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# All-cellulose and all-wood composites by partial dissolution of cotton fabric and wood in ionic liquid

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ABSTRACT

After cotton fabric (CF) and hinoki lumber (HL) were dipped in 1-butyl-3-methylimidazolium chloride (BMIMCl) at 100 °C, the BMIMCl-impregnated CF and HL were hot-pressed to give CF-BMIMCl and HL-BMIMCl composites, respectively. The BMIMCl contained in the composites was removed by Soxhlet extraction, and subsequently annealed to produce all-cellulose and all-wood composites (CF-A and HL-A). The SEM analyses revealed that cellulose fibers combined together for CF-A and the surface of HL-A became smooth, respectively. The XRD measurements indicated that the crystallinity index of cellulose component decreased by the hot press, increased by the extraction, and further increased by the annealing for both the composites. The tensile modulus of CF-A increased with increasing pressure of hot-press. Although tensile strength of HL-A was a little lower than that of original HL, tensile modulus of the former was much higher than that of the latter.



## 1. Introduction

Biocomposites which are composed of matrix resins and natural fibers such as wood and plant fibers have recently gained much attention due to their low cost, environmental friendliness, and their potential to compete with man-made fiber-reinforced composites (Bledzki & Gassan, 1999; John and Thomas, 2008; Mohanty, Misra, & Hinrichsen, 2000). Furthermore, the concept of using bio-based polymers as matrix resins for biocomposites is becoming increasingly important due to dwindling petroleum resources (Faruk, Bleszki, Fink, & Sain, 2012; Koronis, Silva, & Fontul, 2013). Nonetheless, the use of such biocomposites termed as green composites has been limited due to their lower mechanical and thermo-physical properties compared to the synthetic composites.

Recently, a new class of cellulose-based green composites which utilizes cellulose for both the matrix and reinforcement has been investigated. Single-polymer composites based on cellulose are referred to as "all-cellulose composites" (ACCs) and are able to overcome the above drawbacks due to a superior mechanical properties of the matrix cellulose and strong interfacial bonding (Huber, Bickerton, Müssig, Pang, & Staiger, 2012a; Huber, Pang, & Staiger, 2012b; Nishino, Matsuda, & Hirano, 2004). An ACC is synthesized either (i) from completely dissolved cellulose combined with undissolved cellulose and subsequent regeneration to form the matrix phase or (ii) by partial dissolution of the cellulose surface followed by regeneration to form a matrix phase. Ionic liquids (ILs) are loosely defined as salts with a melting temperature lower than 100 °C. Some ILs are known to be powerful dissolving solvents for cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002), lignin (Pu, Jiang, & Ragauskas, 2007) and wood (Kilpeläinen et al., 2007; Sun et al., 2009; Zavrel, Bross, Funke, Büchs, & Spiess, 2009) with important commercial advantages including high dissolution capacity, negligible vapor pressure, ease of recycling, thermal stability and no requirement for pre-treatment or activation of the substrate. The utilization of IL to the second preparation method of ACC has been investigated by some groups using 1-butyl-3-methylimidazolium chloride (BMIMCl) to produce ACC films from microfibrillated cellulose and filter paper (Duchemin, Mathew, & Oksman, 2009), and using 1-butyl-3-methylimidazolium acetate (BMIMAc) to produce 4-layered ACC laminates from linen and rayon textiles (Huber et al., 2012a; Huber et al., 2012b). Although all-wood green composites using ILs and other solvents had not yet been reported, we have much recently reported the all-wood green composites by partial dissolution of wood flour in BMIMCl (Shibata, Yamazoe, Kuribayashi, & Okuyama, 2013). However, the tensile strength and modulus (5.3 MPa and 1.9 GPa) were not so improved as compared with those of the original cedar wood (20.8 MPa and 1.0 GPa) and those of the 4-layered ACC laminates from linen (65.0 MPa and 1.1 GPa). The present study deals with all-wood composites prepared by hot press of BMIMCl-impregnated hinoki lumber (HL),

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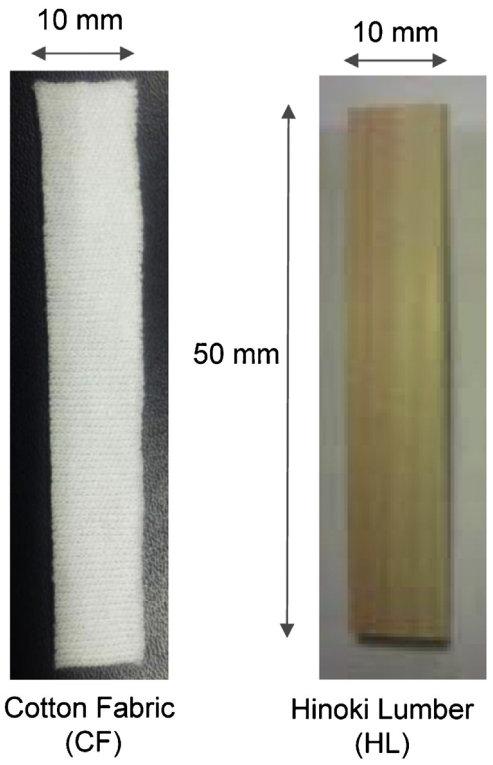


**Fig. 1.** Photographs of CF and HL specimens used in this study.

subsequent extraction of the IL, and then annealing. This study also describes new ACCs using cotton fabric (CF) and BMIMCl. Cotton is a seed fiber which has a higher content of cellulose than flax which is a bast fiber. Typical cellulose contents of cotton and flax are 82.7 and 71%, respectively (Mohanty et al., 2000). The mechanical and thermal properties of the obtained all-wood composites were investigated as compared with the CF-based ACCs.

## 2. Experimental procedures

### 2.1. Materials

1-Butyl-3-methylimidazolium chloride (BMIMCl) was purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). A cotton fabric (CF) of a twill 3/1 weave, a surface mass of 400 g m$^{-2}$ and thickness 0.91 mm was purchased from a local dry-goods store (Yuzawaya Co. Ltd., Narashino, Japan). The lumber of hinoki cypress (*Chamaecyparis obtusa*) (HL) with a thickness of 2.0 mm was purchased from a local home center (Keiyo D2 Co. Ltd., Funabashi, Japan). Fig. 1 shows the photographs of cut specimens of CF and HL. Cellulose (microcrystalline powder, ca. 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).

### 2.2. Preparation of CF composites

After CF with a thickness of 0.91 mm was dried at 100 °C for 24 h, the fabric was cut into a size of 50 mm × 50 mm (1.00 g). The cut CF was dipped into a liquid of BMIMCl at 100 °C for 30 min. The BMIMCl-impregnated CF (CF/BMIMCl) was hot-pressed at a temperature of 150 °C and a pressure of 5, 10 or 15 MPa for 30 min to produce a white BMIMCl-containing CF composite (CF-BMIMCl). The weight of the CF-BMIMCls obtained at 5, 10 and 15 MPa was 1.36, 1.23 and 1.20 g, whose values correspond to the BMIMCl content of 26.5, 18.7 and 16.7%, respectively.

The BMIMCl contained in CF-BMIMCl was removed with acetonitrile at 82 °C for 2 h using a Soxhlet extraction apparatus and then dried at 100 °C for 24 h to give a Soxhlet-extracted CF-BMIMCl composite (CF-S). The weight of the CF-Ss obtained from CF-BMIMCls at 5, 10 and 15 MPa was 1.00, 1.01 and 0.98 g, indicating that the BMIMCl contained in CF-BMIMCl was completely eliminated.

The obtained CF-S was sandwiched between two stainless steel plates and heated at 150 °C for 24 h in an electric oven in order to enhance the crystallinity of cellulose component to produce an all-cellulose composite prepared from CF (CF-A). No weight change by the annealing was observed for all the CF-As.

### 2.3. Preparation of HL composites

After HL with a thickness of 2.0 mm was dried at 100 °C for 24 h, the lumber was cut into a size of 50 mm × 10 mm. The HL specimen (0.45 g) was dipped into a liquid of BMIMCl at 100 °C for 30 min. The BMIMCl-impregnated HL (HL/BMIMCl) was hot-pressed at a temperature of 210 °C and a pressure of 5, 10 or 15 MPa for 30 min to produce a dark brown BMIMCl-containing HL composite (HL-BMIMCl). The weight of the HL-BMIMCls obtained at 5, 10 and 15 MPa was 1.17, 1.17 and 1.18 g, whose values correspond to the BMIMCl content of 61.5, 61.5 and 61.9%, respectively.

The BMIMCl contained in HL-BMIMCl was removed with acetonitrile at 82 °C for 2 h using a Soxhlet extraction apparatus and then dried at 100 °C for 24 h to give a Soxhlet-extracted HL composite (HL-S). The weight of the HL-S was 0.45 g, indicating that the BMIMCl contained in HL-BMIMCl was completely eliminated.

The obtained HL-S was sandwiched between two stainless steel plates and heated at 210 °C for 24 h in an electric oven in order to enhance the crystallinity of cellulose component to produce an all-wood composite prepared from HL (HL-A). No weight change by the annealing was observed for HL-A.

### 2.4. Measurements

FT-IR spectra were measured on a FT-IR 8100 spectrometer (Shimadzu Co. Ltd., Kyoto, Japan) by KBr method. X-ray diffraction (XRD) analysis was performed at ambient temperature on a Rigaku RINT-2100 X-ray diffractometer at a scanning rate of 2.0° min$^{-1}$, using Cu Kα radiation (wavelength, λ = 0.154 nm) at 40 kV and 14 mA. All scans were in the range $2° \le 2\theta \le 40°$ 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* (Segal, Creely, Martin, & Conrad, 1959). It is defined as

$$CrI = \frac{I - I'}{I} \quad (1)$$

where $I$ is the amplitude of the (002) diffraction peak ($2\theta$ = 22.5–22.7°) 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 ($T_5$) was measured on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 20 °C min$^{-1}$ in a nitrogen atmosphere. Tensile tests of the rectangular specimens (length 50 mm, width 10 mm, thickness 2.0–0.4 mm) of CF-A, HL and HL-A were performed at 25 °C using an Autograph AG-I (Shimadzu Co. Ltd., Kyoto, Japan). Span length and testing speed was 25 mm and 10 mm min$^{-1}$. Five specimens were tested for each set of samples, and the mean values and the standard deviation were calculated. The morphology of the samples was observed by field emission-scanning electron microscopy (FE-SEM), using a Hitachi S-4700 machine (Hitachi High-Technologies Corporation, Japan). The surface of sample was sputter coated with gold to provide enhanced conductivity.

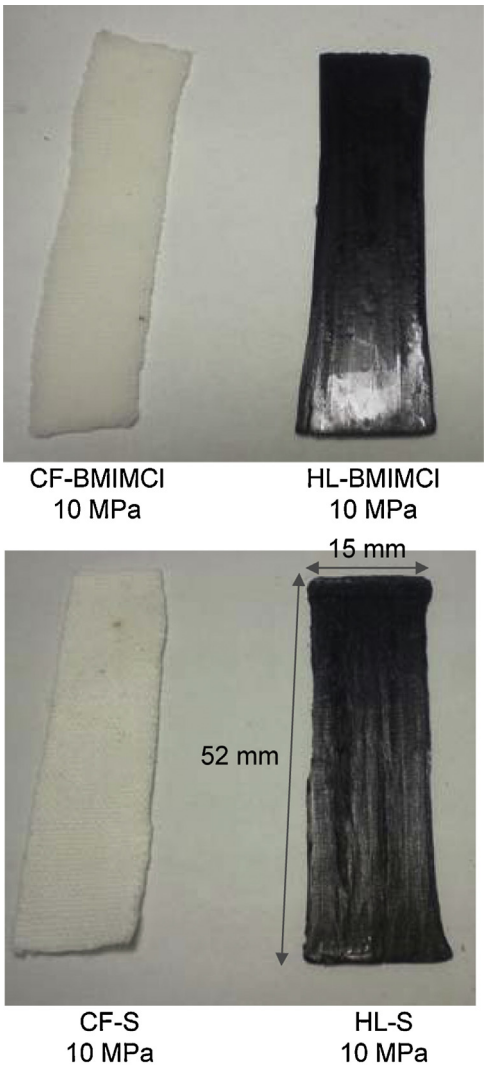


**Fig. 2.** Photographs of CF-BMIMCl, HL-BMIMCl, CF-S and HL-S prepared at the pressure of 10 MPa.

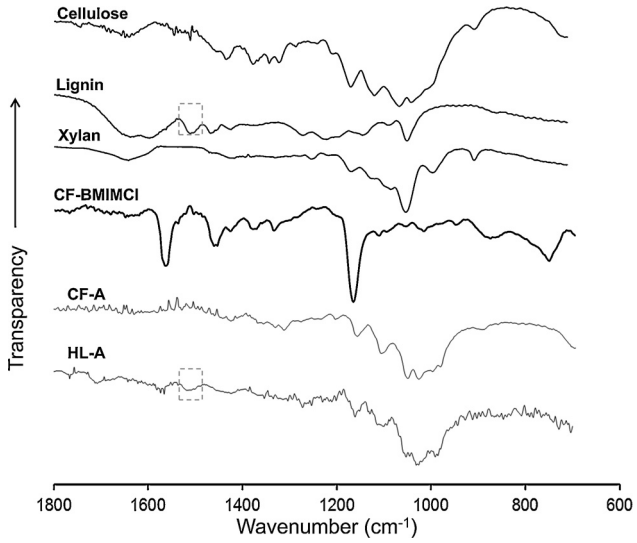


**Fig. 3.** FT-IR spectra of CF-BMIMCl, CF-A and HL-A compared with those of cellulose, lignin and xylan.

## 3. Results and discussion

### 3.1. Characterization and morphology of CF and HL composites

The cut specimens of CF and HL were dipped into excess BMIMCl at 100 °C, taken out, and then pressed at the temperatures of 150 and 210 °C to produce CF-BMIMCl and HL-BMIMCl, respectively. Pressure on the hot press was changed from 5 to 15 MPa. Although the BMIMCl content of CF-BMIMCl decreased with increasing pressure (5 MPa: 26.5%; 10 MPa:18.7%; 15 MPa:16.7%), that of HL-BMIMCl (ca. 62%) was little influenced by the pressure. Fig. 2 shows typical appearance of the CF-BMIMCl and HL-BMIMCl prepared at 10 MPa. The CF-BMIMCl was more rigid and transparent than the original CF. The surface of hinoki changed from unglazed yellowish brown to glossy dark brown by the hot press. The hot press of CF/BMIMCl at the temperatures lower and higher than ca. 150 °C resulted in the formation of a soft cloth with insufficient adhesion of the fibers and the formation of a very thin and translucent film, respectively. The wood surface of HL/BMIMCl started to flatten and colorize at around 200 °C on the hot press, and the temperature higher than 220 °C caused the formation of considerable voids due to some decomposition. The BMIMCl contained in CF-BMIMCl and HL-BMIMCl was removed by the extracted with acetonitrile to produce CF-S and HL-S, respectively. The surface of CF-S was more opaque and whiter than that of CF-BMIMCl, and that of HL-S became matted (Fig. 2). Annealing of CF-S and HL-S at 150 and 210 °C for 24 h produced CF-A and HL-A, respectively. There was little change in appearance of the specimens by the annealing treatment.

Fig. 3 shows FT-IR spectra of CF-BMIMCl, CF-A and HL-A compared with those of cellulose, lignin, and xylan. Cellulose and xylan had characteristic bands at around 1000–1200 $cm^{-1}$ ascribed to alcoholic C—O stretching vibration. Although we did not show the FT-IR spectra of CF and HL, their spectra were substantially the same as those of CF-A and HL-A, respectively. This implies that any specific components of CF and HL were not eliminated by the extraction and annealing processes. It is known that cotton fibers are almost entirely composed of cellulose (90–96% based on weight of fibers). (Abdel-Halim & Al-Deyab, 2013) Actually, the spectra of CF and CF-A were very similar to that of cellulose. Typical contents of cellulose, hemicellulose and lignin for wood chips of hinoki cypress are reported to be 41.2, 25.2 and 29.3% (Moniruzzaman & Ono, 2013). Lignin has a characteristic absorption band distinguishable from cellulose and xylan (a main component of hemicellulose) at around 1500 $cm^{-1}$ ascribed to aromatic ring framework vibration of polyphenol moieties. Actually, the spectra of HL-A (or HL) exhibited the absorption band at around 1500 $cm^{-1}$, which was not observed for those of cellulose and CF-A. The CF-BMIMCl showed the absorption bands related to the C-N stretching vibration at 1167 $cm^{-1}$, and the imidazolidinium framework vibration of BMIMCl at 1562 $cm^{-1}$, indicating that CC-BMIMCl certainly contains BMIMCl. Their absorption bands related to BMIMCl almost completely disappeared for HL-A, implying that the impregnated BMIMCl completely eliminated by the Soxhlet extraction, in agreement the fact that the BMIMCl content calculated from weight change is almost 0%. Similar trends were observed for HL-BMIMCl and HL-A.

Fig. 4 shows the FE-SEM images of the surfaces of CF, CF-As 5, 10 and 15 MPa. The CF is composed of the fabricated cotton fibers whose diameter is ca. 10 μm. In the image of CF-A 5 MPa, although the fibers started to adhere, the shape of fibers was considerably kept. With increasing pressure of the hot press, the fibers flattened and most of fibers combined together at 15 MPa. Fig. 5 shows the FE-SEM cross-sectional images of CF-As 5 and 15 MPa. The voids observed for CF decreased with increasing pressure. Although some voids were observed at 5 MPa, almost the void disappeared at 15 MPa. Fig. 6 shows FE-SEM images of HL, HL-As 5, 10 and 15 MPa. In the photograph of HL, the grain of woody surface is

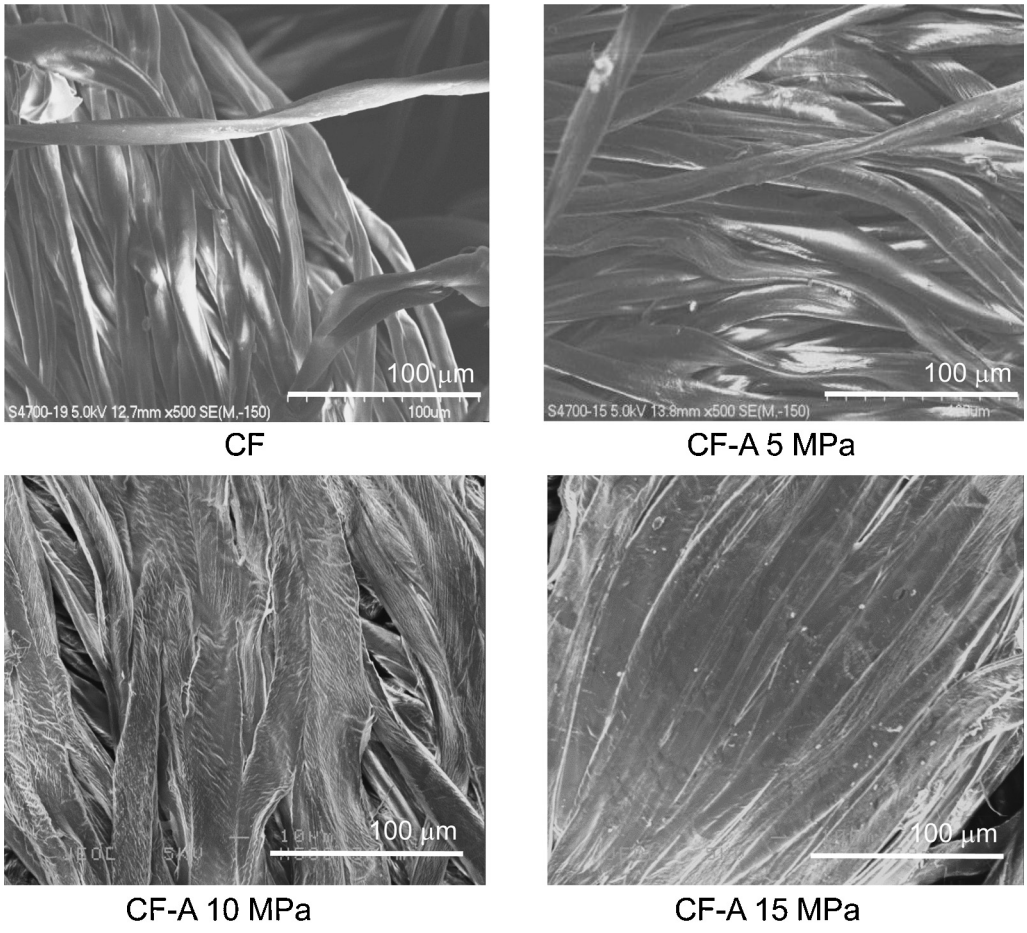


**Fig. 4.** FE-SEM microphotographs of the surfaces of CF and CF-As.

clearly appeared. With increasing pressure, the wood surface flattened, and a smooth surface was obtained at 10 MPa. However, some cracks are appeared at 15 MPa, indicating that woody tissue is somewhat broken by an excess pressure. There was little difference in the cross-section images for HL-As 5, 10 and 15 MPa, because original HL had little void.

Fig. 7 shows XRD profiles of CF and CF-based composites prepared at 15 MPa. CF showed characteristic peaks to cellulose I at $2\theta = 14.7^\circ$ for the (1 0 1) plane, $2\theta = 16.6^\circ$ for the $(1\,0\,\bar{1})$ plane, and $\theta = 22.7^\circ$ for the (0 0 2) plane (Ford, Mendon, Thames, & Rawlins, 2010). The *CrI* (0.84) of CF dropped to 0.40 for CF-BMIMCl, reflecting that considerable amount of crystalline cellulose dissolved into BMIMCl. The finally obtained CF-A had a similar *CrI* (0.85) to original CF (0.84). The CF-As prepared at 5 and 10 MPa had silimar *CrI* to that at 15 MPa, as is summarized in Table 1. The fact that the XRD peaks at around 15, 17 and 23° ascribed to cellulose I structure did not shift for all the CF-based composites indicates that cellulose I structure is kept during a partial dissolution in BMIMCl, extraction and annealing process. Generally, dissolution and regeneration of cellulose I is believed to lead to a transformation to cellulose II, which is reported to be a more stable form of cellulose due to the anti-parallel packing of the single cellulose chains in contrast to parallel packing in cellulose I (Ma, Zhou, Li, Li, & Ou, 2011; Zhao et al., 2009). Regarding the ACCs prepared

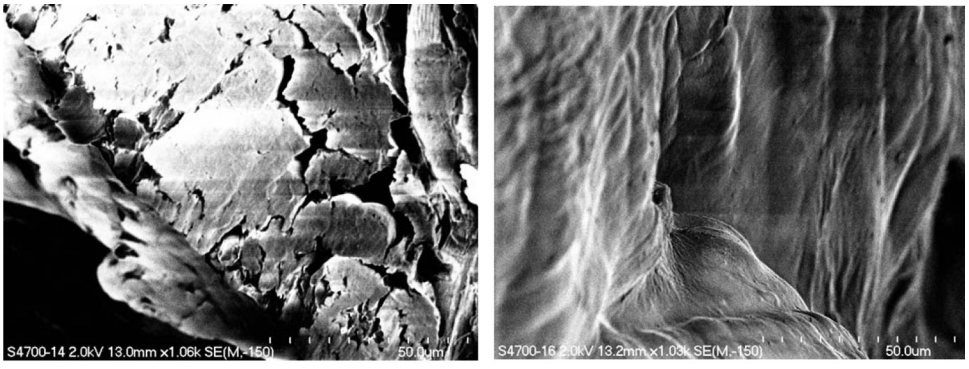


**Fig. 5.** FE-SEM microphotographs of the cross-sections of CF and CF-As.

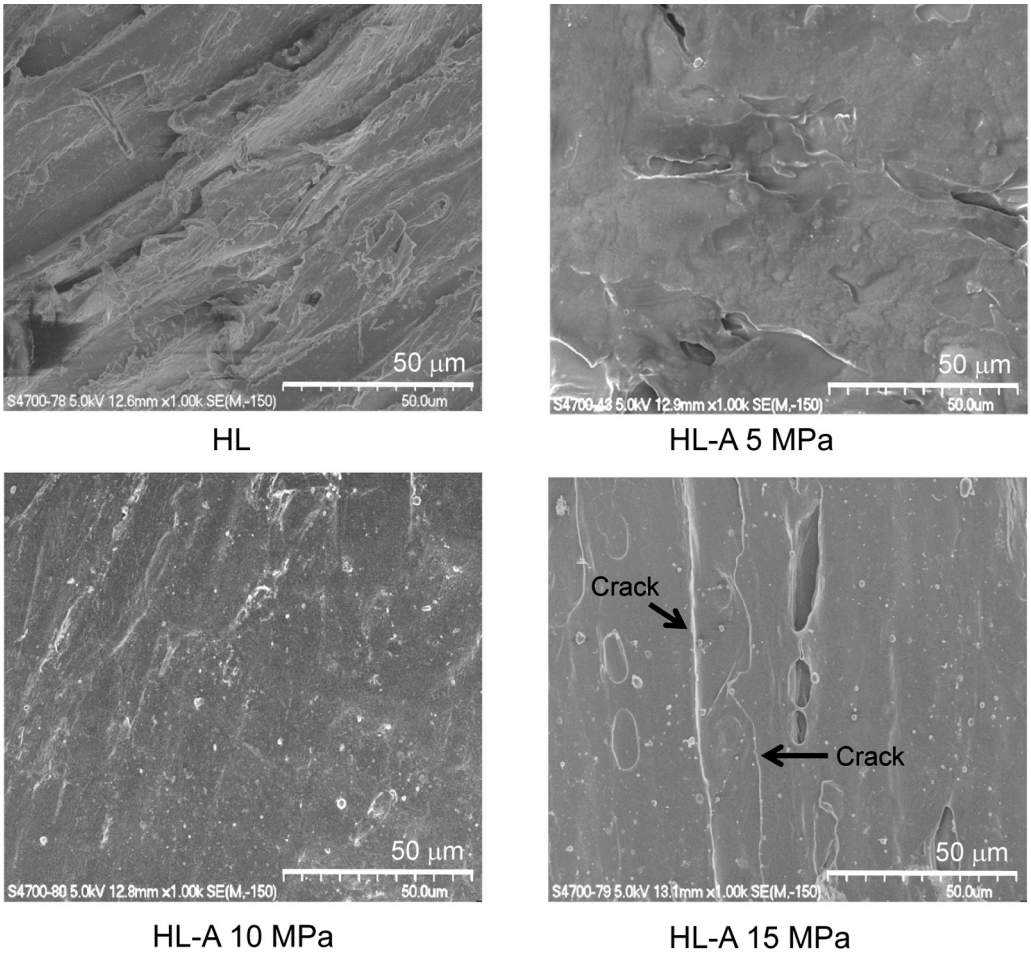


**Fig. 6.** FE-SEM microphotographs of the surfaces of HL and HL-As.

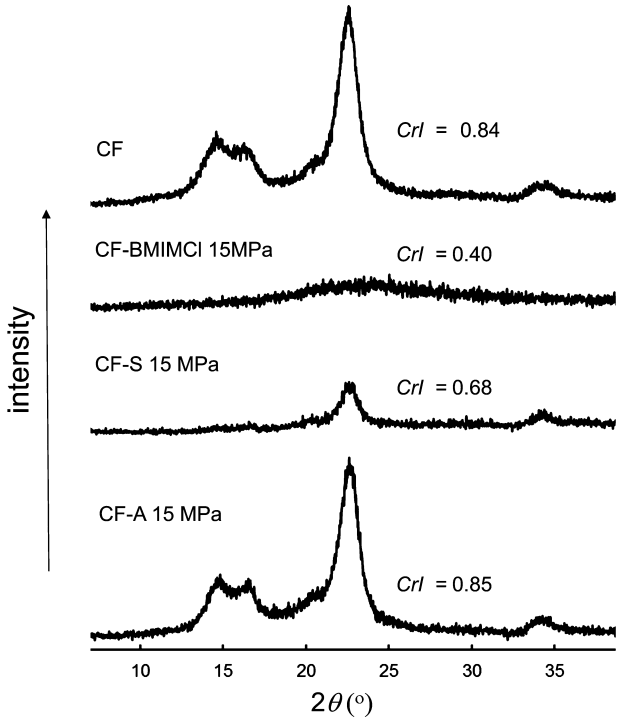


**Fig. 7.** XRD profiles of CF-BMIMCl, CF-S and CF-A prepared at the pressure of 15 MPa compared with that of CF.

by a partial dissolution of cellulose in ILs and regeneration, it had been reported that cellulose I structure is almost maintained for the ACC prepared from microfibrillated cellulose paper and BMIMCl (Duchemin et al., 2009) and the ACC prepared from linen fabrics and BMIMAc (Huber et al., 2012a; Huber et al., 2012b). The unchanged crystalline structure of cellulose I was explained by the dissolution of only minimal amounts of cellulose. In our case, the *CrI* of cellulose I dropped from 84% (CF) to 40% (CF-BMIMCl) by a partial dissolution of cellulose in BMIMCl, again rose to 68% (CF-S) by removal of BMIMCl, and further pulled up to 85% (CF-A) by annealing at 150 °C for 24 h, as was shown in Fig. 7. Although much more evidence is necessary to be reasoned, the *CrI* data suggest that the partial dissolution of cellulose I in BMIMCl does not always lead to a structural change to cellulose II when regenerated.

**Table 1**
*CrI* and $T_5$ of CF, CF-As, HL and HL-As.

| | *CrI* (–) | $T_5$ (°C) |
|---|---|---|
| CF | 0.84 | 346.3 |
| CF-A 5 MPa | 0.84 | 337.3 |
| CF-A 10 MPa | 0.86 | 337.6 |
| CF-A 15 MPa | 0.85 | 343.7 |
| HL | 0.71 | 292.3 |
| HL-A 5 MPa | 0.79 | 287.3 |
| HL-A 10 MPa | 0.81 | 289.4 |
| HL-A 15 MPa | 0.80 | 301.1 |

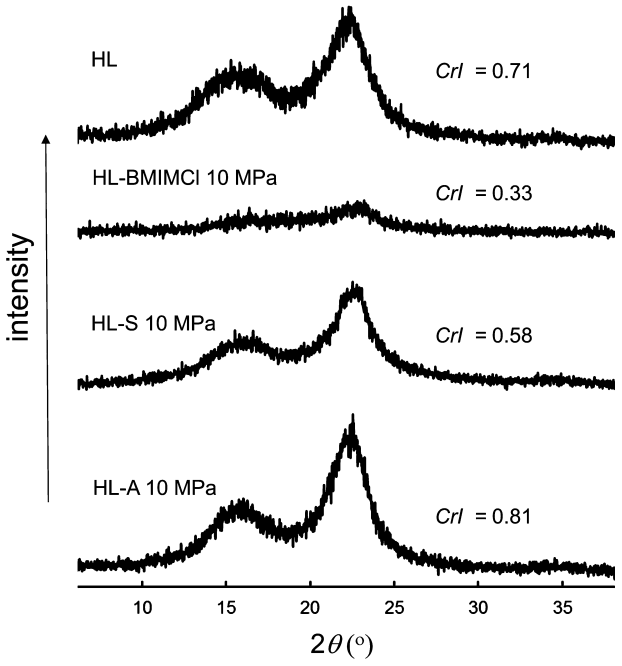


**Fig. 8.** XRD profiles of HL-BMIMCl, HL-S and HL-A prepared at the pressure of 10 MPa compared with that of HL.

Fig. 8 shows XRD profiles of HL and HL-based composites prepared at 10 MPa. The HL had the prominent cellulose I peak at 22.5° for the (0 0 2) plane, however, the characteristic (1 0 1) and (1 0 $\bar{1}$) peaks (2$\theta$ between 15° and 17°) are not distinct as those in CF, but combine into one broad peak at 15.8°. The *CrI* (0.71) of HL which has a lower cellulose content than CF was lower than that of CF (0.84). After the hot press of HL-BMIMCl, *CrI* dropped to 0.33, again increased by the removal of BMIMCl by Soxhlet extraction, and further increased by annealing at 210 °C for 24 h in a similar trend to CF-based composites. The HL-As prepared at 5, 10 and 15 MPa had a comparable *CrI* (0.79–0.81), which was a little higher than the original HL (0.71) (Table 1). The structure of cellulose I was kept for HL-As in the same way as CF-As. It was revealed that cellulose I structure is maintained in case of wood powder regenerated from wood solution in ILs (Kilpeläinen et al., 2007). We had also obtained a similar result for all wood biocomposites prepared by a partial dissolution of wood flour in BMIMCl (Shibata et al., 2013).

### 3.2. Thermal and mechanical properties of CF and HL biocompoistes

Fig. 9 shows TGA curves of CF-As and HL-As. Their 5% weight loss temperatures ($T_5$s) are also summarized in Table 1. Although the $T_5$ of CF-A 15 MPa (343.7 °C) was a little lower than that of CF (346.3 °C), that of HL-A 15 MPa (301.1 °C) was a little higher than that of HL (292.3 °C). We do not know a clear reason, but it may be related to the fact that *CrI* of HL-A 15 MPa (0.80) is higher than that of HL (0.71). In the past studies, it had been reported that an increase of crystallinity for cellulose causes a rise of the thermal degradation temperature (Kadokawa, Murakami, & Kaneko, 2008; Wu, Wang, Li, Li, & Wang, 2009). However, the facts that HL-A 10 MPa with *CrI* 0.81 had a lower $T_5$ than HL-A 15 MPa, and that CF-A 5 MPa which has the same *CrI* to CF showed a lower $T_5$ than CF suggest that other factors than crystallinity may be also related in our case. It is known that the dissolution of cellulose in BMIMC at the temperature higher than 100 °C for several hours caused a considerable reduction of degree of polymerization (DP) (Duchemin et al., 2009; Iguchi, Aida, Watanabe, & Smith, 2013; Lan, Liu, Yue, Sun, & Kennedy, 2011). There is a possibility that the decrease of $T_5$ in this study is related to a reduction of DP of lignocellulosic components caused by the processing under a high temperature with BMIMCl.

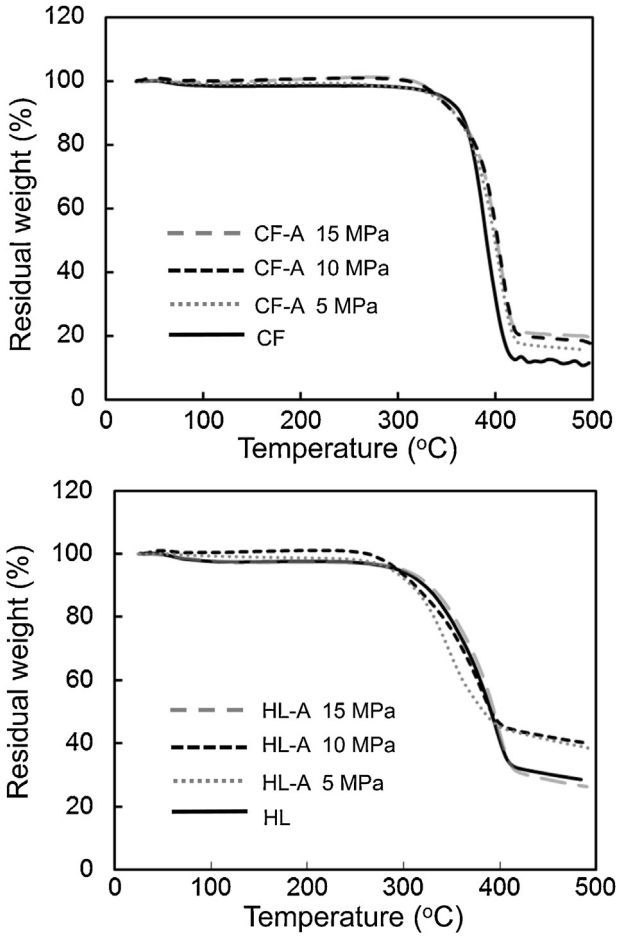


**Fig. 9.** TGA curves of CF, HL, CF-As and HL-As.

Fig. 10 shows the tensile properties of CF-As, HL and HL-As. Although the tensile properties of CF were not measured because the value of cross-sectional area for CF with much voids is inaccurate, it was obvious that CF-As are much stiffer than CF. Tensile modulus for CF-As increased with increasing pressure of hot press, in agreement with the observation of FE-SEM. Elongation at break of CF-As decreased with increasing pressure. Although the average tensile strength for CF-As also increased with increasing pressure, the error bar was relatively large. The tensile strength and modulus of CF-A 15 MPa (22 MPa and 134 MPa) were lower than those of 4-layered linen laminate (46 MPa and 860 MPa). This is attributable to the fact that the tensile strength of the original linen texlite (36 MPa) is much higher than that of CF (5 MPa). Regarding the all-wood composites, although the tensile strength and elongation at break for HL-As were lower than those of HL, tensile modulus for HL-A increased with pressure and became a maximum value (6.33 GPa) at 10 MPa, which was much higher than that of HL (1.31 GPa). The lowering of tensile modulus at 15 MPa should be related to the fact that some cracks were observed for the HL-A prepared at 15 MPa (Fig. 5). The tensile strength and modulus of HL-A 10 MPa (51 MPa and 6.33 GPa) were also much higher than those of all-wood composite prepared from wood flour and BMIMCl (5.3 MPa and 1.9 GPa) (Shibata et al., 2013).

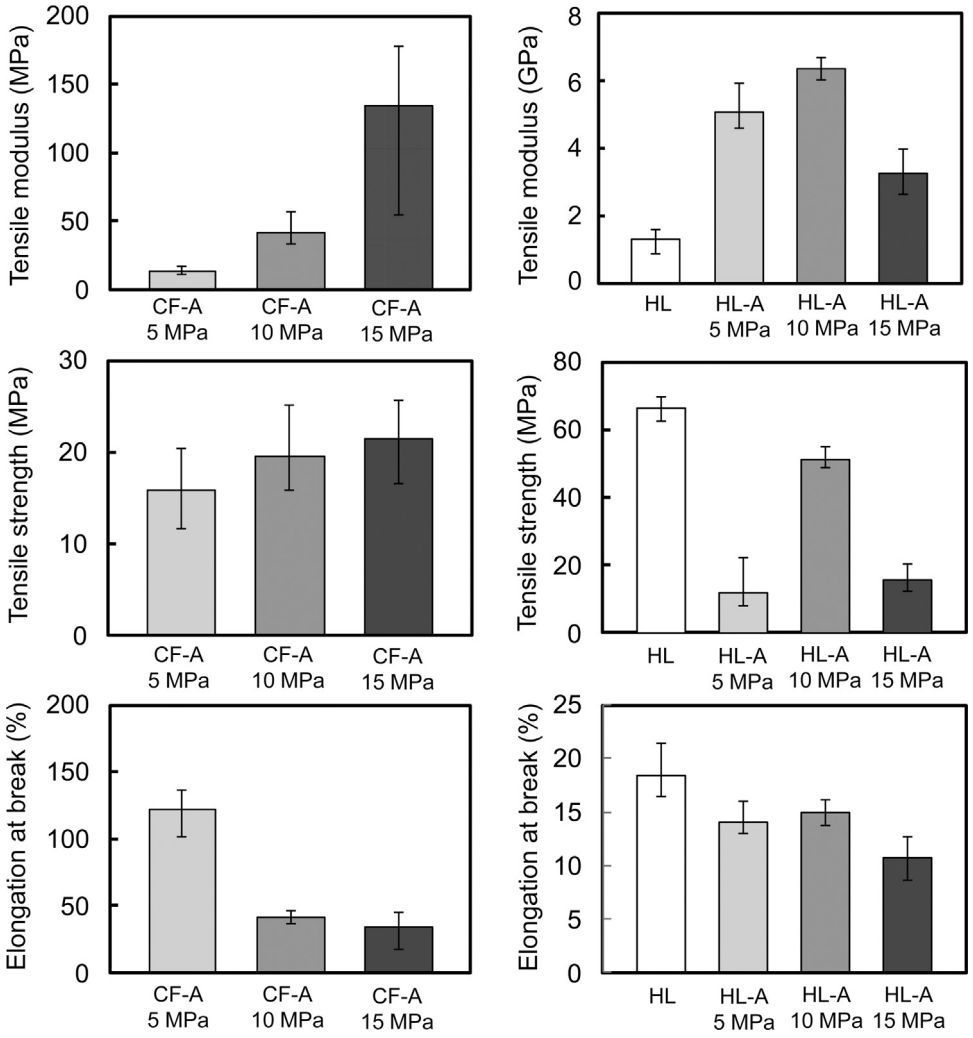


**Fig. 10.** Tensile properties of CF-As, HL and HL-As.

## 4. Conclusions

New ACCs and all-wood composites were prepared from CF and HL, respectively, by hot press of CF/BMIMCl and HL/BMIMCl, Soxhlet extraction, and subsequent annealing. The FT-IR analysis revealed that HL had a higher content of lignin than CF, and that the incorporated BMIMCl was eliminated by the Soxhlet extraction. The FE-SEM analyses revealed that cellulose fibers combined together for CF-A and the surface of HL-A became smooth. The XRD measurements indicated that *CrI* of cellulose component decreased by the hot press, increased by the extraction, and further increased by the annealing for both the composites. The CF-A and HL-A showed almost comparable $T_5$ to the original CF and HL. The tensile modulus of CF-A increased with increasing pressure of hot press. The tensile strength and modulus of HL-A 10 MPa was much higher than those of the all-wood composite prepared from wood flour and BMIMCl.

## Acknowledgements

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