Structure, Tensile and Electromechanical Properties of 1-Butyl-3-Methylimidazolium bis(trifluoromethylsulfonyl)imide Incorporated Cellulose

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Abstract: *The effect of 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (BMITFSI) incorporation on the structure, tensile and electromechanical properties of cellulose was premeditated by scanning electron microscopy, X-ray diffraction, tensile test and bending actuation test. Both cellulose and BMITFSI were found to be thermodynamically compatible and have good miscibility. Addition of 0.02 wt% of BMITFSI resulted in augment of yield strength and Young's modulus; meanwhile they were decreased upon increasing the BMITFSI content. Upon dispersion of 0.1 wt% BMITFSI, the bending displacement of the cellulose actuator was drastically enhanced in comparison with that of cellulose membrane.*

Keywords: Cellulose, Young's modulus, Room Temperature Ionic Liquid, BMITFSI, Bending actuator.

1. INTRODUCTION

Cellulose is one of the well known natural polymer, consists of β-D-glucopyraonosyl units with a (1-4)-β-D-linkage and forms a linear chain through many inter and intra molecular hydrogen bonds [1,2]. Cellulose has been utilized in many fields, such as films for hemodialysis, water resistance, coatings, laminates, optical films, pharmaceuticals, and food and textile industries [3-7]. As one of new applications, cellulose has been rediscovered as a smart material that produces bending displacement under the application of electric field and is termed as electroactive paper (EAPap). Cellulose EAPap was made with cellulose fibers dissolved into a solvent and cast as a sheet. Thin gold electrodes were deposited on both sides of the cellulose paper, and when an electric field was applied across the thickness of the paper, it showed a bending deformation. This newly developed material can be used as a micro-electro mechanical systems (MEMS), such as surface acoustic wave (SAW) sensor, radio frequency identification (RFID) tags and biosensors [8,9] due to its ease of availability, biodegradability and comparatively good physical and mechanical properties.

Room-temperature ionic liquids (RTILs) are compounds consisting entirely of ions that exist in the liquid state around room temperature [10]. As novel attractive solvents, they possess unique properties such as negligible vapor pressure, wide potential windows, high thermal stability, high viscosity, good conductivity and solubility [11]. RTILs containing bis(trifluoromethylsulfonyl) imide (TFSI⁻) are attractive, not only they have many advantages over other RTILs such as wide electrochemical potential window, acceptable ionic conductivity, high thermal stability and negligible vapour pressure [12-14]. Furthermore, RTILs have been incorporated to conventional materials, such as chitosan [15], carbon nanotubes [16], polymer [17,18], and Nafion [19] for improving conductivity and promoting the electron transfer [20]. The combination of RTIL and polymer can create unique materials that might open up new opportunities for studies of direct electrochemistry, biosensors, biocatalysis and solid-state electrochemical devices [21, 22].

In the present investigation, different amount (0.02 wt% ~ 0.1 wt%) of 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (BMITFSI) was incorporated into cellulose during dissolution process to see the changes in structural, tensile and electromechanical properties. Trifluoroacetic acid (TFA) has been utilized to dissolve cotton cellulose pulp because; TFA is one of the non aqueous and non derivatising solvent for cellulose, and can dissolve both native and regenerated cellulose at room temperature within a few days. Unlike other solvent systems for example DMAc/LiCl, TFA requires no curing and washing process to remove remnant solvents upon dissolution and regeneration of cellulose. Furthermore, TFA can be removed from the film by natural

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evaporation due to hydrolysis of trifluoroacetyl ester groups with moisture in the air [23], so that, ionic liquids can be easily entrapped in the cellulose matrix. In this paper, structural changes, tensile and electromechanical properties of BMITFSI incorporated cellulose films are assessed by using Scanning Electron Microscope (SEM), X-ray diffraction (XRD), tensile test and bending displacement measurement.

2. MATERIALS AND METHODS

2.1. Materials

Cotton cellulose pulp (MVE, DPW 4580) was purchased from Buckeye Technologies Co., USA. Trifluoroacetic acid (> 99%) was purchased from Dae-Jung Chemical & Metals Co. Ltd. South Korea. BMITFSI was purchased from Sigma Aldrich, USA.

2.2. Fabrication of BMITFSI Incorporated Celllose

Cotton cellulose pulp was cut into small pieces and heated under reduced pressure at $110^{\circ}C$ for 2 hours. The cotton cellulose pulp, trifluoroacetic acid and BMITFSI at different weight percents (0, 0.02, 0.04, 0.06, 0.08 and 0.1%) were mixed together and allowed for dissolution at an ambient condition. The clear cellulose-BMITFSI solution was poured onto glass petri dish and cured at the ambient condition for 1 day. To ensure complete elimination of the solvent, the cured films were further dried under high vacuum (~ 72 cm Hg) for 2 days. Thickness of the dried samples varied between 33 ~ 35 μm. Sample with 0 wt % BMITFSI is referred as cellulose membrane.

3. CHARACTERIZATION

3.1. SEM and XRD Analysis

The cross sections of the cellulose films were examined with a scanning electron microscope (Hitachi S4300). The films were coated with carbon before the SEM observation. The XRD patterns were recorded with a thin film X-ray diffractometer (X'Pert MPD PRO / Philips) using CuKα target at 40 kV and 50mA, at scanning rate of 0.015°/min. The diffraction angle ranged from 5 to 40°.

3.2. Tensile Test

Tensile test was conducted according to ASTM D-882-97 using a universal testing machine. Two ends of the specimen were fixed between upper and a lower jaw of the instrument with gauge length of 50 mm. Test was performed under the ambient condition with pulling rate of 0.5 mm/min.

3.3. Evaluation of Electromechanical Properties

Electromechanical behavior of BMITFSI incorporated cellulose was evaluated by measuring bending displacement in the presence of electric field. The bending displacement measuring system consists of two laser displacement sensors (Keyence, LK-G85 and LK-G15), current probe (Tektronix, TCP 300), Lab VIEW software on personal computer and function generator (Agilent, 33220A). Gold electrodes were deposited on both sides of the BMITFSI incorporated cellulose films. The sample is held in a gripper that has electric contacts wired to the function generator and current probe. When the function generator sends out the electrical signal to the actuator, it produces a bending displacement, and the laser displacement sensor measures it. All tests were carried out at 25° C and 80% relative humidity condition.

Figure 1. Photographs of Cellulose membrane. and BMITFSI incorporated cellulose with 0.04% and 0.1 %.
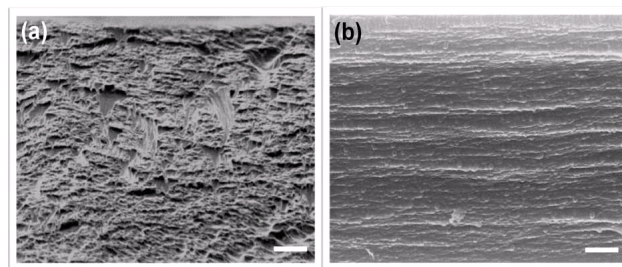

Figure 2. Cross sectional SEM images of (a) Cellulose membrane. (b) 0.1% BMITFSI incorporated cellulose; scale bar 1 μm.

4. RESULTS AND DISCUSSIONS

4.1. Morphological and Structural Studies

Figure 1 shows the photographs of pristine and BMITFSI incorporated cellulose. In Fig. 1, the clarity of cellulose samples incorporated with different amount of BMITFSI was unchanged. Even at 0.1 wt % BMITFSI, the samples were clear, indicating a good thermodynamic mixing of cellulose polymer with BMITFSI. If the ionic liquid and cellulose were not thermodynamically compatible, the cellulose polymer might have phase-separation and form an emulsion as reported for polystyrene-BMIPF6 [24] Cross sections of cellulose membrane and BMITFSI incorporated cellulose were observed by SEM to study this morphological change and miscibility. Figure 2 illustrates the cross sectional SEM images of the cellulose membrane and BMITFSI incorporated cellulose. Cellulose membrane showed a typical compact fibril structure (Fig. 2(a)) having a discontinuous layers. However, it was changed to loosely packed and uniform layered structure upon addition of BMITFSI (Fig. 2(b)). The reason might be due to the entrapment of BMITFSI molecules between cellulose layers during dissolution and regeneration process.

The cellulose has four types of crystal structures, namely cellulose I, II, III and IV that can transform from one to another type [25, 26]. Figure 3 (a) and (b) shows the compared X-ray diffractograms of cotton cellulose pulp and cellulose regenerated from TFA solvent (cellulose membrane). Cotton cellulose pulp exhibited typical cellulose I structure with X-ray diffraction peaks at 15º, 16.8º and 23º assigned to (1 1 0), (1 -1 0) and (2 0 0), respectively [27]. Upon dissolution and regeneration of cotton cellulose pulp in TFA (cellulose membrane), the (1 1 0) peak at $2\theta = 15^{\circ}$ and (1 -1 0) peak at $2\theta = 16.8^{\circ}$ were completely disappeared and showed a new peak at $2\theta = 12.5^{\circ}$, which possess a negligible intensity. Meanwhile (2 0
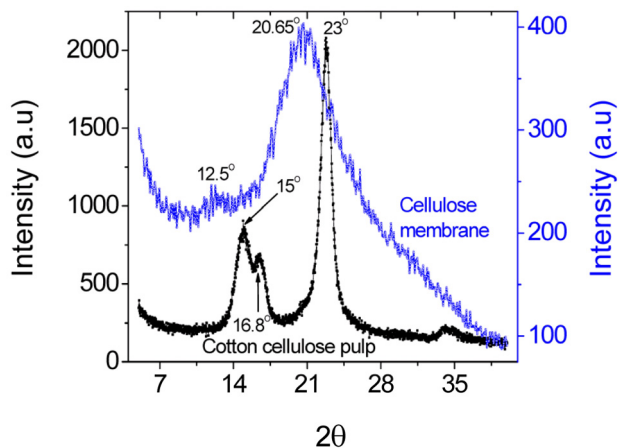
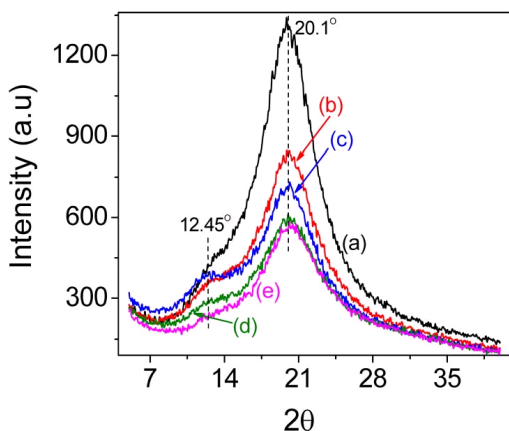Figure 3. Compared X-ray diffractograms of Cotton cellulose pulp and cellulose membrane.

Figure 4. X-ray diffractograms of cellulose incorporated with different amount of BMITFSI : (a) 0.02 %, (b) 0.04 %, (c) 0.06 %, (d) 0.08 % and (e) 0.1 %.

0) peak at $2\theta = 23.0°$ was shifted to $20.7°$, suggesting the transformation of crystalline structure from cellulose I to cellulose II with large amount of amorphous region. Figure 4 shows the X-ray diffractograms of cellulose mixed with different wt. % of BMITFSI. Small shift of peaks at $2\theta = 12.5°$ and $20.7°$ to $12.5°$ and $20.1°$, respectively, were observed upon BMITFSI incorporation. It seems that intensity levels of these peaks were largely dependent on the BMITFSI content. Upon addition of 0.02 wt% BMITFSI, the peak intensities at $2\theta = 12.5°$ and $20.1°$ were greatly enhanced (Fig. 4 a) compare to that of cellulose membrane (Fig. 3 b). The crystallinity of the samples was evaluated by calculating crystallinity index according to Ref. 28. However one should note that, the crystallinity values represents relative parameter, which strongly depends on the calculation method as the separation of crystalline and non-crystalline (amorphous) scattering in cellulose has always somewhat arbitrary procedure [29]. The crystallinity index of the cellulose membrane and 0.02 wt % BMITFSI incorporated cellulose was improved from 0.24 to 0.47. Since TFA is a very strong acid, dissolution and regeneration of cellulose from it may degrade cellu-
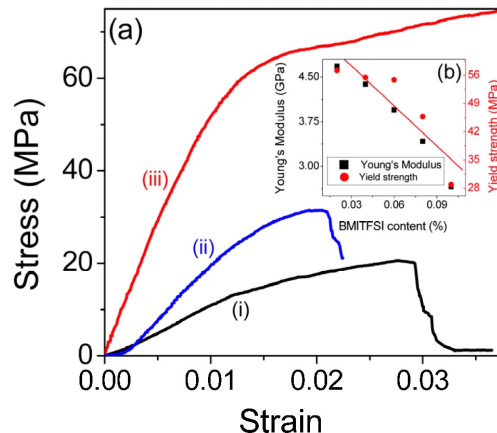

Figure 5. (a) Stress-strain curves of BMITFSI incorporated cellulose; (i) Cellulose membrane, (ii) 0.02% BMITFSI and (iii) 0.1 % BMITFSI. (b) effect of BMITFSI content on yield strength and Young's modulus.

lose chains so as to reduce its crystallinity. However, small amount addition of BMITFSI may inhibit the cellulose degradation to some extent, thereby improve its crystallinity. Conversely, further raise of the BMITFSI content tends to decrease the peak intensities at $2\theta = 12.5°$ and $20.1°$. At 0.1 wt% BMITFSI, the peak at $2\theta = 12.0°$ is almost disappeared, whereas the peak intensity at $2\theta = 20.1°$ came down to half of the cellulose case with 0.02 wt.% BMITFSI.

Crystallinity index of the 0.04, 0.06, 0.08 and 0.1 wt% BMITFSI incorporated cellulose was found to be 0.35, 0.29, 0.21 and 0.18, respectively, suggesting decreased crystallinity (Fig 4 b- e). This might be due to irregular structure of cellulose caused by the introduction of BMITFSI, which might result in lower crystallinity.

4.2. Tensile Properties

Influence of BMITFSI addition on tensile properties of cellulose was examined by taking tensile test. Three samples were tested for each case and averaged the test values. Figure 5 (a) exemplifies the stress-strain curves of cellulose membrane and BMITFSI incorporated cellulose. Yield strength and Young's modulus for cellulose membrane was found to be 13.8 MPa and 1.2 GPa, respectively. 0.02 wt% addition of BMITFSI resulted in augment of these properties to 57.2 MPa and 4.7 GPa, respectively. As mentioned earlier, addition of small amount of BMITFSI may inhibit the cellulose degradation to some extent, by filling the nano pores in the cellulose structure and thereby reduce the surface tension in the developed surface of separation of the internal pores, which leads to improved crystallinity [30]. Similar enhancement in tensile properties of regenerated cellulose has been reported due to addition of mineral oil [30]. On the other hand, further increase of BMITFSI content resulted in almost linear decrease of these properties, reaching to 28.8 MPa and 2.7 GPa, respectively at 0.1 % BMITFSI as shown in Fig 5 (b). This shows a good agreement with the crystallinity values. As the BMITFSI content is increased, it may form secondary bonds to intra- and inter-molecular hydrogen bonds of cellulose chains and spread them apart by positioning themselves between the cellulose chains so as to separate them and reduce their
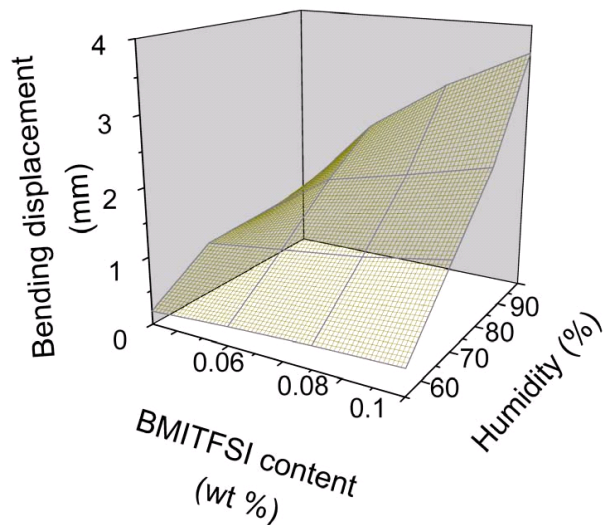
Figure 6. Variation of bending displacement with BMITFSI content and humidity at 0.08 V/μm and 3.5 Hz.

Figure 7. Bending displacement of 0.1 % BMITFSI incorporated cellulose EAPap actuators with varying electric field and frequency at 90%RH, 25°C.

interactions. Because of this consideration, one can foresee a decreasing crystallinity of semi crystalline polymers as suggested by Sperling [31], which leads to reduction in their tensile properties.

4.3. Electromechanical Properties

The BMITFSI content effect on the electromechanical properties of cellulose was evaluated by measuring the bending displacement and electrical power consumption as a function of frequency. It has been reported that performance of cellulose based EAPap actuators strongly depends on the applied electric field and ambient humidity condition [8, 9, 32]. Figure 6 shows bending displacement of the actuators at 80% relative humidity level with varying BMITFSI content in comparison with cellulose membrane. As shown in Fig. 6, cellulose membrane showed a very small displacement output of 0.6 mm. The actuation principle of EAPap is based on the combination of piezoelectricity and ion migration associated with dipole moments of cellulose constituents [9]. Explanation for the low tip displacement of cellulose membrane could be due no presence of ions as TFA is completely removed upon regeneration. Thus, the actuation mechanism of cellulose membrane is more likely based on piezoelectric effect. Nevertheless, dispersion of 0.06 wt. % BMITFSI in the cellulose resulted in 2-fold increase in bending displacement (1.2 mm) compared to that of cellulose membrane.

Further increase of BMITFSI content to 0.08 and 0.1 wt. % increased the bending displacement of the actuator to 3.6 mm and 4.2 mm, respectively. As the BMITFSI content increased, inter- and intra- molecular attraction forces are decreased so as to increase free volume and chain mobility [33]. Also, increased ion content improved its ion mobility and repulsive force between ions, which caused the great improvement in the bending displacement of the actuator. The resonant frequencies for the actuator with 0.06, 0.08 and 0.1 % BMITFSI content were found to be 5.5 Hz, 4.5 Hz and 3.5 Hz, respectively. The resonance frequency of the actuator is decreased with increasing the BMITFSI content. This result is in agreement with the Young's modulus change [34]. For a cantilever
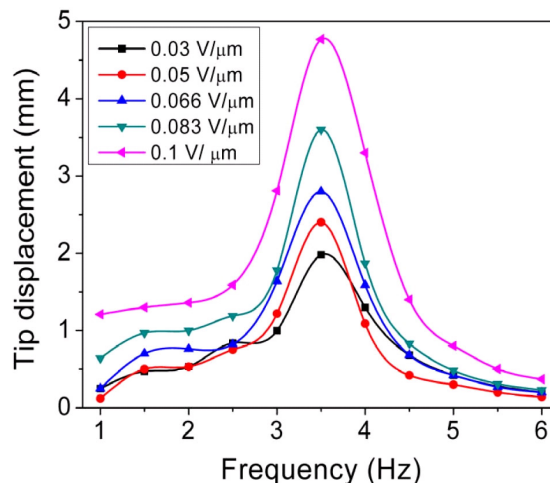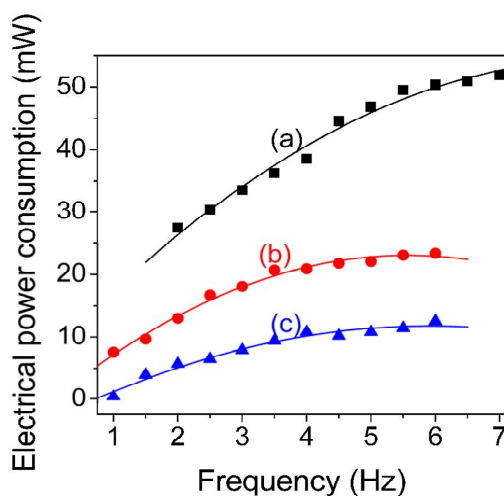

Figure 8. Electrical power consumption of cellulose EAPap actuators with varying BMITFSI content at 80% humidity level; (a) 0.06 %, (b) 0.08 % and (c) 0.1 %.

beam, the first resonance frequency is proportional to the square root of Young's modulus [35].

Figures 7 depict the variation of bending displacement of 0.1 % BMITFSI incorporated cellulose actuator as a function of frequency and electric field at 90% relative humidity. Bending displacement of the actuator increased with increasing the electric field. On increasing the applied electric field from 0.03 V/μm to 0.1 V/μm, the bending displacement was improved from 2.0 to 4.8 mm. Variation of electrical power consumption of the actuator with varying frequency was found by measuring the current consumption shown in Fig. 8. The electrical power consumption of the actuator decreased with increasing the BMITFSI content. This observation is in agreement with our previous results, [36,37]. Buzzeo et

al.[38] have reported the lower energy consumption of RTILs for numerous electrochemical processes. Note that, the electrical power consumption was less than 10 mW at 0.1 wt% BMITFSI.

5. CONCLUSIONS

Room temperature ionic liquid, BMITFSI, incorporated cellulose EAPap actuators were fabricated and their structure, tensile and electromechanical properties were studied. TFA was employed to dissolve cotton cellulose pulp and various amounts of BMITFSI were incorporated during dissolution. When small amount (0.02 wt %) of BMITFSI was incorporated, both crystallinity, Yield strength and Young's modulus of cellulose was enhanced from 0.24, 13.8 MPa and 1.2 GPa to 0.47, 57.2 MPa and 4.7 GPa, respectively, due to hindered cellulose degradation. As the amount of incorporated BMITFSI increased further, these properties were rather decreased and reaching to 0.18, 28.8 MPa and 2.7 GPa, respectively at 0.1 % BMITFSI. It is due to fact that secondary bonds to intra- and inter-molecular hydrogen bonds of cellulose chain are formed so as to spread them apart by positioning themselves between the cellulose chains, thus reducing their interactions. Seven- fold (4.2 mm) in-crease in electromechanical properties of the actuator was observed when 0.1 wt% of BMITFSI was incorporated in the cellulose com-pared to that of cellulose membrane (0.6 mm). The electrical power consumption of cellulose- BMITFSI EAPap actuator was less than 10 mW at 0.1 wt% BMITFSI.

6. ACKNOWLEDGEMENT

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