

Effect of Room Temperature Ionic Liquids Adsorption on Electromechanical Behavior of Cellulose Electro-Active Paper

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Abstract: The cellulose smart material called electro-active paper (EAPap) is made by regenerating cellulose. However, the actuator performance is degraded at low humidity levels. To solve this drawback, EAPap bending actuators were made by activating wet cellulose films in three different room-temperature ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆), 1-butyl-3-methylimidazolium chloride (BMICL) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄). In the results, the actuator performance was dependent on the type of anions in the ionic liquids, in the order of BF₄⁻ > Cl⁻ > PF₆⁻. The BMIBF₄-activated actuator showed the maximum displacement of 3.8 mm with low electrical power consumption at relatively low humidity. However, the BMICL-activated actuator showed a slight degradation of actuator performance. Further performance and durability improvement will be possible once various ionic liquids are blended with cellulose.

Keywords: cellulose, room temperature ionic liquids, bending actuator, durability.

Introduction

Cellulose is one of the well known natural polymer, consists of β -D-glucopyranosyl 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 due to its ease of availability, biodegradability and comparatively good physical and mechanical properties.³⁻⁷ Recently, cellulose has been reported as a smart material that can be used for biomimetic sensor/actuator devices as well as microelectromechanical systems (MEMS).^{8,9} This smart cellulose is termed as electro-active paper (EAPap). The actuation principle of EAPap was found to be a combination of piezoelectric and ion migration effects. EAPap can produce a large bending displacement with low actuation voltage and power consumption. It has merits in terms of lightweight, biodegradability, low cost and abundance.

Cellulose EAPap was made by regenerating cellulose, by dissolving cellulose pulp in *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) solvent system. During regeneration process, the Li⁺(DMAc)_x macrocations were entrapped in cellulose matrix which can damage the electrode, there by reduces its durability. Also, in order to improve its piezoelectric properties and to applying this EAPap material to

various devices, it is necessary to perfectly regenerate the cellulose. Recently we have reported the process of removing solvent and ions from the cellulose films after regenerating in DMAc/LiCl solvent system.^{10,11} However, regeneration of cellulose resulted in reduced performance of actuators at low humidity levels. In other words, it produces bending displacement output at high humidity levels.¹²

Ionic liquid (IL) is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100 °C, or even at room temperature (room temperature ionic liquids, RTILs). At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. Ionic liquids have interesting properties such as nonvolatility, high stability, suitable polarity, high ionic conductivity, and easy recyclability.¹³ Also, RTILs promise lower energy consumption for numerous electrochemical processes.¹⁴ Owing their ideal properties, ILs are receiving much attention as environmentally benign solvents for organic chemical reactions,¹⁵ separations,¹⁶ and for electrochemical applications.¹⁷ Recent developments involve their use for biopolymers,¹⁸ molecular self assemblies¹⁹ and actuators.^{20,21}

This communication reports the improvement in performance of cellulose EAPap actuators at low humidity levels by activating the wet regenerated cellulose films in three different RTILs solutions. The adsorption of RTILs on cellulose surface was characterized by atomic force microscopy (AFM), UV-visible spectroscopy and FTIR. Further,

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the effect of RTILs adsorption on actuator performance was evaluated by measuring bending displacement and durability.

Experimental

Fabrication of RTIL Adsorbed Cellulose Films. Regenerating cellulose from *N,N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) solvent systems was well documented in the literature,^{10,22} and the same reported method was employed with slight modification. In brief, cotton cellulose (16 gm. MVE, DPW 2400) and LiCl (80 gm) were heated at 100 °C for 2 h and LiCl was dissolved in DMAc (720 mL) solvent. An optically transparent cellulose solution was obtained from this process. The resulting cellulose solution was stored for 10 days for complete dissolution of cellulose microfibrils. Cellulose films were prepared by spin coating the solution (Laurell, EDC2-100) on to 8" silicon wafer followed by curing with isopropyl alcohol and deionized water mixture. Resulting cellulose wet films were immersed in to 2% 1-butyl-3-methylimidazolium hexa fluorophosphate (BMIPF₆), 1-butyl-3-methylimidazolium chloride (BMICL) and 1-butyl-3-methylimidazolium tetra fluoroborate (BMIBF₄) for 3 days. Upon drying in room conditions bending actuators were fabricated by depositing very thin gold electrodes of size (40×10) mm on the both sides of film by using a thermal evaporation system.

Characterization of RTIL Adsorbed Cellulose Films. To characterize the adsorption of RTILs on cellulose films,

AFM images were collected in tapping mode by employing Nanoscope multimode IVa (Digital Instruments, NS4A). RMS roughness of cellulose films was measured at five different areas by scanning surface area of 100 μm². UV-Visible spectra in the range of 100-1,000 nm were obtained with a HP Diode array spectrophotometer 8452A. The IR spectra were obtained by BioRAD (Digilab) FTS 3000 spectrometer with KBr beam splitter, detector at 8 cm⁻¹ resolution and 300 scans per sample. The films were cut into very small particles and characterized by FT-IR, to evaluate the adsorption of RTILs on to cellulose films.

Evaluation of Electromechanical Behavior. The bending displacement measuring system is consisted 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). The actuator 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.

Results and Discussion

RMS roughness analysis gives the primary information about the fine scale fluctuations in the effective surface height. Adsorption of RTILs on to regenerated cellulose surface was evaluated by measuring the RMS (R_q) value. Fig-

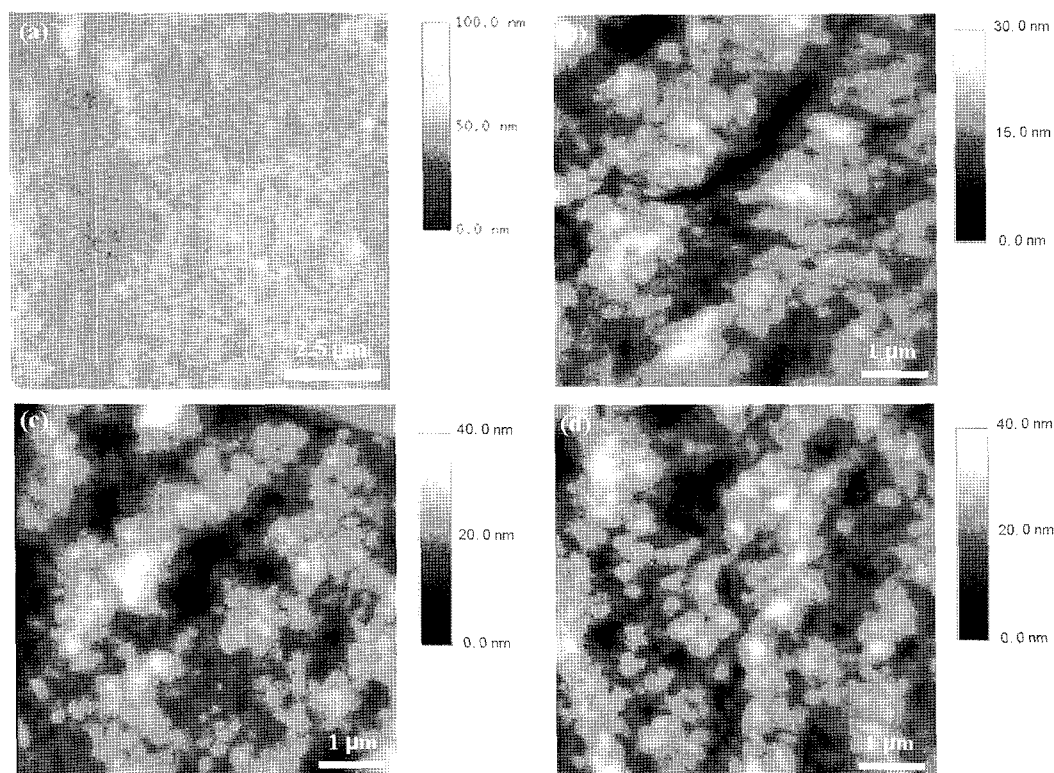


Figure 1. AFM surface images: (a) Pure regenerated cellulose and RTILs adsorbed cellulose, (b) BMIPF₆, (c) BMICL and (d) BMIBF₄.

ure 1 represents the tapping mode AFM surface images of pure regenerated cellulose and RTILs adsorbed cellulose. Comparison of AFM images clearly indicates the adsorption of RTILs onto cellulose surfaces. Further, RMS (R_q) values were measured to quantify the adsorption of RTILs, before measuring RMS (R_q) values; the images were flattened using first-order flattening. Flattening removes image artifacts due to vertical (Z) scanner drift, image bow, skips, and anything else that may have resulted in a vertical offset between scan lines. In the case of the regenerated cellulose, RMS (R_q) value was found to be 2.50 nm and this value was changed to 3.42, 4.70 and 4.88 nm when the cellulose was activated in BMIPF₆, BMICL and BMIBF₄, respectively. The higher values of RMS (R_q) and also, the change in surface morphology of films confirm the presence and adsorption of RTILs on the cellulose film.

Figure 2 illustrates the UV-visible spectra of cellulose films activated in different RTILs; spectrum of pure cellulose was also included for comparison. Pure cellulose film showed a peak at 200 nm when activated in BMIPF₆, and it was shifted to 214 nm. However, when the films were activated in the solutions of BMICL and BMIBF₄, the peak was shifted to 230 nm and also many peaks have been observed in the range of 200–230 nm. It has been reported that, pure BMIPF₄ and BMICL, BMIPF₆ have characteristic UV peaks at 433 and 270 nm, respectively.^{23,24}

Based on the change in RMS (R_q) values from lower to higher values and also the shift in the characteristic UV peak, we arrive to the conclusion that the RTILs was adsorbed on to cellulose film surfaces when activated in RTILs solution.

In order to evaluate the influence of RTILs adsorption on the performance of actuators, cellulose EAPap actuators that were activated in different ionic liquids, were prepared and tested at 25 °C and at two different relative humidity levels (35 and 50%). Influence of different RTIL adsorption

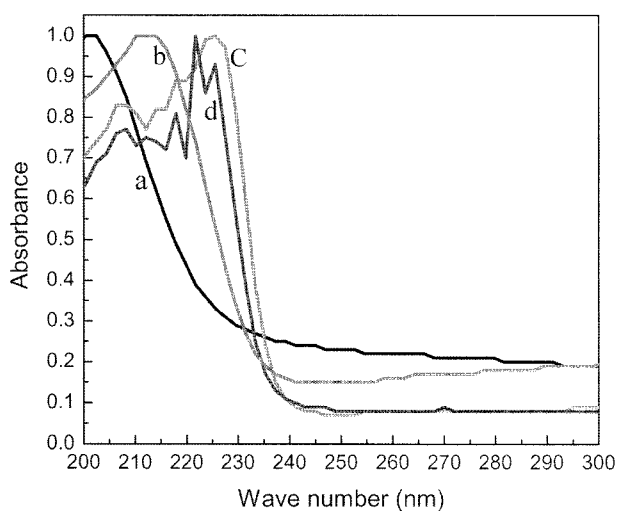


Figure 2. UV-visible spectra of cellulose films activated in different RTILs; (a) Cellulose, (b) BMIPF₆, (c) BMICL, and (d) BMIBF₄.

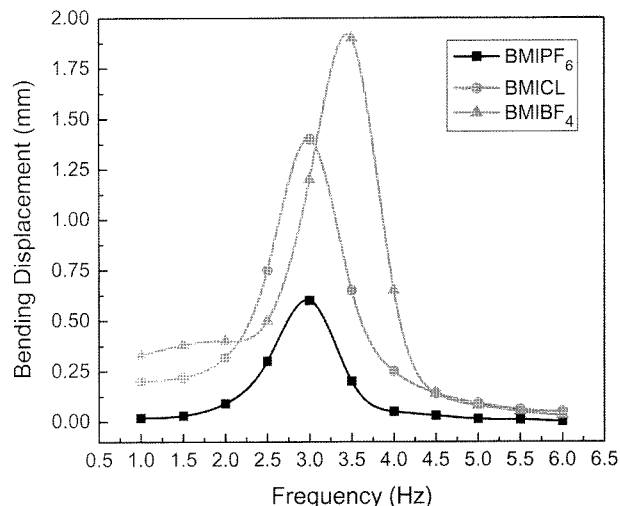


Figure 3. Influence of different RTIL adsorption on bending displacement of actuators at 35% relative humidity.

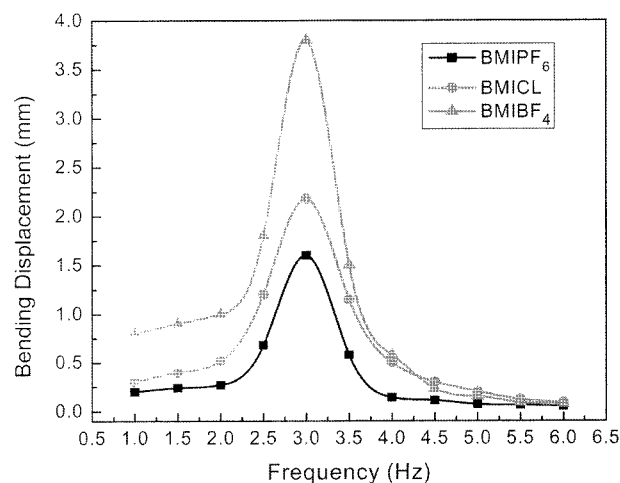


Figure 4. Influence of different RTIL adsorption on bending displacement of actuators at 50% relative humidity.

on the performance of actuators at 35 and 50% relative humidity levels are shown in Figure 3 and Figure 4, respectively. At 35% relative humidity level, the maximum bending displacement of 1.9 mm (4 V, 3.5 Hz) was obtained when the cellulose was activated in BMIBF₄. This is much higher than that of actuators activated in BMICL (1.4 mm, 4 V, 3 Hz) and BMIPF₆ (0.6 mm, 4V, 3 Hz). Note that when the humidity increased to 50% the maximum displacement output of 3.8 mm, 2.2 mm and 1.6 mm were obtained for BMIBF₄, BMICL and BMIPF₆ absorbed EAPap actuators, respectively. As humidity increased, the moisture content of the film increased, and the film became soft which resulted in improved mobility of anions (PF₆⁻, Cl⁻ and BF₄⁻). The improved anion mobility caused a higher bending displacement of the actuator. The maximum displacement of 3.8 mm that was obtained from BMIBF₄ absorbed EAPap at 50% relative humidity, is much higher than that of actuators

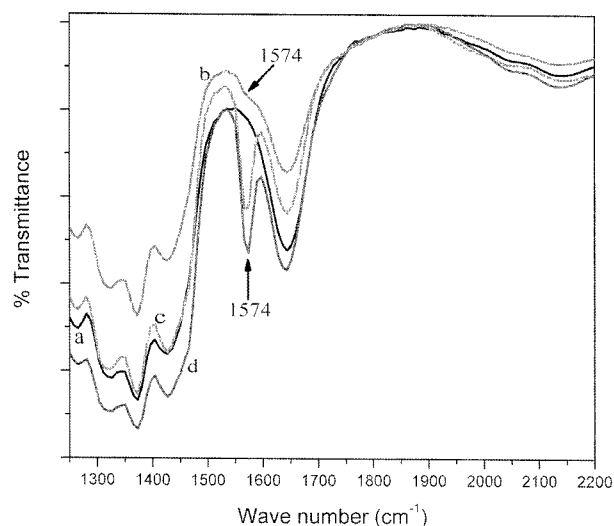


Figure 5. FT-IR spectra of cellulose activated in different ionic liquids; (a) Cellulose, (b) BMIPF₆, (c) BMICL, and (d) BMIBF₄.

based on cellulose-chitosan laminates²⁵ as well as multi walled carbon nanotubes mixed cellulose actuators.¹² From the actuator performance results, it seems that the bending displacement of actuators depends on the type of anions in ionic liquids, in the order of $\text{BF}_4^- > \text{Cl}^- > \text{PF}_6^-$. Although volume of BF_4^- anion (48 \AA^3) is smaller than that of PF_6^- (68 \AA^3)²⁶ it showed a higher displacement at both 35 and 50% humidity levels. In order evaluate this behavior, samples were further subjected to FTIR analysis.

Figure 5 depicts FT-IR spectra of cellulose activated in different ionic liquids in the range of 1250- 2200 cm^{-1} . The spectrum of regenerated cellulose is also shown as a reference. Peak at 1654 cm^{-1} was seen for cellulose. However, when it was activated in RTILs, new peak was appeared at 1574 cm^{-1} , which is assigned to the bending vibration of C-C and C-N for butyl methylimidazolium.²⁷ Note that, the peak intensity at 1574 cm^{-1} for the BMIPF₆ was very small compare to that of BMICL and BMIBF₄ cases. Further, for a rough estimation of the amount of ionic liquids adsorbed in to cellulose surface, the intensity at 1574 cm^{-1} was obtained by calculating the peak height from a local baseline between adjacent valleys, which was automatically calculated at the maximum absorbance found by using OMNIC 4.0 software.²⁸ Peak intensities at 1574 cm^{-1} for BMIPF₆, BMICL and BMIBF₄ cases were 0.002, 0.117 and 0.147, respectively. This result reveals that very small amount of BMIPF₆ was adsorbed

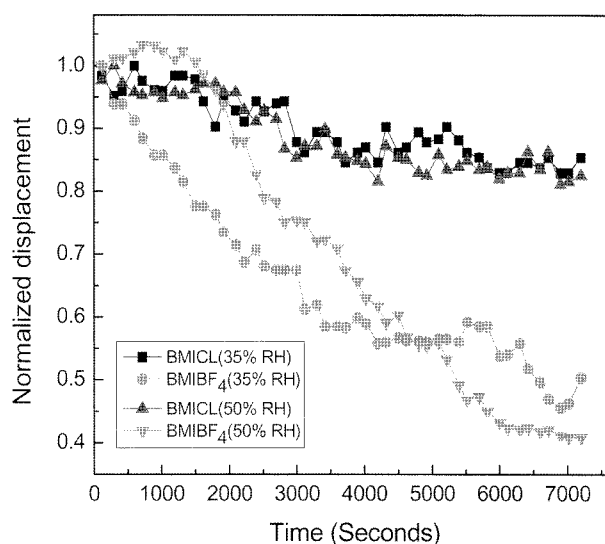


Figure 6. Bending displacement of actuators with time.

into cellulose surface. Since the conductivity of PF_6^- (5.2 mS/cm) is also lower than that of BF_4^- (13 mS/cm)²⁶ it might attribute to small bending displacement of the actuator activated in BMIPF₆ at both 35% and 50% relative humidity levels.

Actuators activated in BMICL and BMIBF₄ exhibited the higher bending displacement than that of BMIPF₆ activated case. To see the durability of these actuators, they were activated continuously more than 11 h at 35% and 50% relative humidity levels. Figure 6 shows the result. Although the BMIBF₄ activated actuator showed higher displacement than that of BMICL activated one, its performance was gradually decreased with time. The performance degradation was 58.3% and 62.9% at 35% and 50% relative humidity levels, respectively. It might be due to the fact that BMIBF₄ is highly hygroscopic. When it was exposed to humid environment continuously for a long duration, it might absorb water and resulted in removal of adsorbed BMIBF₄ from the surface of the actuator. This leads to depletion of ions in the film causing the degraded performance of the actuator. On the other hand, the actuator activated in BMICL showed lower performance degradation. The low performance degradation of BMICL activated actuator might be due to the hydrogen bonding between Cl^- ion and anhydroglucose units of cellulose through hydroxyl protons, and the presence of high localized negative charge on the Cl^- ions.²⁹

Table I. Comparison of Performance and Electrical Power Consumption of Various EAPap Actuator Systems

EAPap Actuator System	Displacement (mm)	Resonance Frequency (Hz)	Electrical Power Consumption (mW)	Humidity Level
Cellulose	3.7	7.5	55	70%
PPy coated cellulose	6.4	6	68	70%
PANI coated cellulose	6.7	5.5	74	70%
BMIBF ₄ activated cellulose	3.8	3	17.9	50%
BMICL activated cellulose	2.2	3	16.9	50%

The electrical power consumed by the actuators was found by measuring the current. About 16.9 and 17.9 mW of electric power were consumed by the actuators activated in BMICL and BMIBF₄, respectively at 50% relative humidity level. These power consumptions are lower than that of the actuators based on cellulose as well as PPy and PANI coated cellulose actuators as shown in Table I. Buzzeo *et al.*¹⁴ have reported the lower energy consumption of RTILs for numerous electrochemical processes. Present observation also reveals that the RTILs are promising for reducing energy consumption for many electromechanical applications.

Conclusions

EAPap actuators were fabricated by using regenerated cellulose films activated in three different RTILs, namely, BMIPF₆, BMICL and BMIBF₄. Bending displacement of the actuators were found to be in the order of BF₄⁻ > Cl⁻ > PF₆⁻. BMICL and BMIBF₄ activated actuators exhibited the maximum output of 2.2 and 3.8 mm respectively with low power consumption (~17 mW) at relatively low humidity level. Although, BMICL activated actuator showed a bit small bending displacement compared with that of BMIBF₄ activated one, it showed very low actuator performance degradation (~19%). This was due to the hydrogen bonding between Cl⁻ ion and anhydroglucose units of cellulose through hydroxyl protons and the presence of high localized negative charge on the Cl⁻ ions. Present investigation suggests that further performance and durability improvement of EAPap actuator is possible by blending various ionic liquids with cellulose.

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