

이온성 액체를 이용한 셀룰로우스 추출

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Regeneration of Cellulose from Ionic Liquids

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Abstract :Ionic liquids based on formate and hydrogen carbonate anions were synthesized for use as solvents for the effective dissolution of cellulose and the regenerated cellulose was in the native lattice.

Key words :Cellulose(셀룰로우스), Ionic Liquid(이온성 액체), Regeneration(추출)

1.INTRODUCTION

Cellulose is one of the most abundant biorenewable resources. Cellulose and its derivatives have been widely used in commercial applications in the fiber, paper, membrane, polymer, and paints industries. Processing cellulose consisting of linear glucose chains from solutions has in particular drawn attention from engineers and scientists. However, this natural renewable polymer is incompatible with water and organic solvents, because of its stiff backbone and close chain packing caused by numerous intermolecular and intramolecular hydrogen bonds. Several solvents dissolving cellulose such as zinc chloride solution have been found to be environmentally and technologically unacceptable.¹⁾ Although the introduction of the now commercialized N-methylmorpholine N-oxide (NMMO) to cellulose processes could address environmental considerations, NMMO is unstable at temperatures above 100 °C.²⁾

Recently, considerable interest has been directed

toward the use of ionic liquids (ILs) as green-solvents, owing to their unique physical properties. ILs generally feature good chemical and thermal stability, non-flammability, and immeasurably low vapor pressure. Rogers et al. first identified 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) as a novel solvent for the dissolution of cellulose. Their discovery of a new solvent system, so called “ionic liquids”, has been expected to bring about progress in the area of cellulose dissolution and to help open up another phase in the cellulose industry.³⁾

However, with respect to Cl⁻, on one hand, it has ability to disrupt hydrogen bonding between chains, but on the other, treatment with IL containing Cl⁻ leads to a progressive reduction in crystallinity and lattice transformation from cellulose I to cellulose II with considerable loss of crystalline order. The difference in crystalline conformation results also in the loss of elastic modulus and decrease in thermal stability.^{4)(a)} Furthermore, most research has focused on chloride anion, and thus little work has been devoted to finding

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more suitable ILs for cellulose dissolution. The question of whether there are other potential ILs for dissolution should be an interesting research theme and a key to the answer would depend on how to design IL structure for cellulose dissolution.

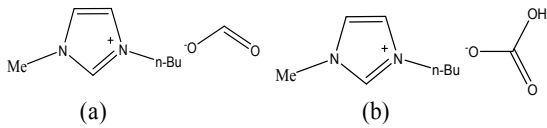


Fig1. Structures of [bmim][HCO₂](a),and[bmim][HCO₃](b)

In this context, we are working to find new and powerful ILs as solvents for cellulose and to evaluate their effects on cellulose dissolution. After some preliminary considerations, we focused on the anion effect of ILs rather than the cation effect and established the following criteria: (1) The candidates should be in a liquid state at room temperature as room temperature ionic liquids (RTILs) can yield the process improvement. (2) The ILs should interfere with the great number of hydrogen bonds in cellulose and thus effectively dissolve cellulose.

2. EXPERIMENTAL

According to the selected criteria, 1-butyl-3-methylimidazolium formate ([bmim][HCO₂]) and 1-butyl-3-methylimidazolium hydrogen carbonate ([bmim][HCO₃]) were evaluated in the present work. [bmim][Cl] was also prepared for comparison with the suggested system. The anions, HCO₂-and HCO₃-, are weak acids against water, which attract proton. The synthesis procedure for [bmim][HCO₂] and [bmim][HCO₃] was divided into two steps. The desired cation was formed, and converted into the corresponding anion, formate and hydrogen carbonate, by anion exchange. A solution of 1-methylimidazole (0.10 mol) and 1-chlorobutane (0.20 mol) was refluxed under nitrogen for 48 h. The unreacted starting materials were removed by extraction with diethyl ether ([bmim][Cl]).

Sodium formate/bicarbonate (40 mmol) was added to a solution of [bmim][Cl] (40 mmol) in MeOH (20mL), and the mixture was stirred at room temperature for 10 h. The

precipitated NaCl(KCl) was filtered off, and was added Methylene Chloride to remove an excess NaCl(KCl), and then dried at 50 °C for 24 h. A viscous paste of 10 wt % cellulose was formed and cellulose was rapidly separated from IL when water was added to the system. Figure 1 shows the structural formula of [bmim][HCO₂] and

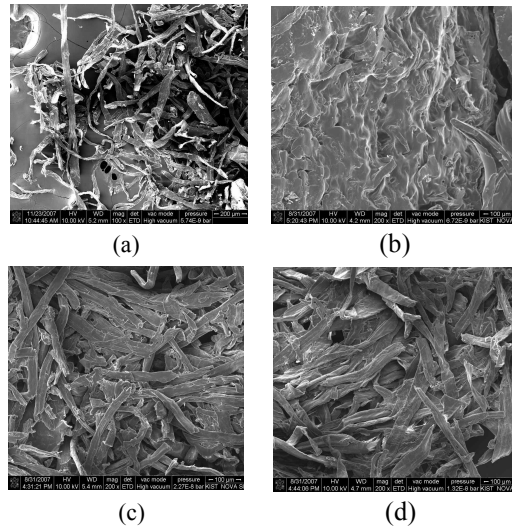


Fig 2. SEM images of native cellulose (a), images of regeneration after dissolution in [bmim][Cl] (b), [bmim][HCO₂](c),and[bmim][HCO₃](d).

[bmim][HCO₃]. Both are in a liquid state at room temperature while [bmim][Cl] has a melting point of 65 °C. The cellulose sample was added to [bmim][Cl], [bmim][HCO₂] and [bmim][HCO₃] at 100 °C.

3. RESULT

SEM photographs were taken of cellulose regenerated from ILs after dissolution, as presented in Figure 2, in order to evaluate morphology changes. Transformation of the cellulose regenerated from [bmim][Cl] after dissolution (CelCl) was observed from the SEM image, as shown in Figure 2(b). Compared to the shapes observed from native cellulose, it was found that the morphology of CelCl was significantly transformed and the original structure had almost disappeared. In contrast, Figure 2(c) and 2(d) show that the morphology was preserved after

regeneration from [bmim][HCO₂](Cel_{HCO₂}) and [bmim][HCO₃](Cel_{HCO₃}), respectively.

The structural changes during dissolution of cellulose were characterized by X-ray diffraction (XRD), as shown in Figure 3. It has been reported that when native cellulose is dissolved and subsequently regenerated from solution, its crystal phase normally transforms from cellulose I to cellulose II.⁴⁾⁻⁶⁾ During dissolution, solvents penetrate cellulose and induce rearrangement of the crystal packing of the polymer chains, leading to a phase transition. This process is irreversible and usually accompanied by a decrease in the crystallinity.⁶⁾

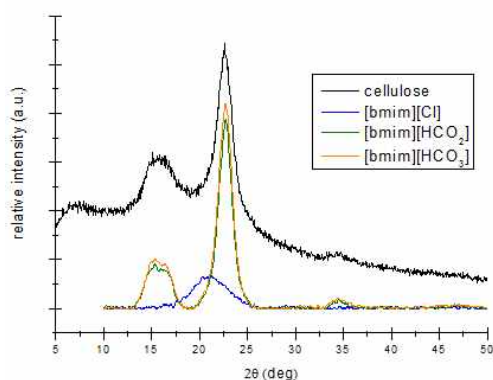


Fig 3. XRD of cellulose regenerated from ILs

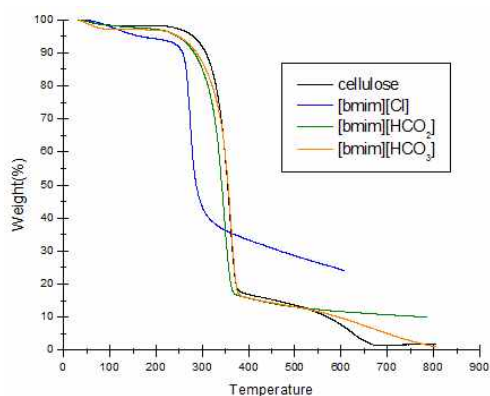


Fig 4. TGA curves of cellulose regenerated from ILs.

After dissolution in [bmim][Cl], as seen in Figure 3, the regenerated cellulose exhibits the the diffraction patterns

of cellulose II and, compared to the native cellulose, the intensity of the diffraction peaks is significantly reduced. On the contrary, when [bmim][HCO₂] and [bmim][HCO₃] were used, the resulting regenerated cellulose structure was still cellulose, as indicated by the typical strong diffraction peak at $2\theta = 22.7^\circ$, representing strong crystalline intensity.^{7),8)} It is of interest that the crystal structure of native polymer can be reproduced, given that regenerated samples with native cellulose I lattice is difficult to secure.^{9),10)} HCO₂- and HCO₃- as weaker proton drawing groups than Cl- may be more effective solvents in terms of cellulose dissolution. Compared to Cl-, the relatively bulky size and weak electronegativity of HCO₂- and HCO₃- have an impact on the dissolution mechanism. The steric effect slows penetration of the anion into the polymer chains, and the appropriate basicity interferes with intermolecular and intramolecular hydrogen bonding in the polymer without breaking the structural network. In contrast, Cl- rapidly disrupts or even breaks intermolecular and intramolecular hydrogen bonding in the dissolution process, ultimately preventing recrystallization.⁴⁾

TGA curves are shown in Figure 4. The two samples regenerated from [bmim][HCO₂] and [bmim][HCO₃] exhibit that their thermal stability is slightly inferior to native cellulose, but comparable. This result suggests that cellulose can be regenerated into the native lattice without change of original properties. However, the curve shows the sample regenerated from [bmim][Cl] has a much lower onset temperature for decomposition as revealed by the previous report.³⁾

4.SUMMARY

Two RTILs, [bmim][HCO₂] and [bmim][HCO₃], were introduced into cellulose dissolution. Cellulose I was regenerated from [bmim][HCO₂] and [bmim][HCO₃], and cellulose II was obtained from [bmim][Cl]. The structure of regenerated cellulose depends on species of anion in ILs. Accordingly, the kind of ILs can act as a selective gate to determine the crystal structure of cellulose regenerated from solution. Because of these unique characteristics, the newly proposed IL systems will

suggest a key step toward the environmentally-benign process and can provide engineers and scientists with more options for selecting a suitable solvent according to their research purpose.

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