

Addition of 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) Imide to Improve the Thermal Stability of Regenerated Cellulose

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ABSTRACT: This article reports the influence of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMITFSI) addition on the thermal and mechanical properties of regenerated cellulose. Scanning electron microscopy, Young's modulus values, thermogravimetric analysis, glass-transition temperature values, and ultraviolet-visible spectroscopy were used to assess the effect of BMITFSI addition on the properties of regenerated cellulose. The addition of a room-temperature ionic liquid, BMITFSI, during the dissolution of cellulose was found to enhance the thermal stability of regenerated cellulose. Compared to other reported plasticizers for regenerated

cellulose, such as glycerol, glycols, water, mineral oil, and α -monoglycerides, the low vapor pressure of BMITFSI led to a long performance with the least evaporation or leaching. In addition, the immiscible nature of BMITFSI in water and its stability against moisture made BMITFSI an effective plasticizer for regenerated cellulose over a broad range of surrounding humidities and temperature conditions. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 750–755, 2011

Key words: biopolymers; blending; FT-IR; thermogravimetric analysis (TGA)s

INTRODUCTION

Cellulose, the most abundant polymer found in nature and produced in a sustainable way, offers many possible applications because it is renewable and biodegradable. Cellulose is used in many applications, such as in films for hemodialysis,¹ water resistance,² sensors,³ and actuators.⁴ Even though cellulose has advantages over other petroleum-based polymers, its applications have been limited because of the presence of a large number of intramolecular and intermolecular hydrogen bonds.

Plasticization is a very simple and useful method for improving the mechanical properties of polymers. Plasticizers are low-molecular-weight resins or liquids that form secondary bonds to the polymer chains and spread them apart, so as to improve the flexibility and processability of polymers.⁵ Many compounds, such as glycerol, glycols, water, mineral oil, and α -monoglycerides, have been used as plasticizers of cellulosic materials.^{6–8} Although these compounds are fairly effective, they suffer from mobility

and volatility and, hence, are lost by migration or evaporation. They are also so highly hygroscopic that their effectiveness as plasticizers largely depends on the ambient humidity and temperature conditions.⁹

Ionic liquids (ILs) are salts in which ions are poorly coordinated; this results in them being liquids below 100°C or even at room temperature [room-temperature ionic liquids (RTILs)]. ILs have interesting properties, such as nonvolatility, high stability, suitable polarity, and high ionic conductivity.¹⁰ RTILs containing bis(trifluoromethylsulfonyl) imide are especially attractive because they have many advantages compared to other common ILs, namely, a wide electrochemical potential window, an acceptable ionic conductivity, a high thermal stability, and a negligible vapor pressure. They are also hydrophobic and stable against moisture.^{11–14}

Our research group developed a cellulose as a smart material that can be used for sensors, actuators, and microelectromechanical system devices. This material is called *electroactive paper* (EAPap) and is made by regenerating cellulose.⁴ In this article, we report its enhanced thermal stability of regenerated cellulose by the simple addition of an RTIL, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMITFSI). The influence of BMITFSI addition on the properties of regenerated cellulose was measured in terms of Young's modulus, thermogravimetric analysis (TGA), and the

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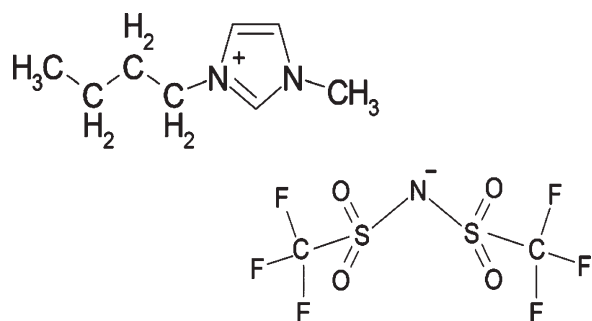


Figure 1 Scheme of BMITFSI.

glass-transition temperature (T_g). Figure 1 shows the scheme of BMITFSI.

EXPERIMENTAL

Materials

Cotton cellulose (MVE, DPW 4580) was purchased from Buckeye Technologies Inc. (Tennessee, USA). Trifluoroacetic acid (TFA; >99%) was purchased from Dae-Jung Chemical and Metals Co., Ltd. (Gyeonggi-Do, South Korea). BMITFSI (HPLC grade) was purchased from Sigma-Aldrich.

Sample preparation

Samples of regenerated cellulose composed of BMITFSI were prepared by the dissolution of cotton pulp in TFA with different weight percentages of BMITFSI (0.01, 0.02, 0.03, 0.04, 0.06, 0.08, and 0.1 wt %). Upon complete dissolution, the clear mixture solutions were poured onto glass Petri dishes and cured under ambient conditions for 1 day. By evaporating TFA, we changed the cast films to regenerated cellulose films. To ensure the complete elimination of TFA, the regenerated cellulose films were further dried under high vacuum for 2 days. TFA was used to dissolve cotton cellulose because TFA is a non-aqueous and nonderivatizing solvent for cellulose and can dissolve both native and regenerated cellulose at room temperature within a few days. Unlike other solvent systems, for example, *N,N*-dimethylacetamide/LiCl, TFA requires no curing or washing processes to remove remnant solvents upon the dissolution and regeneration of cellulose. Furthermore, TFA can be removed from the film by natural evaporation by the hydrolysis of trifluoroacetyl ester groups with moisture in the air¹⁵ so that ILs can be easily incorporated into cellulose.

Characterization

The cross sections of the samples were examined with scanning electron microscopy (SEM; Hitachi S4300) (Hitachi, Tokyo, Japan). The films were

coated with carbon *in vacuo* before SEM observation employing E102 ion sputter from HITACHI (Tokyo, Japan). IR spectra were obtained with a Bio-Rad FTS 3000 spectrometer from Digilab (Cambridge, USA) with KBr beam splitter, detector at 8 cm^{-1} resolution and 300 scans per sample. Ultraviolet-visible (UV-vis) spectra in the range 200–250 nm were obtained with a diode array spectrophotometer (HP 8452A, Hewlett Packard, Waldbronn, Germany).

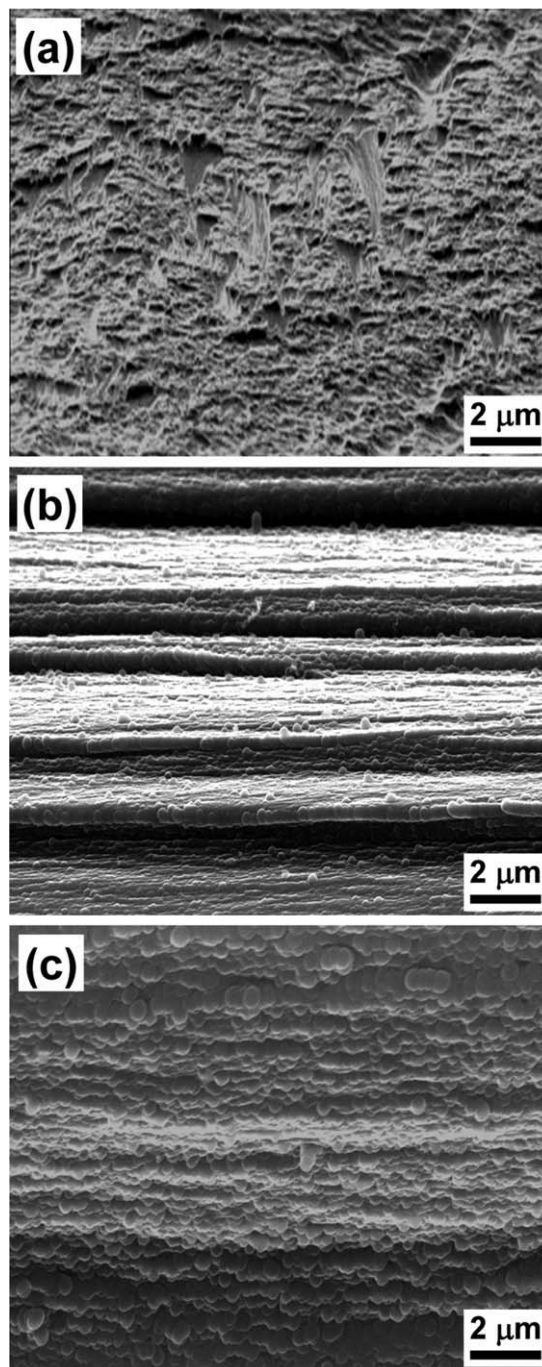


Figure 2 Cross-sectional SEM images of regenerated cellulose films with different BMITFSI contents: (a) pristine cellulose, (b) 0.06% BMITFSI, and (c) 0.1% BMITFSI.

TABLE I
Thermal Stability of Cellulose Mixed with Different Amounts of BMITFSI

BMITFSI content (%)	Mass loss at 200°C (wt %)	Mass loss at 300°C (wt %)
0 (bulk cellulose)	5.7 ± 1.5	19.9 ± 4.6
0.01	3.2 ± 1.2	19.1 ± 4.0
0.02	3.0 ± 1.1	18.1 ± 3.5
0.03	2.8 ± 0.9	16.2 ± 2.8
0.04	2.6 ± 0.9	14.2 ± 2.3
0.06	2.1 ± 0.7	10.6 ± 1.9
0.08	1.9 ± 0.5	8.6 ± 1.3
0.1	1.3 ± 0.3	2.3 ± 0.9

The thermal stability and T_g of the samples were analyzed by TGA (Netzsch, STA 409 PC) from (NETZSCH-Geratebau GmbH, Selb., Germany) and differential scanning calorimetry (Netzsch, DSC 200F3), respectively. The films were cut into pieces, and the weight loss of the samples was analyzed by the burning of samples (10–15 mg) in air with heating up to 700°C at a heating rate of 10°C/min.

Tensile testing was conducted according to ASTM D 882-97 with a universal testing machine manufactured locally by Hanvac system, Incheon, South Korea. Two ends of the specimen were fixed between the upper and lower jaws of the instrument with a gauge length of 50 mm. The test was performed under ambient conditions with a pulling rate of 0.5 mm/min.

RESULTS AND DISCUSSION

Figure 2 depicts the SEM images taken at the cross section of the samples when the BMITFSI content was 0 (pristine cellulose), 0.06, and 0.1%. Pristine regenerated cellulose showed a typical compact fibril structure [Fig. 2(a)] having a discontinuous layers. TFA is a very strong acid; the dissolution and regeneration of cellulose in it was mainly responsible for the disturbed structure. On the other hand, the addition of BMITFSI molecules changed it to a uniform layered structure. The reason might have been the entrapment of BMITFSI molecules between cellulose layers during the dissolution and regeneration process.

The mass losses of BMITFSI mixed cellulose at 200 and 300°C were calculated with TGA and are shown in Table I. Bulk cellulose exhibited mass losses of 5.7 ± 1.5 and $19.9 \pm 4.6\%$ at 200 and 300°C, respectively. In wood fibers, the potential water absorption sites are hydroxyl and carboxyl groups. Thus, a large mass loss might be attributed to the loss of water absorbed from the surrounding environment and the remnant solvent. These values decreased to 3.2 ± 1.2 and $19.1 \pm 4.0\%$, respectively, with the

addition of 0.01 wt % BMITFSI and tended to decrease further with increasing BMITFSI content. Finally, with the addition of 0.1 wt % BMITFSI, the mass losses of cellulose at 200 and 300°C were found to be 1.3 ± 0.3 and $2.3 \pm 0.9\%$, respectively. Figure 3 illustrates the compared mass losses of pristine regenerated cellulose and the regenerated cellulose incorporated with 0.1 wt % BMITFSI. The thermal degradation temperature of cellulose was enhanced from 350 ± 10 to $380 \pm 15^\circ\text{C}$ with the addition of BMITFSI molecules. ILs have been reported to have a high thermal stability with very little evaporative loss beyond 300°C;¹⁶ this characteristic of ILs might have been responsible for the improved thermal stability of the regenerated cellulose with BMITFSI addition.

Plasticizers are expected to reduce the Young's modulus, tensile strength, and T_g of polymers and to increase their flexibility, elongation at break, toughness, dielectric constant, and power factor.¹⁷ Figure 4(a) shows the BMITFSI content effect on the T_g values of the regenerated cellulose. The T_g value of regenerated cellulose decreased with increasing BMITFSI content, and there was a remarkably linear relationship between T_g and the BMITFSI content. The T_g value of regenerated cellulose was reduced to $229 \pm 12^\circ\text{C}$ at 0.1 wt % BMITFSI. Generally, plasticizers are relatively low-molecular-weight compounds added to polymers during processing to reduce the intermolecular bond strength by positioning themselves between the polymer molecules, thus separating them and reducing their interactions.¹⁸

Figure 4(b) shows the variation in Young's modulus of the regenerated cellulose with various amounts of BMITFSI. The Young's moduli of the samples

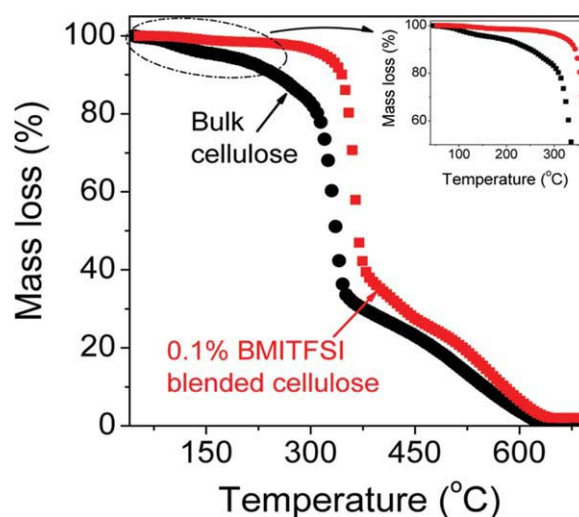


Figure 3 TGA curves of the pristine cellulose and BMITFSI-incorporated cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

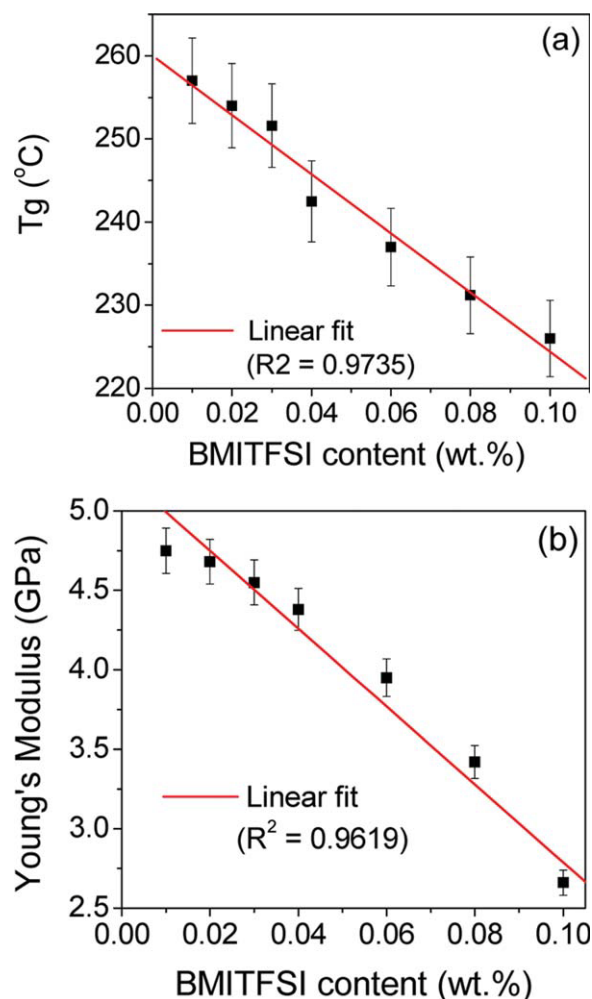


Figure 4 (a) Effect of the BMITFSI content on T_g of cellulose and (b) variation in the Young's modulus of regenerated cellulose loaded with different amounts of BMITFSI. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

were determined according to ASTM D 882-97 under ambient conditions. The Young's modulus results show a similar tendency to that of the T_g results and indicate that BMITFSI indeed acted as a plasticizer of cellulose. The incorporation of BMITFSI into cellulose caused the breaking of hydrogen bonds and reduced their interactions; therefore, the material was made softer and more pliable. This also

allowed the polymer chains to deform more easily and T_g and the melting temperature to be lowered. Because of these, we may have foreseen a decrease in the crystallinity of semicrystalline polymers with increasing plasticizer content, as suggested by Sperling.¹⁹ A comparison of the properties of BMITFSI-loaded regenerated cellulose with those of reported cellulose plasticizers is shown in Table II. The properties of the BMITFSI-loaded regenerated cellulose were on par with those of other reported cellulose plasticizers.

Figure 5 shows the UV-vis spectra of BMITFSI-incorporated cellulose. A new peak appeared around 217 nm with the addition of 0.01% BMITFSI. As the BMITFSI content was increased to 0.02 and 0.03%, the intensity of the peak increased and shifted to a lower position (213 nm). Further increases in the BMITFSI amount resulted in increases in the peak. However, the position of the peak remained unaltered at 212 nm up to 0.08%; conversely, at 0.1% BMITFSI, the peak became broader. This shift of the peak with BMITFSI content suggested the possibility of intermolecular interactions between the cellulose and BMITFSI molecules.

Figure 6 shows the FTIR spectra of the O-H stretching vibrations of the BMITFSI-incorporated cellulose at wave numbers of 3000–3700 cm^{-1} . We ascertained that the pristine cellulose showed a broad OH peak in the range 3000–3700 cm^{-1} . This hydrogen-bonded O-H stretching band could indeed be resolved into two bands with Opus software (Bruker Optik GmbH, Ettlingen, Germany) with base line correction under the assumption that all of the vibration modes followed a Lorentzian distribution, as shown in Figure 7. In Figure 7, bands 1 (3244 cm^{-1}) and 2 (3434 cm^{-1}) are related to the intermolecular hydrogen bonding of 6-OH...O-3' and the sum of valence vibrations of H-bonded OH groups and the intramolecular hydrogen bonding of 2-OH...O-6,^{20,21} respectively. As shown in Figure 6, up to a 0.04% BMITFSI loading, the intensity of the OH absorption band remained the same. As the BMITFSI loading increased beyond 0.04%, the peak maxima of the blend systems started shifting to a higher wave number (data are not shown for 0.01,

TABLE II
Properties of the BMITFSI-Loaded Regenerated Cellulose Versus Reported Cellulose Plasticizers

	Weight loss (%)	Degradation temperature (°C)	Tensile strength (MPa)	Reference
Glycerol-plasticized cellulose composite	7.1	370	Not reported	23
Glycerin-plasticized regenerated cellulose	Not reported	Not reported	41.5 MPa	8
Glycerol-plasticized starch-cellulose composite	~ 12	~ 370	12	24
Glycerin α -monocaproate regenerated cellulose	Not reported	Not reported	65.1	8
BMITFSI (0.1%)-added regenerated cellulose	2.3 \pm 0.9	380 \pm 15	29	This study

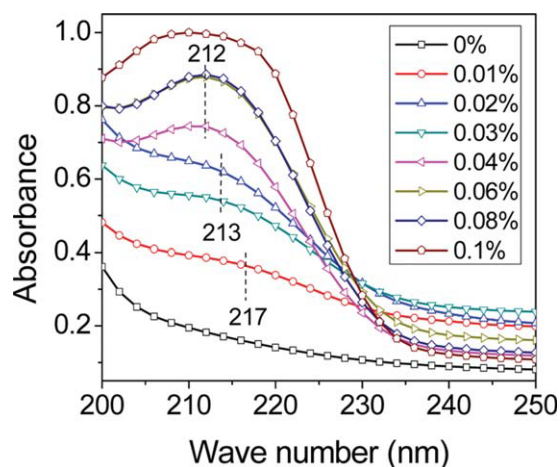


Figure 5 UV-vis spectra of the BMITFSI-incorporated cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.02, 0.03, 0.06, and 0.08% loadings). Finally, at a 0.1% BMITFSI loading, the maximum peak of the system shifted to a higher wave number by more than 15 cm^{-1} . The dissolution of cellulose in TFA occurred by the swelling of cellulose pulp; this was followed by the rupture of tight hydrogen bonds of cellulose due to the hydrogen bonding of O—H and C—F groups.²² BMITFSI had no significant OH absorption band. However, it possessed a large number of C—F groups, which were attributed to increased interaction between O—H and C—F groups.

In summary, shifts in the peak maxima of the OH absorption band to higher wave numbers with

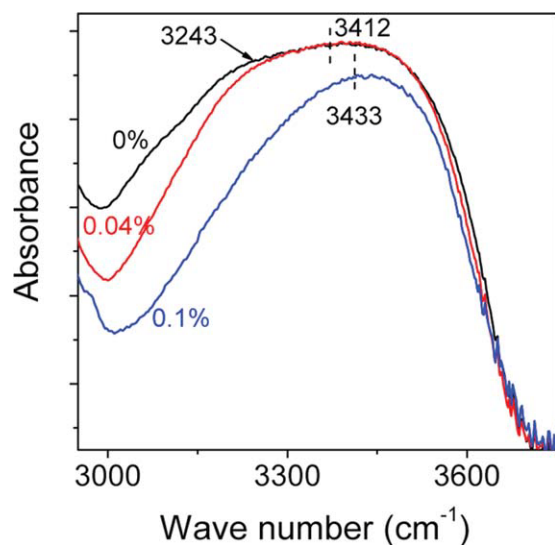


Figure 6 FTIR spectra of the O—H stretching vibrations of the BMITFSI-incorporated cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

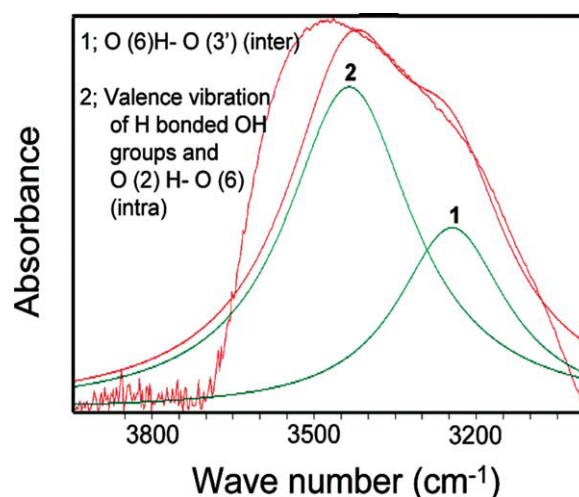


Figure 7 Resolution of hydrogen-bonded OH stretching for the pristine cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increasing BMITFSI loading suggested intermolecular interactions between the cellulose and BMITFSI molecules. In other words, the incorporation of BMITFSI molecules into cellulose during its dissolution process caused hydrogen bonds to break so as to decrease chain cohesion and spread them apart. Thus, BMITFSI reduced polymer-polymer chain bonding and provided an increase in the mobility of cellulose chains; this caused a reduction in T_g . This results in soft and more easily deformable cellulose.

The main disadvantages of cellulose plasticizers reported so far include mobility and volatility, and hence, they are easily lost by migration or

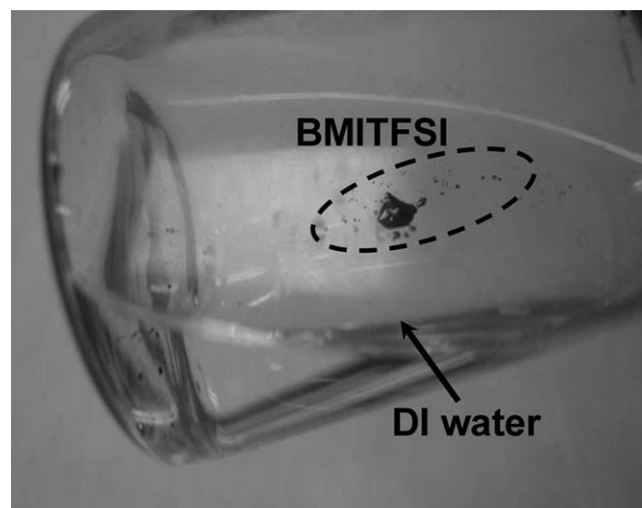


Figure 8 Photograph demonstrating the immiscible nature of BMITFSI in deionized (DI) water.

evaporation. They are also extremely hygroscopic; hence, their effectiveness varies with the surrounding conditions, namely, with the temperature and humidity.^{8,9} In this aspect, BMITFSI is particularly promising because it is highly immiscible in water, as shown in Figure 8, and typically has no detectable vapor pressure; this could enable it to perform as a cellulose plasticizer with significantly extended lifetimes. Further, as a typical example, regenerated cellulose incorporated with 0.1 wt % BMITFSI was washed with water, and its mechanical and thermal properties were reassessed. The weight loss at 300°C, degradation temperature, and tensile strength of the sample after washing with water were found to be $3.1 \pm 1.0\%$, $375 \pm 12^\circ\text{C}$, and $32.4 \pm 1.94\text{ MPa}$, respectively. The properties of water-washed samples were almost the same as those of the samples before water washing. Because BMITFSI is highly immiscible in water (Fig. 8), it may have been retained in the cellulose matrix with the least leaching.

CONCLUSIONS

In conclusion, the simple addition of the RTIL BMITFSI during the dissolution process greatly enhanced the thermal stability of regenerated cellulose. The mass losses of BMITFSI-added cellulose at 200 and 300°C tended to decrease with increasing BMITFSI content. The thermal degradation temperature of cellulose was enhanced from 350 ± 10 to $380 \pm 15^\circ\text{C}$ with the addition of BMITFSI; the superior thermal stability of IL under high temperature might have been mainly responsible for the improved thermal stability of cellulose. UV-vis and FTIR spectroscopy analyses suggested intermolecular interaction between the cellulose and BMITFSI molecules. Because BMITFSI has a negligible vapor pressure, nonvolatility, a hydrophobic nature, and stabil-

ity against moisture, BMITFSI could be a promising candidate as a plasticizer of cellulose.

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