We investigate the reactivity and viscosity properties of macromolecules from wood such as cellulose and xylan in ionic liquids, which has ability to liquefy wood. The macromolecules from wood were treated with ionic liquids at 120 °C. The obtained ionic liquid insoluble residue was weighed and calculated yield of residue. We discussed for reactivity of the macromolecules from wood by changes of residual concentration with ionic liquid treatment. Viscosity measurements were performed for macromolecules from wood/ionic liquid solution. Huggins coefficient was calculated by resulting viscosity measurements. With Huggins coefficient we investigate state of macromolecules from wood in ionic liquids. It was assumed that cellulose would be dispersed in 1-ethyl-3-methylimidazolium chloride and would probably aggregate in 1-ethyl-3-methylimidazolium acetate. It was thought that the state of macromolecules from wood in ionic liquids influence on their reactivity in ionic liquids.

Key Words
Ionic liquids, Macromolecules from wood, Molecular properties, Reactivity, Viscosity

1. Introduction

Since the dawn of history, human being have engaged in a comfortable life while advances in science and technology. Especially since the Industrial Revolution, our living standards have been enhanced by utilization of fossil resources such as oil and coal. In particular, oil among fossil resources is useful as raw materials of chemical products and synthetic resins. However, mass consumption of fossil fuels affects the global environment and causes global warming. With the depletion of fossil resources, energy issues are becoming more serious. Recently, a great deal of attention has been focused on biomass resources as alternatives to fossil resources. Wood is a promising resource among various biomass because of its huge stocks and inedible characteristics, which means that its utilization poses no threat to food supply. Because wood is characterized as a carbon neutral, the utilization of wood as an alternative to fossil resources can contribute to the suppression of the increase in carbon dioxide concentration in the atmosphere. In recent years, there have been increased efforts to promote the use of wood. Thus, research on the effective utilization of wood plays an important role.

Various methods have been proposed for the energy and chemical conversion technology for wood. A lot of studies have been performed so far with respect to chemical conversion of wood such as acid hydrolysis 1), enzymatic saccharification 2), hot-compressed water treatment 3), pyrolysis 4) 5) and supercritical fluid treatment 6).

A great deal of attention has been focused on processing technology of wood by the ionic liquids in recent
years. Ionic liquids are salt having their melting points at ambient temperature. They are expected as a novel green solvent because of a unique characteristic such as negligible vapor pressure, thermal and chemical stability, nonflammability and a high solubility power. It has been known that some ionic liquids as solvent can be recycled several times 7). Several studies have been reported for chemical synthesis in ionic liquids as reaction media 8), 9) or catalyst 10) ~ 12). Ionic liquids have also been applied for the extraction of chemical substances 13) ~ 16). Since it was reported that certain ionic liquids can dissolve cellulose 15), much attention has been focused on the reactivity and solubility of wood which is constituted cellulose, hemicellulose and lignin in ionic liquid. It is reported that 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) can liquefy all the constituents of wood. The solubilized polysaccharides such as cellulose and hemicellulose in [C2mim][Cl] are depolymerized to low molecular weight compounds such as glucose, mannose, levoglucosan and 5-hydroxymethylfurfural 18). It is also revealed that the atmosphere in the reaction system affects the liquefaction behavior of wood in the ionic liquid 27). Moreover, the difference of liquefaction behavior between softwood and hardwood has been reported, Japanese beech (hardwood) was more easily liquefied than Western red cedar (softwood) 19), 1-Ethyl-3-methylimidazolium acetate ([C2mim][Ac]) can completely liquefy wood 19), Kilpeläinen et al. have reported the solubility of wood in various imidazolium-based ionic liquids 20). It has been reported that 1-ethylpyridinium bromide has the ability to liquefy wood and liquefies lignin and hemicellulose preferentially 21). Especially for cellulose which is macromolecule from wood, several studies on the reactivity in ionic liquids have been reported so far. Solubility and reaction behavior of cellulose in various ionic liquids were reported 22) ~ 25). The solubilized cellulose in [C2mim][Cl] is degraded to low molecular weight compounds such as glucose, cellobiose, 5-hydroxymethylfurfural and levoglucosan. Moreover, the polymer which is different from the cellulose is produced with progress of the reaction 26). The more detailed degradation behavior of cellulose in [C2mim][Cl] has been revealed 27). Some studies on derivatization of cellulose in ionic liquids have been reported 28). The derivatization of hemicelluloses in ionic liquids has been reported 29). Froschauer et al. reported that phosphate-based ionic liquids have ability as selective solvents for xylan 30).

To elucidate more detailed reactivity and solubility of polymer to solution, molecular characterization of polymer in solution are necessary. For molecular characterization of polymer in solution, viscosimetry is mainly employed. Staudinger established the concept of polymer by finding the correlation between viscosity and molecular weight of polymer. Huggins has reported that aggregation states of polymer are found by solution viscosity 31). Mead et al. and Kreamer reported the molecular properties of polymer solution 32) ~ 33).

For cellulose as macromolecules from wood, many studies on the molecular properties in various solutions have been reported so far. Rheological properties and gelation of cellulose solution has been reported 34). Tamai et al. performed viscosity measurements on solution of cellulose/ LiCl/1,3-dimethyl-2-imidazolidinone (DMI) and obtained Huggins coefficients of 0.3~0.4. They revealed that cellulose was dispersed in the solution homogeneously 35). For cellulose from various biomass in LiCl/N,N-dimethylacetamide (DMAc) solution, light scattering and rheological properties have been reported 36) ~ 38). The aggregate structure of mercerized cellulose in LiCl/N,N-dimethylacetamide (DMAc) solution has been revealed 39) ~ 40). Yanagisawa et al. reported that cellulose behaves as typical semiflexible chains in good solvent 41). Several studies on the solution properties of xylan which is one of hemicelluloses have been reported 42) ~ 43). The rheological properties of water-soluble galactoglucomannan solution have also been reported 44). The glucomannan from konjac solution indicates high Huggins coefficient value and it has been suggested that macromolecule of konjac glucomannan is aggregated in solution 45).

For ionic liquids solution, several studies have been reported 46) ~ 48). Gerick et al. investigated the rheological properties of cellulose/ionic liquids, [C2mim][Ac] and 1-butyl-3-methylimidazolium chloride. These cellulose/ionic liquids solutions showed Newtonian and it is revealed that [C2mim][Ac] is a theta solvent to cellulose 49). Sescousse et al. reported the rheological properties of cellulose/imidazolium-based ionic liquids solutions 50). Moreover, for cellulose/ [C2mim][Ac] solution, rheological properties 52) has also been reported.

As described above, many studies on the reaction behavior of macromolecules from wood in ionic liquids has been reported. However, there are few studies on the molecular properties of macromolecules from wood in ionic liquids such as their aggregation states and affinity to the ionic liquid. Molecular properties of macromolecules from wood in ionic liquids are important for understanding the detailed reactivity between macromolecules from wood and ionic liquids. In addition, those are necessary to consider effective utilization of wood by the ionic liquid processing technology. In this study, therefore, we investigated the molecular properties of macromolecules from wood such as cellulose and hemicelluloses in ionic liquids, which has the ability to liquefy wood.
2. Materials and methods

2.1 Samples and chemicals

Whatman CF-1 was used as cellulose sample, which is fluffy fibrous. Its molecular weight and crystallinity is 6.88 \times 10^{14} \text{ g mol}^{-1} and 64.2\% \text{ [52]}, respectively. Xylan from beech was used as xylan sample, which is fine powder and purchased from Tokyo Chemical Industry. Its molecular weight is 2.26 \times 10^{12} \text{ g mol}^{-1}. Cellulose and xylan were dried in an oven at 105 °C for 24 h before use to obtain oven-dried samples. The ionic liquids, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) and 1-ethyl-3-methylimidazolium acetate ([C2mim][Ac]), were purchased from Tokyo Chemical Industry and Sigma-Aldrich, respectively. The chemical structure of [C2mim][Cl] and [C2mim][Ac] are shown in Fig. 1. Cellobiose, xylobiose, acetic acid, sodium chlorite, and ethanol were purchased from Wako Pure Chemical Industries. Delignified xylan was prepared for comparison with purchased xylan which was fine powder and purchased from T o k y o Chemical Industry. Its molecular weight is 2.26 \times 10^{12} \text{ g mol}^{-1}. Each sample was measured at 120 °C in a 100-ml flask. After complete dissolution of the sample, the obtained was diluted to specific viscosity (ηsp) of each sample were determined by measuring value of viscosity. Huggins coefficient was determined by equation (1).

\[
\frac{\eta_{sp}}{C} = [\eta] + k' [\eta]^2 c
\]  

Where \( k' \) is Huggins coefficient, \( C \) is the concentration of the sample solution, and \([\eta]\) is the intrinsic viscosity. Intrinsic viscosity is the extrapolation of reduced viscosity to value at zero solute concentration. By equation (1), Huggins plot was created. In addition, Mead-Fuoss plot was created from equation (2).

\[
\ln \frac{\eta_{sp}}{C} = [\eta] + (\frac{1}{2} - k') [\eta]^2 c
\]

2.2 Treatment for macromolecules from wood with ionic liquids

3 g of [C2mim][Cl] or [C2mim][Ac] was heated at 120 °C in a 100-ml flask. After sufficient heating, 0.18 g of cellulose or xylan was added into the flask. At specified reaction times, 20 µL of the reaction media was taken and homogeneously mixed with 180 µL of distilled water. These mixtures were then filtered through a 0.45-µm filter and the filtrates were analyzed by high-performance liquid chromatography (HPLC) (Shimadzu Corporation) under the following conditions: column, Shodex Sugar KS-801; flow rate, 1 mL/min; eluent, H2O; detector, RID; column temperature, 80 °C.

2.3 Treatment for disaccharides with ionic liquids

6 g of [C2mim][Cl] or [C2mim][Ac] was heated at 120 °C in a 100-ml flask. After sufficient heating, 0.18 g of the sample was added into the flask. After complete dissolution of the sample, the obtained was diluted to prescribed concentrations by adding [C2mim][Cl] or [C2mim][Ac], and these solutions were studied on their viscosities. Complete dissolution of the sample was confirmed visually. All viscosity measurements were carried out using a tuning fork vibro viscometers (SV-1A, A&D Company, Limited, measurement accuracy: ±5%). The viscosities of the samples were measured at 120 °C. Each sample was loaded into glass vessel, and it was heated and kept temperature in oil bath. The relative viscosity (ηrel) and specific viscosity (ηsp) of each sample were determined by measuring value of viscosity. Huggins coefficient was determined by equation (1).

3. Results and discussion

3.1 Reactivity of macromolecules from wood in ionic liquids

Fig. 2 shows the changes in the concentration of cellulose during the treatment with [C2mim][Cl]. With the progress of the ionic liquid treatment, concentration of cellulose decreases due to decomposition. Irrespective of the concentration of the cellulose charged, similar decrease rate in Ln C was observed up to 3 h of treatment. For 30 g/L of
charged concentration, large change in Ln C was observed at 4 h. The reasons of this large change in Ln C is unclear.

Fig. 3 shows changes of Ln C of two types of xylans. Marked difference was observed between xylan without delignification and delignified xylan in their reactivity. For xylan without delignification, pronounced difference by charged concentration was observed in Fig. 3 (a). In 30 and 12 g/L of charged concentration, significant decrease of Ln C was not seen after 24 h of treatment. In contrast, Ln C was decreased greatly up to 8 h in case of 3 g/L of charged concentration. It is considered that reactivity of xylan without delignification varies depending on its charged concentration. From Fig. 3 (b), the significant difference of reactivity by charged concentration was not seen for delignified xylan. With the progress of the ionic liquid treatment, Ln C decreases and large decrease of Ln C was observed at 8 or 12 h. A comparison of the results in Fig. 3 (a) and (b) suggests that lignin has a great influence on the reactivity of xylan in \([\text{C2mim}]\text{[Cl]}\).

Fig. 4 shows the changes of Ln C of cellulose treated with \([\text{C2mim}]\text{[Ac]}\). Similar decomposition behavior was found for each charged concentration. In \([\text{C2mim}]\text{[Ac]}\), it is considered that reactivity of cellulose does not depend on the charged concentration. In comparison with \([\text{C2mim}]\text{[Cl]}\)
(Fig. 2), a similar tendency to reactivity in [C2mim][Cl] was observed.

The reactivity of xylan in [C2mim][Ac] is illustrated in Fig. 5. In 30 and 12 g/L of charged concentration of xylan without delignification (Fig. 5 (a)), similar decrease rate of Ln C was seen up to 12 h of treatment. In contrast, Ln C in 3 g/L of charged concentration was decreased greater than those in case of 30 and 12 g/L. From Fig. 5 (b), a large decrease of Ln C with [C2mim][Ac] treatment is not seen in delignified xylan. In addition, reactivity does not depend on the charged concentration of delignified xylan. Comparing with the results in [C2mim][Cl] (Fig. 3 (b)), [C2mim][Ac] has a low ability to decompose xylan.

From these results, it was suggested that difference of reactivity for macromolecules from wood depends on the species of ionic liquids and samples. As the cause of difference by ionic liquids ([C2mim][Cl] and [C2mim][Ac]), two factors are considered. One is that the differences in decomposition rate of cellulose and xylan depends on the stability of β-1,4-bond in both polymers. The other is that the viscosity properties of macromolecules from wood in ionic liquids are likely to influence the reactivity.

3.2 Stability of β-1,4-bond in cellulose and xylan

To investigate the stability of β-1,4-bond in cellulose and xylan, cellobiose and xylobiose were selected as the units of cellulose and xylan, respectively. The decomposition rates of cellobiose and xylobiose in ionic liquids can indicate the stability of their β-1,4-bond.

Fig. 6 shows the changes of Ln C of cellobiose and...
xylobiose in ionic liquids. For decomposition rate of these disaccharides in [C2mim][Cl], significant difference was observed from Fig. 6 (a). Xylobiose was found to be easily decomposed than cellobiose in [C2mim][Cl], indicating that β-1,4-bond of cellobiose is more stable than that of xylobiose in [C2mim][Cl]. From Fig. 6 (b), similar trend was shown for decomposition of the disaccharides in [C2mim][Ac]. At 60 min of treatment, both disaccharides are mostly decomposed. In [C2mim][Ac], it is considered that cellobiose and xylobiose have comparable degradability. Compared [C2mim][Cl] with [C2mim][Ac], it revealed that cellobiose has a very high decomposition ability than [C2mim][Cl].

3.3 Viscosity properties of macromolecules from wood in ionic liquids

To investigate viscosity properties of macromolecules from wood in ionic liquids, macromolecules from wood/ionic liquids solutions were studied on their viscosity.

Fig. 7 shows Huggins and Mead-Fuoss plots for cellulose in ionic liquids. The obtained plots were possible to approximate as a straight line. Huggins coefficient k’ is calculated from the slope of the approximation line. Huggins coefficient k’ for cellulose in [C2mim][Cl] and [C2mim][Ac] is 0.57 and 0.93, respectively. Fig. 8 shows Huggins plots for xylan without delignification in [C2mim][Cl] and [C2mim][Ac] solution. Because the linear approximation could not be obtained by these plots, k’ was not calculated. Fig. 9 shows Huggins and Mead-Fuoss plots for delignified xylan in [C2mim][Cl] and [C2mim][Ac] solution. Comparing [C2mim][Cl] with [C2mim][Ac], marked difference for Huggins coefficient was not observed. k’ of [C2mim][Cl] and [C2mim][Ac] is 0.99 and 1.07, respectively. From Figs. 8 and 9, it is clear that lignin greatly affects the molecular properties of xylan in ionic liquids.

It is reported that when the polymer cannot be uniformly dispersed in the solvent at the molecular level,
the relationship between $c$ and $\eta_0/c$ does not form a straight line \(^{53}\). Since lignin is hydrophobic although xylan and ionic liquids used in this study are hydrophilic, it can be inferred that lignin in xylan was associated with each other, and xylan without delignification could not be uniformly dispersed in the ionic liquids. While, it is known that lignin is covalently bound to xylan which is a linear polymer. Thus, lignin is considered to be part of the branches of xylan. It is reported that the polymers with branches are aggregated with each other and cannot be uniformly dispersed in the solvent at the molecular level \(^{56}\). This may be also why xylan without delignification could not be uniformly dispersed in the ionic liquids used in this study. The dispersion of delignified xylan in the ionic liquids is thought to be improved because the amount of lignin is reduced in it.

In general, Huggins coefficient for common polymers ranges from 0.3 to 0.6. Higher $k'$ and $1<k'$ indicates the aggregation of macromolecules. Although it is difficult to elucidate the state of macromolecules from wood in ionic liquids only from Huggins coefficient, it is presumed that cellulose is dispersed in [C2mim][Cl] solution. Compared with [C2mim][Cl], cellulose may be aggregated in [C2mim][Ac]. High value of $k'$ may indicate that xylan is aggregated in both ionic liquids solution.

3.4 Factors causing the differences in reactivity in ionic liquids

Fig. 6 indicates that stability of $\beta$-1,4-bond in cellobiose is different from that in xylobiose during [C2mim][Cl] treatment. It is clear that the stability of $\beta$-1,4-bond in disaccharides depends on the type of ionic liquids used. In addition, it is found that $\beta$-1,4-bond in disaccharides is more scissile in [C2mim][Ac] than in [C2mim][Cl]. Compared with Fig. 4, however, significant difference on decomposition rate was not observed. For two types of xylan, a marked difference was found as shown in Fig. 3. The decomposition of xylan without delignification was suppressed because of its aggregation in the ionic liquids as described above. It is thought that the higher the concentration of both type of xylan in the ionic liquids added, the more their aggregation proceeds. Therefore, the decomposition rate of both type of xylan may become slower as the concentration of xylan added in the ionic liquids increases. These results revealed that the stability of $\beta$-1,4-bond is not a major factor in the reactivity of macromolecules from wood in ionic liquids. From Fig. 7, it is considered that the state of macromolecules from wood in ionic liquids affects the reactivity of macromolecules from wood. Fig. 6 indicates that [C2mim][Ac] has very high decomposition ability than [C2mim][Cl]. However, from Fig. 3 (b) and Fig. 5 (b), it was clear that [C2mim][Ac] has a lower ability to decompose delignified xylan than [C2mim][Cl]. From the above discussion, it seems that the stability of $\beta$-1,4-bond is not a major factor in the reactivity of macromolecules from wood in ionic liquids. The reactivity of macromolecules from wood depends on the state of macromolecules from wood in ionic liquids.

4. Conclusions

In this study, we investigated the reactivity and viscosity properties of macromolecules from wood such as cellulose and xylan in two types of ionic liquids, [C2mim][Cl] and [C2mim][Ac]. Marked difference by charged concentration was not observed for cellulose in both ionic liquids. For xylan without delignification, it was revealed that the reactivity depends on the charged concentration. Comparing with xylan without delignification to delignified
xylan, significant difference of reactivity was found. It is clear that lignin has great influence on the reactivity of xylan. What affects the reactivity of macromolecules from wood in ionic liquids? We have highlighted two factors: the stability of β-1,4-bond and the viscosity properties of cellulose and xylan in ionic liquids. The stability of β-1,4-bond was investigated by decomposition rate of disaccharides such as cellobiose and xylobiose. It is clear that lignin greatly influences the reactivity of macromolecules from wood. Thus, it was investigated with Huggins coefficient. It was assumed that cellulose is dispersed in [C2mim][Cl] and may be aggregated in [C2mim][Ac]. For xylan without delignification, Huggins coefficient could not be obtained. The delignified xylan solutions showed high Huggins coefficient, presumably indicating that delignified xylan aggregates in both the ionic liquids. In addition, it was clear that lignin greatly influences the reactivity of macromolecules from xylan. What affects the reactivity of macromolecules from wood in ionic liquids? We have highlighted two factors: the stability of β-1,4-bond and the viscosity properties of cellulose and xylan in ionic liquids. The stability of β-1,4-bond was investigated by decomposition rate of disaccharides such as cellobiose and xylobiose. It is clear that lignin greatly influences the reactivity of macromolecules from wood. Thus, it was investigated with Huggins coefficient. It was assumed that cellulose is dispersed in [C2mim][Cl] and may be aggregated in [C2mim][Ac]. For xylan without delignification, Huggins coefficient could not be obtained. The delignified xylan solutions showed high Huggins coefficient, presumably indicating that delignified xylan aggregates in both the ionic liquids. In addition, it was clear that lignin greatly influences the reactivity of macromolecules from xylan. Consequently, it was revealed that the reactivity of macromolecules from wood depends on their states in the solvent than the stability of their β-1,4-bond.

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