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Swelling Behaviors of Natural Cellulose in Ionic Liquid Aqueous Solutions

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ABSTRACT: In the study, a series of methylimidazolium ionic liquids were prepared, including five acidic and seven neutral ionic liquids; and the effects of these ionic liquids on swelling behavior of bagasse cellulose were investigated. The focus of this work is to investigate the relationship between the properties of ionic liquids and the swelling capacity. The swelling absorbency for cellulose in the acidic ionic liquid aqueous solutions was less than in distilled water. It was found that the partial hydrolysis on cellulose surface occurred along with swelling simultaneously. In neutral ionic liquid aqueous solutions, the nonlinearity of swelling ability with the alkyl chain length was discovered. It could be attributed to the dual role of hydrophobic interactions and steric effects provided by cations. Furthermore, small polarizable anions also contribute to the swelling of cellulose to some extent. The properties of treated cellulose were also investigated and compared with the native fibers by scanning electron microscopy. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40199.

KEYWORDS: cellulose and other wood products; ionic liquids; swelling

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INTRODUCTION

Cellulose is the most abundant renewable biopolymer composed of anhydroglucose units by *β*-glycosidic bonds. For instance, a typical chemical analysis of bagasse is: 45–55% cellulose, 20–25% hemicellulose, and 18–24% lignin. It exhibits several promising properties, including hydrophilicity, good biodegradability, biocompatibility, low toxicity, and capacity for broad chemical modification.[1,2] In the past few decades, there has been increased interest in cellulose as an important raw material for many industrial fields.[1] Therefore, the swelling of cellulose by different media (acids, bases, and organic solvents) is an important initial step in several processes, such as mercerization and functionalization/derivatization of cellulose under homogeneous and heterogeneous reaction conditions.[3,4]

In recent years, many technologies used in cellulose processing are not very environmentally desirable. Meanwhile, the high crystal structure owing to the hydrogen bond network between hydroxyl groups also restricts the conversion and other application of cellulose. As potential environment-friendly green solvents, ionic liquids have gained considerable attention. They are molten salts with a melting point below 100°C. Compared with traditional volatile organic solvents, ionic liquids have many fascinating characteristics, including high thermal stability, negligible vapor pressure, non-flammability, tunable solubility, and recyclability.[5] Consequently, ionic liquids have attracted increasing attention in biopolymer field, including cellulose regeneration,[6] derivatization,[7] hydrolysis,[8] etc.

Two key aspects are unavoidable in the research of the swelling of cellulose, which are the structural characteristics of cellulose and the physico-chemical properties of the medium.[9] Concerning the former, the degree of polymerization, index of crystallinity, and the morphological characteristics of cellulose have been studied in detail.[3,9,10] Some other works[9,11] focus on the swelling phenomenon in traditional organic solvents. While with regard to the properties of the swelling medium, little information can be found about the new emerging ionic liquids until now. In our study, the medium is a series of imidazolium ionic liquid solution, and the object of swelling is bagasse cellulose not the microcrystalline cellulose. As far as we know, there has been no systematic investigation for bagasse cellulose swelling in imidazolium ionic liquids.

On the basis of above background, the present work aims to investigate the swelling behaviors of bagasse cellulose in ionic liquids aqueous solution. In this work, twelve imidazolium ionic liquids were employed, including five acidic ionic liquids and seven neutral ionic liquids, in order to study the effects on equilibrium absorbency and swelling rate. This implies important information in the further research and application of ionic liquids in cellulose materials.

EXPERIMENTAL

Materials

Sugarcane bagasse was supplied by a local sugar factory. It was first dried in sunlight and then cut into small pieces (1–3 cm). Then the sliced bagasse was dewaxed and ground in a pulverizing mill to pass through a 40-mesh sieve. The powders underwent pre-treatment with H_2O at 60–80°C for 2 h. Then they were further dried overnight in an oven at 60°C before use.

Twelve investigated ionic liquids were as follows:

1. 1-Propyl sulfonic acid-3-methylimidazolium hydrogensulfate, noted([C_3SO_3Hmim]HSO_4),
2. 1-Propyl sulfonic acid-3-methylimidazolium chloride, noted ([C_3SO_3Hmim]Cl),
3. 1-Methylimidazolium hydrogensulfate, noted ([Hmim] HSO_4),
4. 1-Propyl sulfonic acid-3-methylimidazolium dihydrogenphosphate, noted([C_3SO_3Hmim]H_2PO_4),
5. 1-Butyl-3-methylimidazolium hydrogensulfate, noted ([Bmim]HSO_4),
6. 1-Allyl-3-methylimidazolium chloride, noted ([Amim]Cl),
7. 1-Butyl-3-methylimidazolium chloride, noted ([Bmim]Cl),
8. 1-Butyl-3-methylimidazolium bromide, noted ([Bmim]Br),
9. 1-Ethyl-3-methylimidazolium bromide, noted ([Emim]Br),
10. 1-Pentyl -3-methylimidazolium bromide, noted ([Pemim] Br),
11. 1-Hexyl-3-methylimidazolium bromide, noted ([Hexmim] Br),
12. 1-Propyl-3-methylimidazolium bromide, noted ([Prmim] Br).

The structures of ionic liquids used in this study are displayed in Figure 1 and their purities are all above 97%. To remove the coexisting water in the IL, the IL has been kept in the vacuum drying oven at 50°C for 24 h. All other chemical reagents, purchased from commercial sources in China, were analytical grade or higher in purity.

Preparation of Cellulose

Cellulose was prepared by addition of 4 g oven dried bagasse powder to 160 mL 7% sodium hydroxide solution in a 250-mL three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. The mixture was kept at 70°C for 8 h. This removed the greater part of lignin and a large part of hemicellulose. Because of persistent discoloration the product was subsequently bleached with sodium hydroxide/hydrogen peroxide mixture to remove residual lignin and hemicellulose. The bleached cellulose fibers were washed repeatedly with distilled water until the solution reached a neutral pH. The obtained cellulose fibers were completely dried and weighed. Then the cellulose fibers were ground in a pulverizing mill and further sieved through a 40–100 mesh sieve. Powdered celluloses (40–100 mesh) were kept at 40°C in a vacuum oven for 24 h before use.

Swelling of Cellulose in Solvents

A mesh bottle containing pre-weighted dry cellulose was immersed in excessive ionic liquid solution and kept undisturbed for 24 h at 50°C until swelling equilibrium was reached.

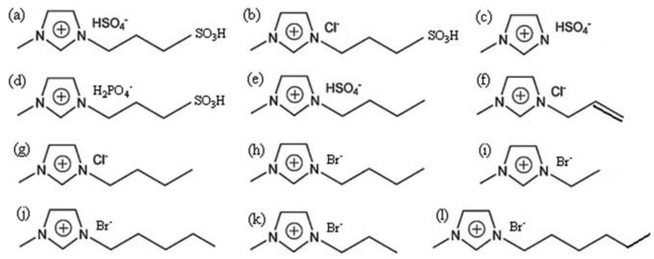

Figure 1. Ionic liquids used in the experiments. (a) [C_3SO_3Hmim]HSO_4, (b) [C_3SO_3Hmim]Cl, (c) [Hmim]HSO_4, (d) [C_3SO_3Hmim]H_2PO_4, (e) [Bmim]HSO_4, (f) [Amim]Cl, (g)[Bmim]Cl, (h) [Bmim]Br, (i) [Emim]Br, (j) [Pemim]Br, (k) [Prmim]Br, (l) [Hexmim]Br.

Then the mesh bottle was removed and centrifuged. Subsequently, the mesh plus cellulose was quickly weighted. After weighing the mesh bottle containing the swollen cellulose, the equilibrium absorption can be calculated using the following equation:

$$Q=(w_2-w_1)/w \quad (1)$$

where Q is the absorption ratio defined as grams of liquid per gram of sample, w_1 and w_2 are the mass (g) of the mesh bottle containing the sample before and after swelling, respectively, w is the mass (g) of sample before swelling.[9]

Swelling rate of the cellulose was measured according to the following process. The mesh bottle containing pre-weighted cellulose was poured into excessive ionic liquid solution at 50°C. At certain time intervals, the liquid absorbency of cellulose was measured according to eq. (1).

The cellulose-containing mesh bottle was introduced into an epoxide separation tube (shown in Figure 2). The latter was introduced into the centrifuge metal tube. There is enough space between the bottom of (b) and (c), so that the solvent could be completely separated from cellulose by high-speed centrifugation.

Analytical Methods

The yield of the total reducing sugars (TRS) was measured by phenol-sulfuric acid method. A mixture containing 0.5 mL swelling solution, 1.5 mL distilled water, 1 mL 5% phenol, and 5 mL 98% concentrated sulfuric acid was prepared. Then the absorbance was measured at 490 nm using UV–vis spectrophotometer. The concentration of TRS was calculated based on the standard curve obtained with glucose.

Scanning electron microscopy (SEM) photographs of virgin bagasse cellulose and treated fibers surfaces were captured using JSM-7500F (JEOL Co Ltd., Tokyo, Japan). In this case, the cellulose samples were coated with gold using the sputtering technique and scanned at room temperature.

RESULTS AND DISCUSSION

Swelling Behaviors of Cellulose in Acidic Ionic Liquids Solution

Performance Comparison of ILs. The five acidic ionic liquids employed in this study all belong to protic solvents. They include [C_3SO_3Hmim]HSO_4, [C_3SO_3Hmim]Cl, [Hmim]HSO_4, [C_3SO_3Hmim]H_2PO_4, and [Bmim]HSO_4, respectively. Ionic

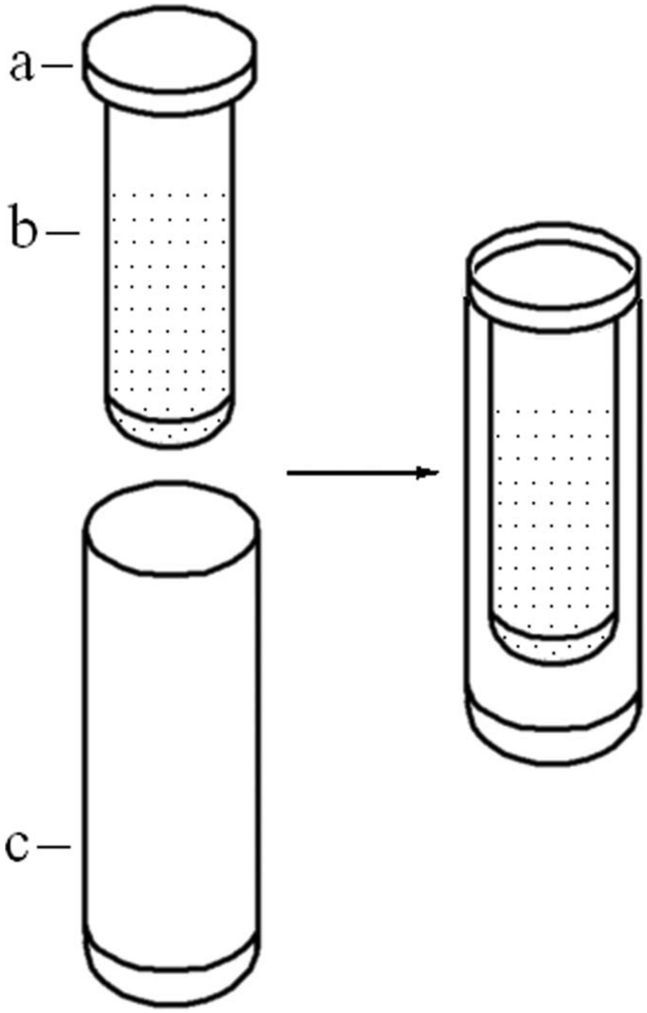

Figure 2. Schematic representation of the epoxide tube employed for the removal of mechanically retained solvent. (The cellulose-containing mesh is placed in tube (b); the latter is closed with stopper (a), and inserted in (c)).

liquids with active hydrogen may bear on the relative importance for swelling effects. Because several inter- as well as intramolecular hydrogen-bonding could be formed due to their functional nature (hydrogen-bond donors or acceptors). Their pH values were measured in the 0.2 mol/L aqueous solution at 25°C by pH meter (PHS-25, China), which were 0.52, 0.83, 1.02, 1.18, and 1.20, successively.

The performance of the selected ionic liquids was compared under the same molar concentrations (0.5 mol/L aqueous solution) at 50°C for 24 h, and the result is shown in Figure 3(a). It can be seen that the absorbency for cellulose in acidic ionic liquids solution is less than that in distilled water, and there is no significant difference among the acidic ionic liquids. As it is known, cellulose is three-dimensional networks of hydrophilic polymers. When cellulose is placed in water, the water diffuses into the polymer matrix, and then causes its swelling. This diffusion process involves migration of water into pre-existing or dynamically formed spaces between macromolecular chains. While in ionic liquid solution, the partial hydrolysis on cellulose

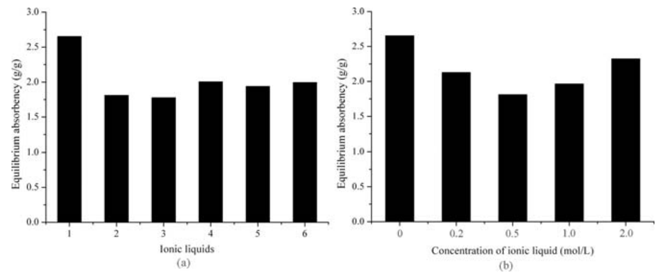

Figure 3. The effect of ILs type and concentration on the swelling behaviors of cellulose: (a) 1-H_2O, 2-[C_3SO_3Hmim]HSO_4, 3-[C_3SO_3Hmim]Cl, 4-[Hmim]HSO_4, 5-[C_3SO_3Hmim]H_2PO_4, 6-[Bmim]HSO_4).

surface occurs along with swelling simultaneously. As for the hydrolysis products, a preliminary analysis with phenol-sulfuric acid method was employed to illustrate the occurrence of the TRS.[12] Subsequently, in order to further illustrate this phenomenon, different concentrations (0.2 mol/L, 0.5 mol/L, 1.0 mol/L, 2.0 mol/L) of ionic liquid [C_3SO_3Hmim]HSO_4 were carried out to investigate their effect on the equilibrium swelling ratio. As shown in Figure 3(b), the swelling ratio decreases obviously first then increases. Meanwhile, the TRS content was also studied in liquid, and the results are shown in Figure 4. It was obvious that the yield of TRS dramatically increased, when the concentration was increased from 0.2 mol/L to 2.0 mol/L. The results are consistent with the previous hypothesis. Carlsson et al.[13] also found that the swelling of wood pulps is maximal at about neutrality and depressed at both low and high pH values. Hence, the results of cellulose swelling in acidic ionic liquid, to some extent, can provide basic information for cellulose hydrolysis.

Effects of Acidic Ionic Liquid on Swelling Rate. In practical applications, swelling rate is important information besides the swelling equilibrium. Figure 5 shows the swelling kinetics of cellulose in ionic liquid solution and DMSO. It can be seen that the swelling rate of cellulose in ionic liquid solution slowly reduced from 0.5 h to 7 h. On the contrary, the swelling rate in

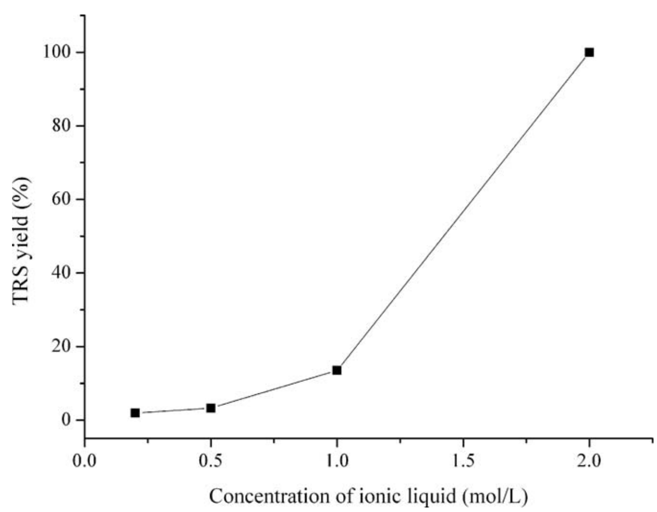

Figure 4. Concentration course of the TRS during the swelling of cellulose (the maximum amount in curve was taken to be 100%).

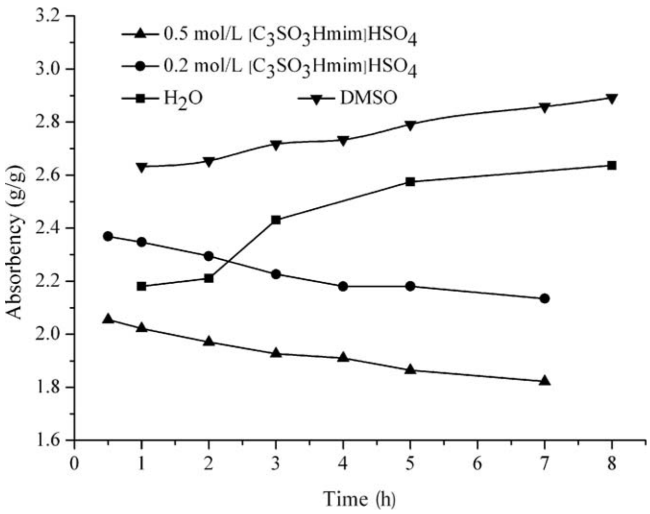

Figure 5. The swelling rate of cellulose in different solution.

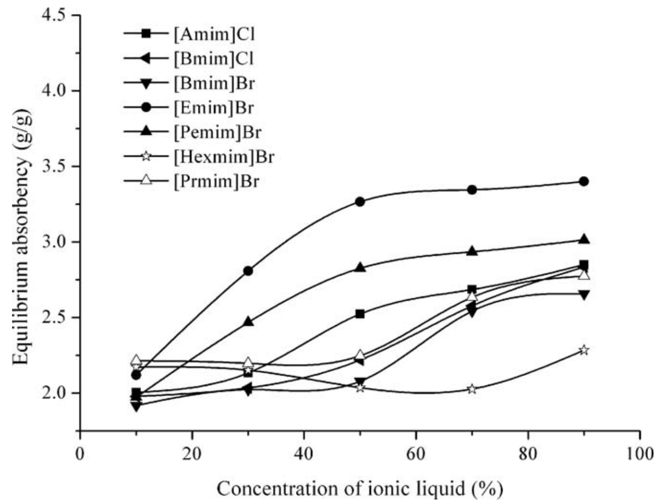

Figure 6. The effect of ILs type on the swelling behaviors of cellulose.

both distilled water and DMSO increased slightly and then began to level off. These behaviors result from the hydrolysis caused by acidic ionic liquids in some degree. And the relatively higher swelling ratio in DMSO may be attributed to its higher hydrogen-bond basicity than water. It has been reported that the hydrogen-bond basicity of solvent is important for cellulose dissolution in terms of the Kamlet–Taft equation.[14] DMSO exhibits a value of 0.76,[15] which is much higher than that of water (0.38).[16] These results indicated that the acidic ionic liquid is an effective catalyst for cellulose hydrolysis, as well as DMSO is an efficient solvent for cellulose swelling and dissolution, which could lay the foundation for future work in the homogeneous catalytic hydrolysis of cellulose.

Swelling Behaviors of Cellulose in Neutral Ionic Liquids Solution

Comparison of Performance of ILs. As shown in Figure 1, seven neutral ionic liquids (f–l) were employed to investigate the effect of structure on swelling. The cations of selected ionic liquids are all based on 1-alkyl-3-methylimidazolium. The swelling mechanism of cellulose in ionic liquids involves the oxygen and hydrogen atoms of cellulose-OH in the formation of electron donor–acceptor (EDA) complexes interacting with ionic liquid.[17] Accordingly, the cations of ionic liquids act as the electron acceptor center and the anions as the electron donor center.

In this section, the performance of the chosen ionic liquids was compared under the same concentration at 50°C for 24 h. Figure 6 presents the variation of equilibrium absorbency for cellulose in various concentrations of ionic liquids. The results showed that a relatively small cation is often efficient in swelling cellulose. It can be seen that 1-ethyl-3-methylimidazolium cation, $[Emim]^+$, is more powerful in swelling of cellulose than other observed cations due to its smaller size. When the cation becomes larger, the ability to form hydrogen bonds with cellulose will decrease. This discovery was also confirmed by Zhao et al.[18] While from the odd-number carbon chain, 1-pentyl-3-methylimidazolium bromide was the most efficient one for cellulose swelling. This discovery is consistent with the odd-even effect observed by Erdmenger in his investigation for cellulose dissolution.[19] This nonlinearity of swelling ability with the alkyl chain length should be attributed to the dual role of hydrophobic interactions and steric effects caused by cations. Moreover, it was found that task-specific ionic liquids, as a series of special ILs containing functional groups[20] (e.g., double bond, hydroxyl, sulfonic group, etc.), also have effects on cellulose swelling. For example, [Amim]C1, with a double bond, is effective for cellulose swelling. Furthermore, the performance of [Bmim]C1 and [Bmim]Br was compared. The former exhibits higher swelling ratios than the latter. This result could be ascribed to the fact that the electronegativity of the chloride anion is larger than bromide anion. Additionally, the smaller radius of chloride anion also makes a great contribution to the higher swelling ratio.

Effects of Neutral Ionic Liquid on Swelling Rate. The swelling behavior of cellulose in [Amim]C1 and [Emim]Br aqueous solutions with different concentrations is shown in Figure 7. It can be seen that the swelling in [Amim]C1 aqueous solution decreased with time and then began to level off. However, in

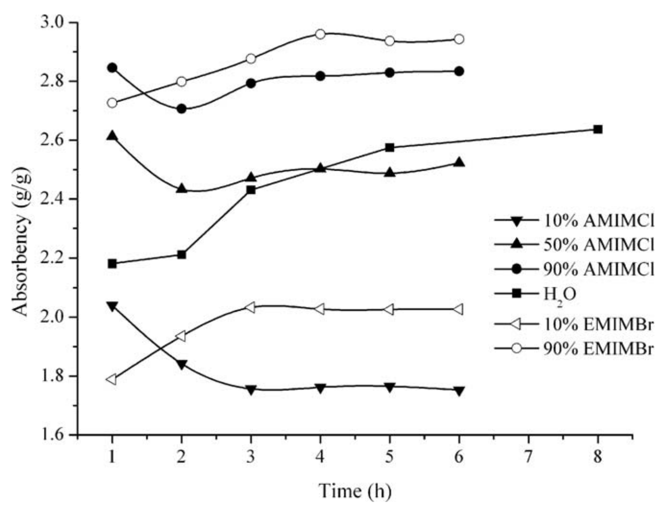

Figure 7. The swelling rate of cellulose in neutral ionic liquid solution.

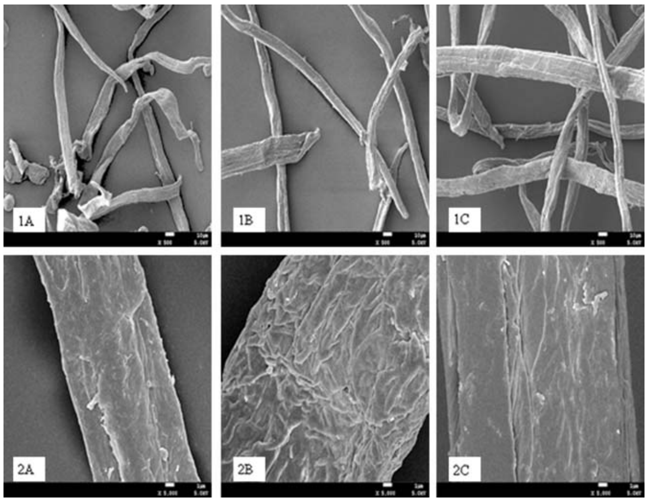

Figure 8. Scanning electron micrographs of (A) Untreated bagasse cellulose, (B) Bagasse cellulose swelled in acidic ionic liquid, and (C) Bagasse cellulose treated with neutral ionic liquid (Micrographs 1A, 1B, and 1C are for cellulose (500×), micrographs 2A, 2B, and 2C are for cellulose (5000×)).

the analysis of TRS, almost no TRS was detected in the neutral ionic liquid aqueous solution after swelling. The result indicated that no degradation of cellulose occurred in the neutral ionic liquid aqueous solution. Therefore, the changing of swelling rate of cellulose could be attributed to partial dissolution on its surface. In contrast, the swelling in [Emim]Br aqueous solution increased with time and then began to level off. Meanwhile, the swelling ratio of cellulose was obviously raised with the increasing concentration of the ionic liquid. The result indicated that they are powerful solvents to swell or dissolve cellulose. Therefore, the neutral ionic liquid can act as ideal medium in cellulose application.

Scanning Electron Microscopy Analysis

Figure 8 shows that the SEM micrographs of the original ground bagasse (A), the cellulose after swelling in acidic ionic liquid (B), and cellulose treated with neutral ionic liquid (C).

The diameter of the swollen bagasse fiber was much bigger than that of virgin sample. It is interesting to observe a large roughness on the surface of cellulose treated with acidic ionic liquid solution. However, the virgin cellulose (2A) as well as the fiber treated with neutral ionic liquid (2C) has a smooth surface. The significant difference presents that the swelling in acidic ionic liquid solution leads to modification in the biopolymer supramolecular structure. These behaviors are in agreement with the results in the above works. Therefore, the neutral ionic liquids are possibly potential direct solvents for cellulose. Conversely, the roughness on the surface of cellulose treated with acidic ionic liquid solution indicates that the swelling generates modification in the biopolymer supramolecular structure. Comparatively, a smoother surface on fiber treated with neutral ionic liquid shows that neutral ionic liquid possibly is a desired direct solvent for cellulose.

Therefore, in the application of catalytic conversion of cellulose, the neutral ionic liquid can be considered as a useful medium in the presence of acidic ionic liquid, which serves as a catalyst. Thus, it will promote mass and heat transfer, and then enhance the catalytic activity.

CONCLUSIONS

Twelve ionic liquids, including five acidic ionic liquids and seven neutral ionic liquids, have been used in order to study the swelling behavior of bagasse cellulose. For the acidic ionic liquid solutions, the absorbency for cellulose is less in distilled water, while no significant difference among the acidic ionic liquids. It was found that the hydrolysis on cellulose surface occurs along with swelling simultaneously. In the neutral ionic liquid solutions, the effect of alkyl chain length ranging from C_2 to C_6 was systematically investigated. Generally, relatively small cations are often efficient in swelling cellulose, whereas from the odd-number carbon chain, [Pemim]Br was the most efficient one for cellulose swelling at 50°C. This nonlinearity of swelling ability with the alkyl chain length could be ascribed to the dual role of hydrophobic interactions and steric effects caused by cations. Additionally, a larger electronegativity as well as smaller radius of anion can make a great contribution to a higher swelling ratio. This may be due to its small polarization effect. Furthermore, SEM shows a comparison of surface structure between native cellulose and treated fibers.

The swelling behaviors present important information for cellulose conversion in our future work. In the catalytic conversion of cellulose, the neutral ionic liquid will be considered as the medium, and acidic ionic liquid can serve as a catalyst simultaneously. Thus, the combined system will promote mass and heat transfer, and then the catalytic activity is enhanced.

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