wt %; sulfur 4%), and xylan from birch wood (Fluka) were purchased from Sigma-Aldrich Japan K. K. (Tokyo, Japan).

Preparation of WF/BMIC and BF/BMIC Composites

A mixture of WF 4.00 g and BMIC 2.67 g was stirred for 10 min at 100°C. Approximately two-thirds volume of the compound was put on a set of three molds kept at 210°C, which is composed of a stainless steel plate ($250 \times 200 \times 2$ mm^3) with three rectangular holes (55×10 mm^2), a poly(tetrafluoroethyl-ene) film ($250 \times 200 \times 0.10$ mm^3) and a stainless steel plate ($250 \times 200 \times 3$ mm^3), piled in that order. Thereafter, a poly(-tetrafluoroethylene) film ($250 \times 200 \times 0.10$ mm^3) and a stainless steel plate ($250 \times 200 \times 3$ mm^3) were covered and compression-molded at pressure of 25 MPa and temperature of 210°C for 3 min. After a relief of the pressurization, residual one-third volume of the compound was added and again compression-molded at 25 MPa and 210°C for 10 min. The molds were cooled to room temperature, three rectangular specimens ($55 \times 10 \times 2$ mm^3) of PWF/BMIC sheet with BMIC content 40 wt % (WF/BMIC) were taken out of the molds. In a similar manner to WF/BMIC, BF/BMIC composites with BMIC content of 40 wt % (BF/BMIC) were prepared using BF instead of WF.

Extraction of BMIC from WF/BMIC and BF/BMIC Composites

The WF/BMIC composite ($55 \times 10 \times 2$ mm^3, 1.07 g) was heated at 60°C for 2 h in ethanol 200 mL. After the sheet taken out was again heated at 60°C for 2 h in a fresh ethanol 200 mL, the resulting sheet was dried *in vacuo* at 60°C for 24 h to produce an extracted WF/BMIC (WF/BMIC-E) biocomposite ($49 \times 8.9 \times 1.8$ mm^3, 0.68 g). As BMIC content of the original sheet was 40 wt %, that of WF/BMIC-E was calculated to be 5.9 wt % from the change of sample weight on the assumption that woody components are not extracted with ethanol. In a similar manner to WF/BMIC-E, an extracted BF/BMIC (BF/BMIC-E) biocomposite was prepared using BF/BMIC instead of WF/BMIC.

Annealing of WF/BMIC-E and BF/BMIC-E Biocomposites

The WF/BMIC-E biocomposite ($49 \times 8.9 \times 1.8$ mm^3, 0.68 g) sandwiched between two stainless steel plates ($250 \times 200 \times 3$ mm^3) was annealed at 200°C for 24 h in an electric oven to produce an annealed WF/BMIC-E (WF/BMIC-A) biocomposite ($50 \times 9.0 \times 1.5$ mm^3, 0.68 g). The BMIC content did not substantially change between WF/BMIC-E and WF/BMIC-A. In a similar manner to WF/BMIC-A, an annealed BF/BMIC-E (BF/BMIC-A) biocomposite was prepared using BF/BMIC-E instead of WF/BMIC-E.

Measurements

Photographs of the compounds were took by IXY 930IS digital camera (Canon, Tokyo, Japan). Fourier transform infrared (FTIR) spectra were measured on a FTIR 8100 spectrometer (Shimadzu, Kyoto, Japan) by KBr or ATR method. X-ray diffraction (XRD) analysis was performed at ambient temperature on a Rigaku (Tokyo, Japan) RINT-2100 X-ray diffractometer, using Cu Kα radiation (wavelength, $\lambda = 0.154$ nm) at 40 kV and 14 mA. All scans were in the range $2° \leq 2\theta \leq 40°$ at a scanning rate of $1.0°$ min^{-1} and a step size of 0.01°. The relative amount of crystallinity was evaluated using Segal's crystallinity index CrI.[25] It is defined as:

$$CrI = (I - I')/I \qquad (1)$$

where, I is the amplitude of the (200) diffraction peak (typically for 2θ 22°) and I' is the amplitude of the plot at $2\theta = 18°$. The latter value (I') is used as an indicator of the intensity of amorphous cellulose. The 5% weight loss temperature was measured on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 20°C/min in a nitrogen atmosphere. Tensile test of the rectangular specimen (length 55–47 mm, width 10–8 mm, thickness 2–1.5 mm) was performed at 25°C using an Autograph AG-I (Shimadzu). Span length and testing speed was 25 mm and 10 mm/min. Five specimens were tested for each set of samples, and the mean values and the standard deviation were calculated. The particle size distribution of WF and BF was measured by a sieve analysis using testing sieves with 24, 35, 60, 100, 250, and 400 mesh (Tyler) of Tokyo Screen (Tokyo, Japan) equipped a mechanical sieve shaker. The morphology of the composite samples was observed by scanning electron microscopy (SEM), using a JSM-6300 machine (JEOL, Tokyo, Japan). The surface of the composite sample was sputter coated with gold to provide enhanced conductivity.

RESULTS AND DISCUSSION

Characterization and Morphology of WF/BMIC and BF/BMIC Composites

The solubility of cellulose pulp[3] and thermomechanical Southern pine pulp[12] in BMIC is reported to be 10 wt % at 100°C and 5 wt % at 130°C, respectively. As we intended to prepare a fiber-reinforced composite where most of the woody fibers are remaining in the composite, a weight ratio of WF (or BF) to BMIC was fixed to 60/40 in this study, which is much higher than the ratio necessary to dissolve WF (or BF). The prepared WF/BMIC 60/40 and BF/BMIC 60/40 compounds were powdery at room temperature. Figure 1 shows the photographs of the WF/BMIC and BF/BMIC compounds pressed at various
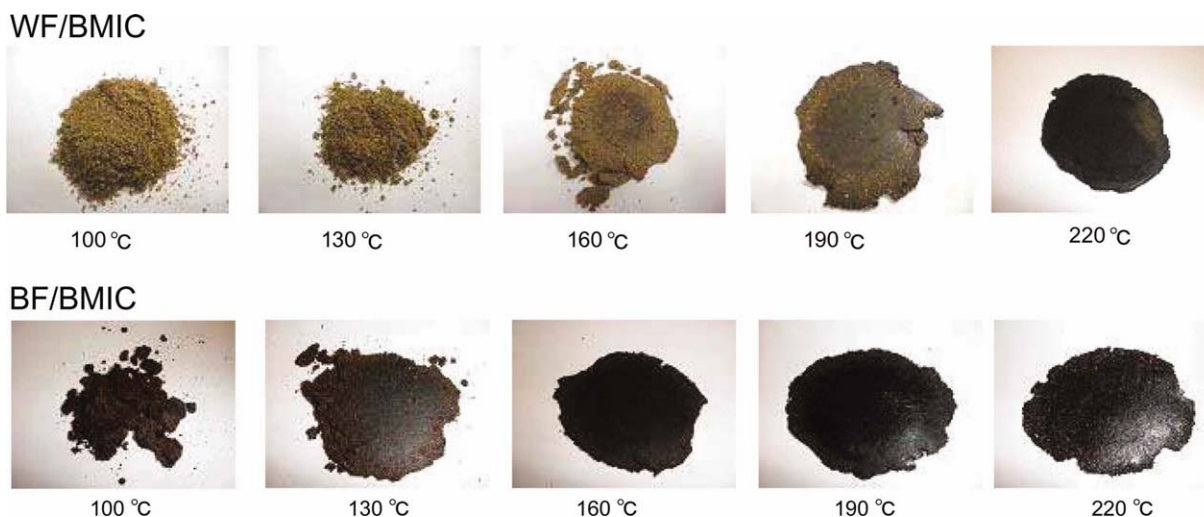
Figure 1. Photographs of the WF/BMIC and BF/BMIC compounds pressed at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperatures. The prepared WF/BMIC 60/40 and BF/BMIC 60/40 compounds were powdery at room temperature. The WF particles for WF/BMIC started to adhere at 160°C, and almost particles joined together between 190 and 220°C. On the other hand, the particles for BF/BMIC started to adhere at 130°C, and almost particles joined together at around 190°C. As deep coloration was observed at 220°C or above, the temperature of compression molding was fixed to 210°C.

Figure 2 shows the FTIR spectra of WF and BF compared with those of MCC, lignin, and xylan. MCC and xylan had characteristic absorption peaks at around 1000–1200 cm^{-1} based on the vibrations of C—OH, C—O—C and pyranose ring.[26–28] Lignin had a characteristic absorption peak at around 1600 cm^{-1} ascribed to aromatic ri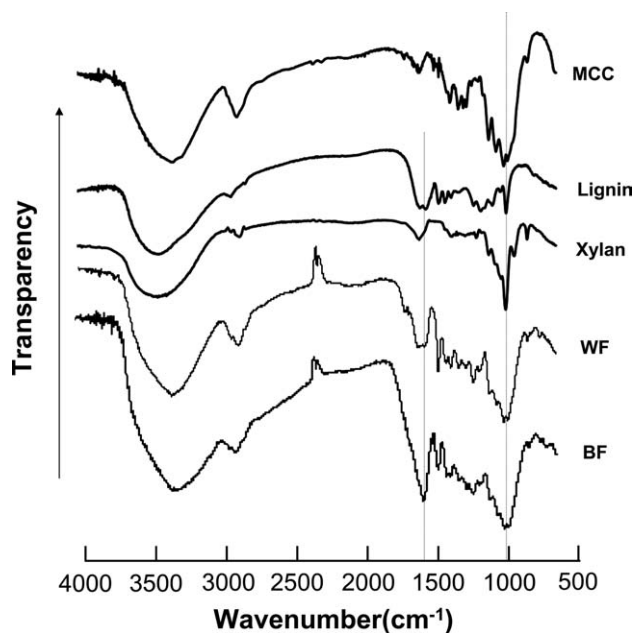ng framework vibration of polyphenol moieties.[29,30] The spectra of WF and BF are basically overlapping of those of MCC, lignin, and xylan. What the absorption peak intensity at around 1600 cm^{-1} relative to the peaks at around 1200–1000 cm^{-1} for BF is stronger than that for WF indicates that BF has a higher content of lignin than WF does.

Figure 3 shows the FTIR spectra of WF/BMIC, WF/BMIC-E, and WF/BMIC-A compared with those of WF and BMIC. BMIC exhibited an intense peak at 1167 cm^{-1} ascribed to C—N stretching vibration. WF/BMIC also showed the C—N stretching vibration peak, indicating that WF and BMIC are certainly compounded. Although the peak based on C—N bond in the spectrum of WF/BMIC-E diminished relative to that of WF/
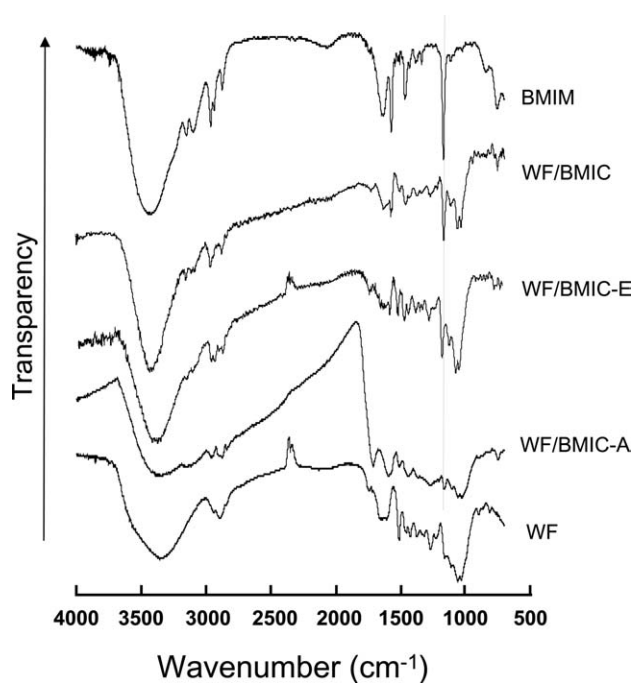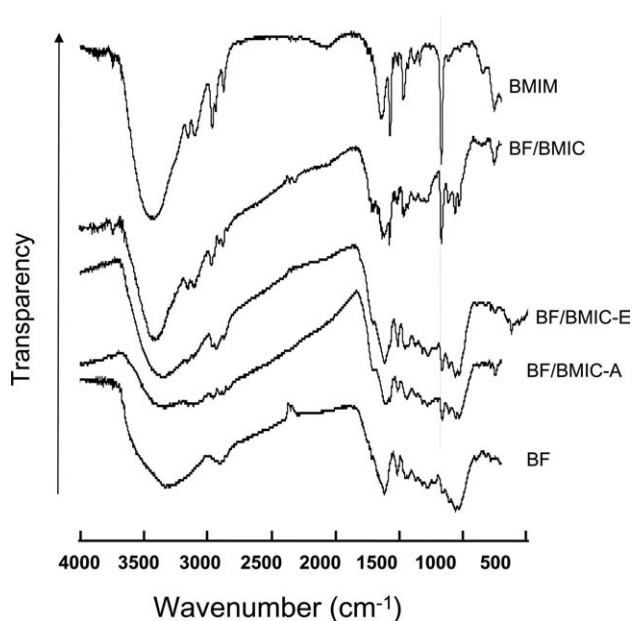

Figure 2. FTIR spectra of MCC, lignin, xylan, WF, and BF.

Figure 3. FTIR spectra of BMIC, WF/BMIC composites, and WF.

Figure 4. FTIR spectra of BMIC, BF/BMIC composites, and BF.

Figure 6. Particle size distributions of WF and BF.

BMIC, the peak did not disappear, indicating considerable amounts of BMIC is eliminated in agreement with the BMIC content of WF/BMIC-E (5.9 wt %) calculated from the change of weight. There was little difference on the IR spectral pattern between WF/BMIC-E and WF/BMIC-A. The FTIR spectra of BF-based composites showed a similar trend to those of the WF-based composites, as are shown in Figure 4.

Figure 5 shows XRD patterns of WF-based and BF-based composites compared with MCC. WF and WF-based composites had the prominent cellulose I peak at 22°, denoting the (200) reflection, however, the characteristic (1$\bar{1}$0) and (110) peaks (2θ
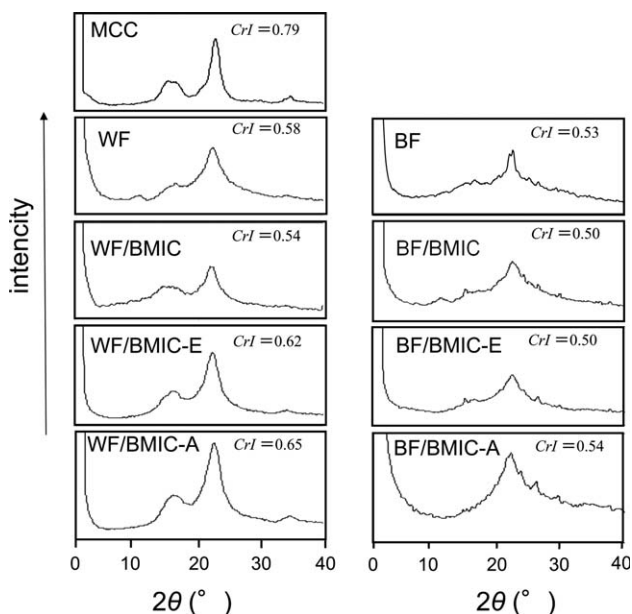

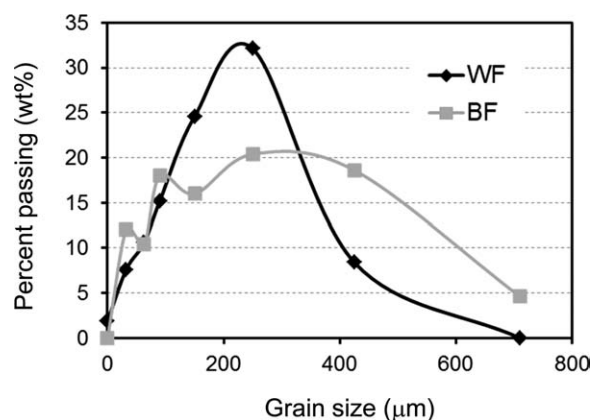**Figure 5.** XRD profiles of MCC, WF, WF/BMIC composites, BF, and BF/BMIC composites.

between 15° and 17°) are not distinct as those in MCC but combine into one broad peak at 16°. The fact that the XRD peak at around 22° ascribed to cellulose I structure did not shift for all the WF-based composites indicates that cellulose I structure is kept during a partial dissolution in BMIC, extraction, and annealing process. It is known that the crystalline structure is transformed from cellulose I to cellulose II in case of the cellulose regenerated from ILs.[23,30,31] However, it is reported that cellulose II structure is not formed in case of wood powder regenerated from the wood dissolved in ILs in consistent with our result.[12] In case of WF-based materials, the value of CrI decreased from 0.58 to 0.54 by a partial dissolution of WF in BMIC, increased to 0.62 by the extraction of BMIC with ethanol, and then increased to 0.65 by annealing. This result suggests that some amounts of crystalline cellulose precipitated from an isotropic sol or gel of cellulose and BMIC after the extraction of BMIC, and some of the residual amorphous cellulose crystallized during the annealing at 200°C in a similar manner to the removal of solvent and subsequent annealing for an isotropic solution of general semicrystalline polymer. On the other hand, BF and BF-based composites showed broader XRD peaks than the corresponding WF-based materials, probably due to the presence of needle-like particles and a wider particle size distribution for BF. Although the value of CrI did not increase by the extraction treatment of BF/BMIC, the value increased from 0.50 to 0.54 by annealing.

Figure 6 shows the particle size distribution of WF and BF. Although the particle size with the largest weight fraction is 250–425 μm for both WF and BF, BF had a wider size distribution than WF. Figure 7 shows SEM microphotographs of WF- and BF-based materials. WF contained some rectangular particles of 0.6–0.2 mm in length and 0.2–0.1 mm in width. BF contained some needle-like particles of 1.0–0.5 mm in length and less than 0.1 mm in width. It is obvious that wood particles of WF/BMIC and BF/BMIC partially dissolved in BMIC and adhere to each other. However, it appeared that the adhesion of some large particles of WF is not good. The surface of BF/BMIC was smoother than that of WF/BMIC in agreement with the fact that BF has a higher fraction of fine particles (<100 μm) than WF does. The surface of the composites became a little rougher by the extraction of BMIC for both the
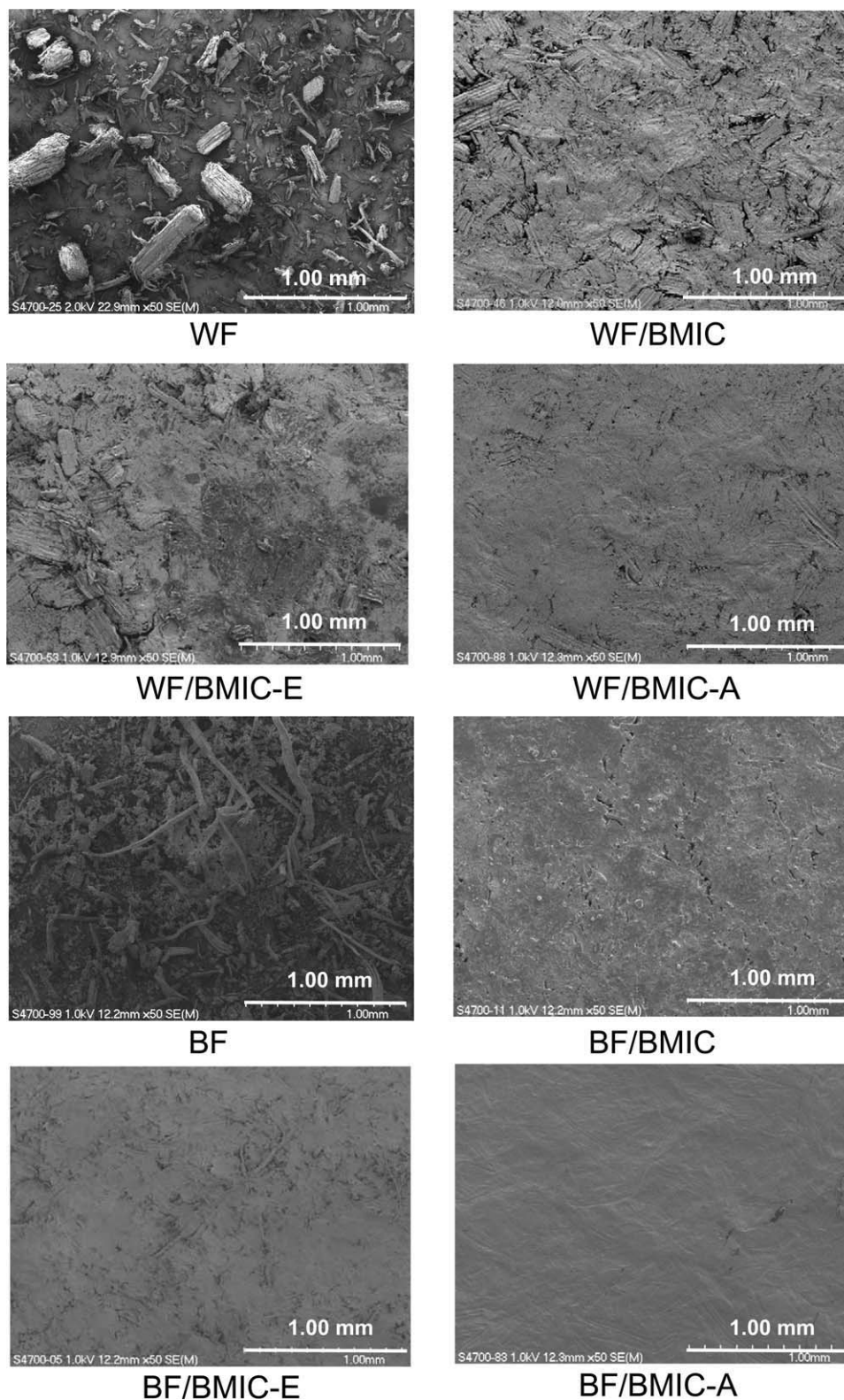
Figure 7. SEM microphotographs of WF, WF/BMIC composites, BF, and BF/BMIC composites.

WF/BMIC-E and BF/BMIC-E. The surfaces of WF/BMIC-A and BF/BMIC-A were much smoother than those of WF/BMIC-E and BF/BMIC-E. It is suggested that the wood particles further adhered by the action of residual BMIC in WF/BMIC-E and BF/BMIC-E during the annealing at 200°C for 24 h. When WF/BMIC composite with BMIC content 30 wt % was similarly
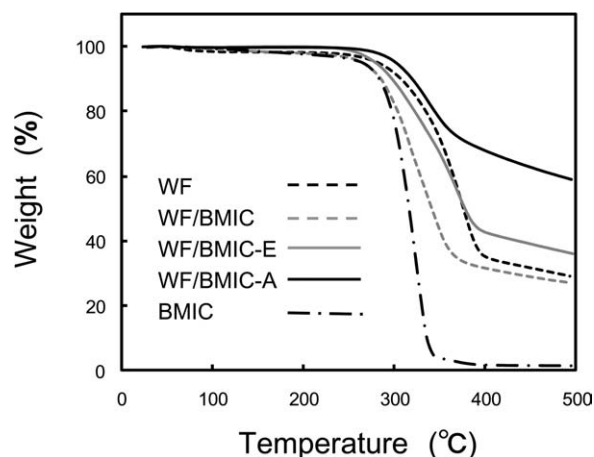
Figure 8. TGA curves of WF, WF/BMIC composites, and BMIC.

prepared, its surface was much rougher than that of the composite with BMIC content 40 wt % (WF/BMIC), as is not shown in the figure. When the BMIC content is 50 wt %, although the surface of the composite with BMIC was as smooth as that of WF/BMIC, the composite after extraction of BMIC had considerable amount of cracks. As a result, the best result was obtained when BMIC content is 40 wt %.

Thermal and Tensile Properties of WF/BMIC and BF/BMIC Composites

Figure 8 shows TGA curves of WF, BMIC, and the WF/BMIC composites. Their 5% weight loss temperatures (T_ds) are also summarized in Table I. The T_ds of WF/BMIC and BF/BMIC were lower than those of WF and BF, respectively, corresponding to the fact that T_d of BMIC is lower than those of WF and BF. The T_ds of WF/BMIC-E and BF/BMIC-E were higher than those of WF/BMIC and BF/BMIC, respectively, because the former contain lower BMIC content than the latter. Furthermore, WF/BMIC-A and BF/BMIC-A showed higher T_ds than WF/BMIC-E and BF/BMIC-E. As the former composites have higher crystallinity of cellulose than the latter composites, this result is in consistent with the already reported results that an increase of crystallinity for cellulose causes a rise of the thermal degradation temperature.[32–34]

Tensile properties of WF/BMICs and BF/BMICs are shown in Figure 9. The BF/BMIC had higher tensile strength, modulus, and elongation at break than WF/BMIC. This result should be attributed to the fact that WF/BMIC has much more cracks

Table I. 5% Weight Loss Temperatures of WF, BF, and the WF/BMIC and BF/BMIC Composites

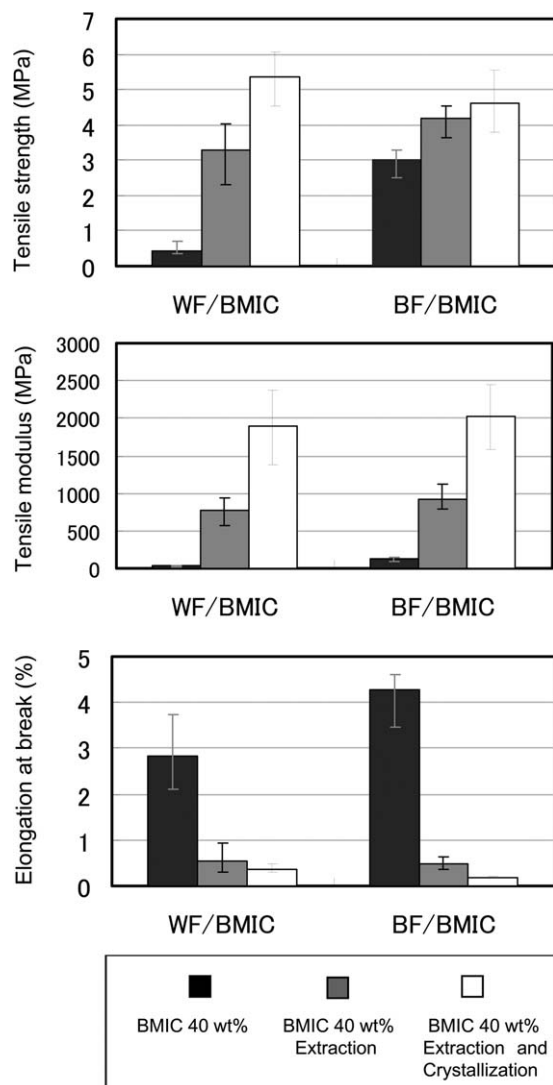| Sample	5% Weight loss temperature (°C)	Sample	5% Weight loss temperature (°C)
WF	293	BF	283
WF/BMIC	271	BF/BMIC	276
WF/BMIC-E	280	BF/BMIC-E	291
WF/BMIC-A	303	BF/BMIC-A	314
BMIC	272		

Figure 9. Tensile properties of WF/BMIC composites, and BF/BMIC composites.

than BF/BMIC as is shown in Figure 6. The tensile strength and modulus considerably increased by the extraction of BMIC and further increased by the annealing treatment for both the WF- and BF-based composites. Although the tensile strengths of WF/BMIC-A (5.3 MPa) and BF/BMIC-A (4.6 MPa) were lower than those of native cedar wood (20.8 MPa), the tensile moduli of WF/BMIC-A (1.9 GPa) and BF/BMIC-A (2.0 GPa) were higher than that of cedar wood (1.0 GPa). This result indicates that all-wood biocomposites in this study are more stiff and brittle materials than the native wood. If it is possible to prepare the biocomposite with much less microcracks by optimizing the particle size of WF and BF, BMIC content, and compression molding condition, the biocomposite with a much higher strength should be obtained. At the present stage, the WF(BF)/BMIC-A biocomposites contain relatively expensive BMIC of about 6 wt %. We are now under investigation on the condition of extraction and recycling of BMIC to develop the biocomposites with high cost performance.

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CONCLUSIONS

The WF/BMIC and BF/BMIC composites were prepared by the compression molding of mixtures of WF and BMIC, and BF and BMIC at 210°C. The BMIC contained in the WF/BMIC and BF/BMIC was twice extracted with ethanol at 60°C to afford WF/BMIC-E and BF/BMIC-E, which were subsequently annealed at 200°C for 24 h to produce WF/BMIC-A and BF/BMIC-A. The FTIR analysis revealed that WF has a higher content of cellulose and a lower content of lignin than BF does, and that the BMIC content diminished by the extraction process. The SEM analyses showed that woody particles joined together by the compression molding of WF/BMIC and BF/BMIC compounds, and that the extraction of BMIC roughened the surface and the annealing again smoothed the surface due to the fusion of the residual BMIC and woody particles. The XRD measurements indicated that the annealing enhanced the crystallinity of cellulose component. The tensile strength, tensile modulus, and 5% weight loss temperature of the biocomposites increased by the extraction of BMIC and further increased by the annealing.

REFERENCES

1. Nakagawa, S. *Shinrinboeki (Forest Pests)* **2000,** *49*, 204.

2. Zhbankov, R. G. *J. Mol. Struct.* **1992,** *270*, 523.

3. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002,** *124*, 4974.

4. Huber, G. W.; Iborra, S. Corma, A. *Chem. Rev.* **2006,** *106*, 4044.

5. Fukaya, Y.; Hayashi, K.; Wada, M.; Ohno, H. *Green Chem.* **2008,** *10*, 44.

6. Fukaya, Y.; Sugimoto, A.; Ohno, H. *Biomacromol.* **2006,** *7*, 3295.

7. Xie, H. L.; Shi, T. J. *Holzforschung* **2006,** *60*, 509.

8. Zavrel, M.; Bross, D.; Funke, M.; Büchs, J.; Spiess, A. C. *Biores. Technol.* **2009,** *100*, 2580.

9. Zhang, H.; Wu, J.; Zhang, J.; He, J. S. *Macromolecules* **2005,** *38*, 8272.

10. Zhao, H.; Baker, G. A.; Song, Z. Y.; Olubajo, O.; Crittle, T.; Peters, D. *Green Chem.* **2008,** *10*, 696.

11. Mäki-Arvela, P.; Anugwom, I.; Virtanen, P.; Sjöholm, R.; Mikkola, J. P. *Indust.Crops Products* **2010,** *32*, 175.

12. Kilpeläinen, I.; Xie, H.; King, A.; Granstrom, M.; Heikkinen, S.; Argyropoulos, D. S. *J. Agric. Food. Chem.* **2007,** *55*, 9142.

13. Pu, Y. Q.; Jiang, N.; Ragauskas, A. J. *J. Wood Chem. Technol.* **2007,** *27*, 23.

14. Barthel, S.; Heinze, T. *Green Chem.* **2006,** *8*, 301.

15. Heinze, T.; Schwikal, K.; Barthel, S. *Macromol. Biosci.* **2005,** *5*, 520.

16. Schlufter, K.; Schmauder, H. P.; Dorn, S.; Heinze, T. *Macromol. Rapid Commun.* **2006,** *27*, 1670.

17. Xie, H.; King, A.; Kilpelainen, I.; Granstrom, M.; Argyropoulos, D. S. *Biomacromolecule* **2007,** *8*, 3740.

18. Wu, J.; Zhang, J.; Zhang, H.; He, J. S.; Ren, Q.; Cuo, M. *Biomacromolecule* **2004,** *5*, 266.

19. Fort, D. A.; Swatloski, R. P.; Moyna, P.; Rogers, R. D.; Moyna, G. *Chem. Commun.* **2006,** 714.

20. Bagheri, M.; Rodiguez, H.; Swatloski, R.P.; Spear, S. K.; Daly, D.T.; Rogers, R. D. *Biomacromolecule* **2008,** *9*, 381.

21. Turner M. B; Spear S. K.; Holbrey J. D.; Rogers R. D. *Biomacrmolecule* **2004,** *5*, 1379.

22. Duchemin, B. J. C.; Mathew, A. P.; Oksman, K. *Compos. Part A* **2009,** *40*, 2031.

23. Ma, H.; Zhou, B.; Li, H. S.; Li, Y.Q.; Ou, S. Y. *Carbohydr. Polym.* **2011,** *84*, 381.

24. Simmons, T. L.; Lee, S. H.; Miao, J.; Miyauchi, M.; Park, T.-J.; Bale, S. S.; Pangule, R.; Bult, J.; Martin, J. G.; Dordick, J. S.; Linhardt, R. J. *Wood Sci. Technol.* **2011,** *45*, 719.

25. Segal, I.; Creely, J. J.; Martin, A. E., Jr.; Conrad, C. M. *Text. Res. J.* **1959,** *29*, 786.

26. Kacuráková, M.; Ebringerová, A.; Hirsch, J.; Hromádková, Z. J. *Sci. Food Agric.* **1994,** *66*, 423.

27. Kacuráková, M.; Capek, P.; Sasinková, V.; Wellner, N.; Ebringerová, A. *Carbohydr. Polym.* **2000,** *43*, 195.

28. Lan, W.; Liu, C.-F.; Yue, F.-X.; Sun, R.-C.; Kennedy, J. F. *Carbohydr. Polym.* **2011,** *86*, 672.

29. Kacuráková, M.; Wellner, N.; Ebringerová, A.; Hromádková, Z.; Wilson, R. H.; Belton, P. S. *Food Hydrocolloids* **1999,** *13*, 35.

30. Sun, N.; Rahman, M.; Qin, Y.; Maxim, M. L.; Rodríguez, H.; Rogers, R. D. *Green Chem.* **2009,** *11*, 646.

31. Zhai, W.; Chen, H. Z.; Ma, R. Y. *Beijing Huagong Daxue Xuebao. Ziran Kexueban* **2007,** *34*, 8272.

32. Kadakawa, J.; Murakami, M.; Kaneko, Y. *Compos. Sci. Technol.* **2008,** *68*, 493.

33. Kadakawa, J.; Murakami, M.; Kaneko, Y. *Carbohydr. Res.* **2008,** *343*, 769.

34. Wu, R. L.; Wang, X. L; Li, F.; Li, H. Z.; Wang, Y. Z. *Biores. Technol.* **2009,** *100*, 2569.