Effect of Li$^+$ Ions on Structure, Properties, and Actuation of Cellulose Electro-Active Paper Actuator

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ABSTRACT: We have reported an electro-active paper actuator from regenerated cellulose. After dissolving cellulose fibers with a solution of lithium chloride in *N,N*-dimethylacetamide, cellulose was regenerated by combining distillation of cellulose solution along with washing with the mixture of deionized water, isopropyl alcohol, and running water. However, the effect of Li$^+$ ions on structure, properties, and the actuation behavior of the actuator was not studied. This article describes the changes in these parameters when the Li$^+$ ions are removed by subjecting it to different running water exposure time. The structure and properties of cellulose electro-active paper and its actuation behavior were studied. As Li$^+$ ions content reduced from 4354.17 to 10.26 ppm by increasing the exposure time of running water, crystallinity, Young's modulus, and bending displacement decreased. Details about the investigation have been explained. This elimination of ions is important to increase the piezoelectric effect in EAPap by decreasing the ion migration effect. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2260–2265, 2008

Key words: regenerated cellulose; lithium ion; running water exposure; electro-active paper; bending actuator

INTRODUCTION

Because of the lack of availability of the source materials, recent researches have been focused on the development and applications of new materials, which are produced from naturally occurring polymers, such as polysaccharides,[1] proteins,[2,3] lipids,[4,5] and so on. The benefits of using these natural polymers include ease of availability, biodegradability, and comparatively good physical and mechanical properties.[6–9] However, their use is limited due to the difficulty in processing and fabrication, because of the polar moieties included in their backbones. Cellulose is one of well-known natural polymers. Cellulose consists of β-D-glucopyranosyl units with a (1-4)-β-D-linkage and forms a linear chain through many inter and intramolecular hydrogen bonds. Also cellulose is actively used in a variety of products such as hemodialysis material[10] and water-resistant material.

Cellulose has been discovered as a smart material that can be used as sensor and actuator materials.[11] This smart material has been termed as electro active paper (EAPap).[12] Cellulose EAPap is made with a cellulose film. Cellulose film can be made by dissolving cellulose fibers into a solution and casting it.

Once the cast solution is coagulated in water, it is converted back to pure cellulose. Figure 1 shows the concept of EAPap actuator made with cellulose.[11] It produces bending displacement in the presence of an electric field on the electrodes.

Cellulose can be regenerated from a solution of lithium chloride (LiCl) in *N,N*-dimethylacetamide (DMAc).[13] This LiCl/DMAc solvent system has been used to form films and fibers of cellulose as well as chitin and aromatic polyamides. A solution of lithium chloride in DMAc represents a solvent system, which is very common in cellulose chemistry. Because of the fact that the mixture is able to affect dissolution of cellulose within a certain concentration range of LiCl and cellulose, it is widely used for analytical purposes and in organic synthesis.[13–15] Recently, we reported the method of regenerating solvent-free and ion-free cellulose by combining distillation of cellulose, washing with the mixture of deionized (DI) water–isopropyl alcohol (IPA), and running water technique.[16] In this article, we present in detail how lithium ions influence the properties and structure of regenerated cellulose as well as actuation behavior of EAPap made by this cellulose. The structure and properties were studied by scanning electron microscope (SEM), X-ray diffraction (XRD), thermo gravimetric analysis (TGA), inductively coupled plasma mass spectroscopy (ICP–MS), electron diffraction X-ray spectroscopy (EDS), and tensile test, and its actuation behavior by tip displacement measurement.

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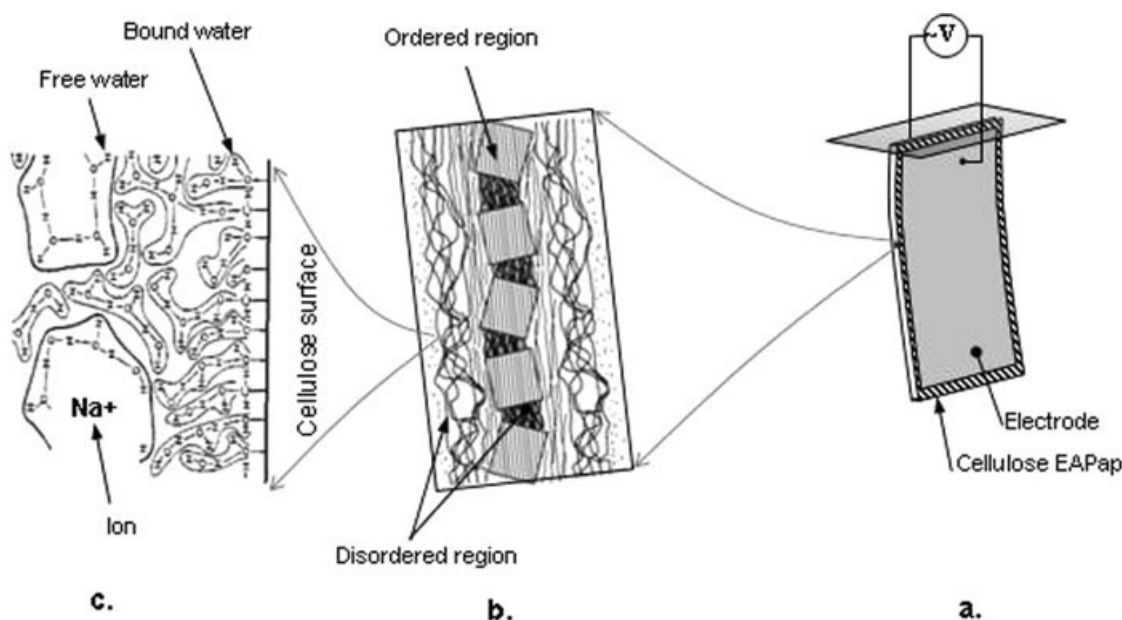Contract grant sponsors: KOSEF/MOST, BK21.

Figure 1 Concept of electroactive paper actuator: (a) cellulose microfibril has ordered crystalline regions and disordered regions, (b) EAPap is made from cellulose paper on which gold electrodes are deposited on both sides, (c) water molecules are bonded with hydroxyls on the cellulose surface (bound water) or clustered in free state (free water).

EXPERIMENTAL

Materials

Cotton cellulose (MVE, DPW 4580) was purchased from Buckeye Technologies Co. N,N-Dimethylacetamide (DMAc) (anhydrous, 99.8% purity) was purchased from Sigma Aldrich. Extra pure lithium chloride was carefully dried with molecular sieves 1 week before use, and DMAc was purchased from Junsei Chemicals Co., Japan.

Preparation of cellulose solution and films

Cellulose and LiCl were heated under reduced pressure at $110°C$ for an hour, and the LiCl was dissolved in DMAc. Then, cellulose was mixed with LiCl-DMAc solution and heated at $155°C$, followed by cooling to $40°C$ for 2 h. The detailed procedure of preparing cellulose solution may be found elsewhere.[17,18] The prepared cellulose solution was poured on a circular glass substrate mounted on a spin coater and uniformly coated on it by the coater. The solution with the glass substrate was put into a glass bath filled with solvent mixture of DI water: IPA (60 : 40). It was cured under pressing with load for 12 h and naturally dried in room condition. Resulting cellulose film is named as NR. The cured cellulose film with DI water: IPA mixture was exposed to running water 6, 12, and 24 h, named as 6HR, 12HR, and 1DR, respectively.

Characterization

The XRD patterns were recorded with thin film X-ray diffractometer using CuKα target at 40 kV and 50 mA, at scanning rate of $0.015°/min$. The diffraction angle ranged from $5°$ to $40°$. Thermal gravimetric analysis (TGA) was performed by TG-DTA (NETZSCH, STA 409 PC). The films were cut in pieces, and weight loss of samples was analyzed by burning 10–15 mg of the pieces in air with heating up to $500°C$ and heating rate ($20°C/min$). Li^+ ion concentration in cellulose film was analyzed by inductive coupled plasma mass spectrometer (ICP-MS, Perkin Elmer, ELAN6100). Cellulose films (100 mg) were dissolved in strong acid ($HCl : HNO_3 = 1 : 3$) by heating at $200°C$, and the solutions were analyzed after dilution with DI water. The surfaces of the films were examined with a scanning electron microscope (Hitachi S4300). The films were coated with platinum under vacuum conditions before the SEM experiments. Mechanical properties of the prepared cellulose films were measured by an in-house testing system. Two sensors were used in the testing system. Load cell (Daecell Korea, UU-K010) was used to measure the applied load. Linear scale system (Sony Japan, GB-BA/SR128-015) was used to measure moving distance, while the load was applied and bending displacement test was performed according to the method described elsewhere.[19]

RESULTS AND DISCUSSION

Table I gives the amount of Li^+ ions and Cl^- present in samples after exposure to running water, measured by ICP-MS and EDS, respectively. As reported earlier, Li^+ ions are pulled out from cellulose–LiCl

TABLE I
Li$^+$, Cl$^-$, Yield Strength, and Young's Modulus of the Films

Sample	Li^{+a} (ppm)	Cl^{-b} (Atomic %)	Yield strength (MPa)	Young's modulus (GPa)	Thickness (μm)
NR	4354.17	4.81	61.87 ± 1.28	3.38 ± 0.11	20 ± 0.9
6HR	25.75	3.83	73.51 ± 2.01	3.54 ± 0.19	19 ± 1.2
12HR	13.73	2.45	77.30 ± 1.54	2.92 ± 0.12	20 ± 1.2
1DR	10.26	1.24	79.26 ± 1.77	2.70 ± 0.14	20 ± 1.1

[a] Measured by ICP-MS.
[b] Measured by cross-sectional EDS of the samples.

complex,[17] since Li$^+$ ions are highly polar and LiCl behaves as a typical ionic compound although Li$^+$ ion is very small. However, it is a very clear evidence from the EDS analysis that the chloride anions were also pulled out of cellulose matrix. This is due to the fact that a high negative charge is localized on the Cl$^-$ ions of molecular complex formed,[20] which causes the Cl$^-$ ions to be pulled out of cellulose matrix along with Li$^+$ ions when the films are subjected to running water.

Figure 2 depicts the cross-sectional SEM images for the samples with different running water time. The cross section of no running water film shows a rough, loosely packed fibrillar structure. This may be due to the presence of Li$^+$ ions as well as the rem-

nant DMAc solvent entrapped between the cellulose layers in the film after washing with DI: IPA mixture. However, the cross sectional morphologies of cellulose films were improved with increase in the running water exposure time from 6 to 24 h, which show more compact and uniformly generated cellulose-layered structures. This is due to the elimination of Li$^+$ ions and remnant solvent in the cellulose films.

Further, the samples were subjected to TGA to study the effect of Li$^+$ ions on the thermal stability. Figure 3 depicts the TGA graphs for the cellulose samples, and the weight loss calculation for the NR sample is shown in Figure 4. The TGA traces indicate a defined and rapid weight loss (WL$_1$) at 146°C
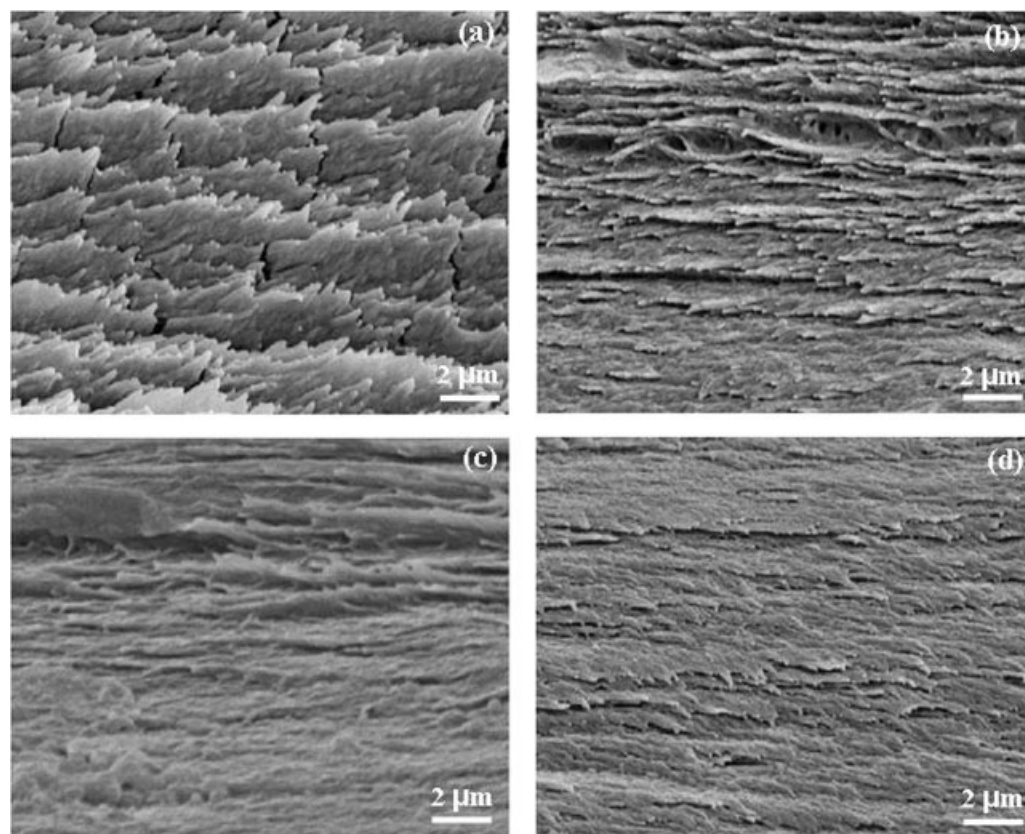

Figure 2 Cross-sectional SEM images of the samples: (a) washed with DI water: IPA mixture (60 : 40), (b) 6 h running water, (c) 12 h running water, (d) 1 day running water.
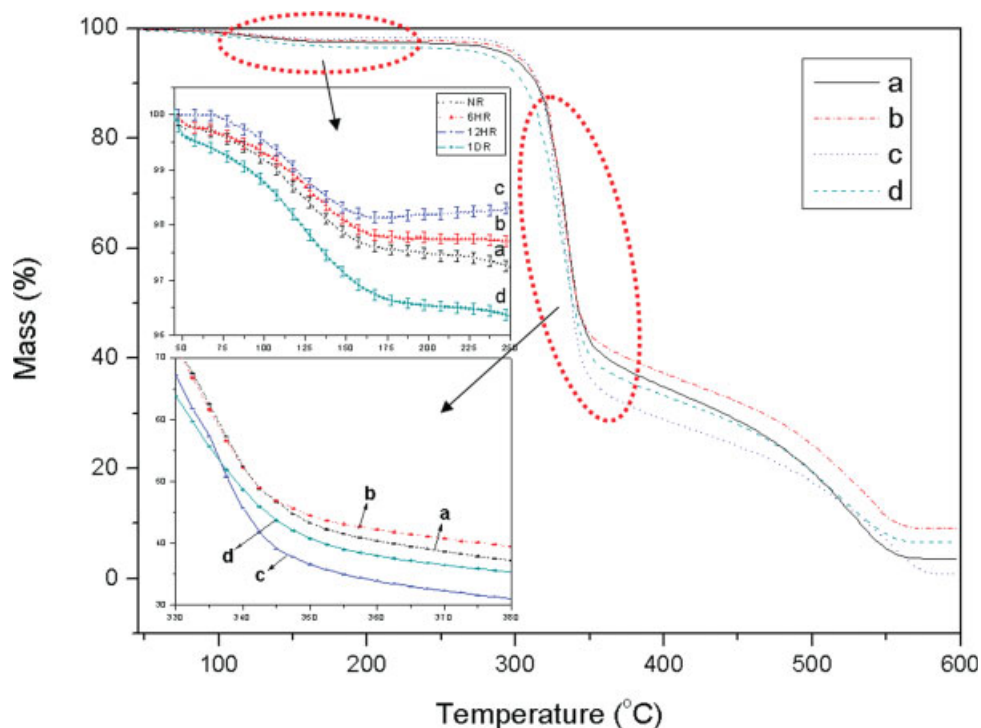
Figure 3 Thermogravimetric analysis (TGA) of the samples: (a) washed with DI water: IPA mixture (60 : 40), (b) 6 h running water, (c) 12 h running water, (d) 1 day running water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and a more gradual weight loss (WL_2) over a wider temperature range (146–340°C). The first weight loss resulted from the loss of remnant solvent and dehydration, and the second weight loss was from the decomposition, which represents the thermal stability of the polymers.[21] It is also reported that, the first weight loss attributed to liberation of aliphatic compounds and decarboxylation and the second to decomposition of aromatic moieties.[22,23] WL_1 for the samples NR, 6HR, 12HR, and 1DR samples were 2.41, 2.16, 2.02, and 2.76%, and that of WL_2 were 40.26, 41.16, 47.31, 42.12%, respectively. It is observed that WL_1 decreases with the increase of running water exposure time from 6 to 12 h, which indicates the loss of Li^+ ions and remnant solvent when films are subjected to running water. However, this value increased to 2.76% when the film was exposed to 24 h; it may be due to the absorption of water when the film is exposed to running water for a long time.

XRD patterns of the samples are shown in Figure 5. From the diffractograms, it is observed that the intensity at 2θ is around 12° and 22° decreased after exposing to running water for 6, 12, and 24 h, which indicates the poor crystallinity upon exposure to running water. In the wood fiber system, the potential adsorption sites are hydroxyl groups and carboxyl groups,[24] and this adsorption of water to accessible cellulose hydroxyl groups increases the chain mobility by weakening intramolecular hydrogen bonds,[25] and reduced crystallinity may be attributed to the absence of interchain hydrogen bonds.[26] Further, the samples were subjected to tensile test to investigate the influence of Li^+ ions on the yield strength and Young's modulus. Last two columns of Table I show the result that Young's modulus
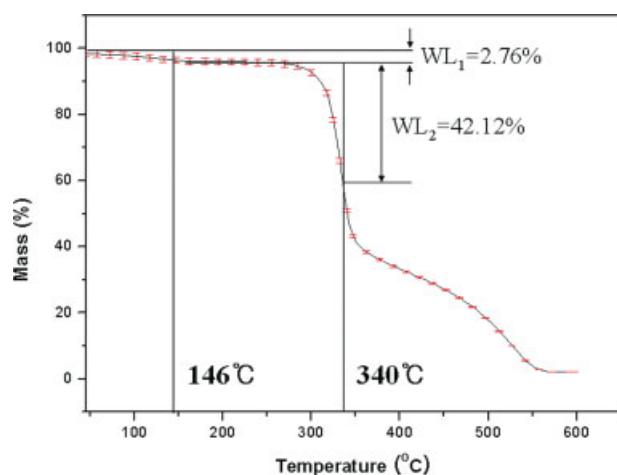

Figure 4 Thermo gravimetric analysis (TGA) of the sample washed with DI water: IPA mixture (60 : 40) with weight-loss calculations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decreased to 2.70 GPa upon exposure to running water for 24 h, showing a good agreement with that of XRD measurement. However, the yield strength increased to 79.26 MPa after exposing to running water for 24 h, which may be the plasticizing effect of water, as it is reported that water is a cellulose plasticizer and has a good plasticizing effect.[27–29] Normally, yield strength is associated with ductile behavior of materials, which means that it is not directly related to Young's modulus.

To evaluate the actuation behavior, gold electrodes were coated on both side of the prepared cellulose films using physical vapor deposition system (SHE-6D-350T), which is termed as EAPap. When an electric field was applied on the electrode, it generates a bending displacement. Figure 6 depicts the bending displacement of cellulose EAPap actuator made by subjecting to different running water exposure times with the actuation frequency variation. Test conditions were 70% relative humidity, 25°C temperature, and 3 V_{PP} actuation voltage. It is observed that the resonant frequency shifted from 7.0 to 6.5, 5.0, and 4.5 Hz upon exposure to 6, 12, and 24 h running water time, respectively. Also, note that the maximum bending displacement was reduced with the running water exposure time. The actuation mechanism of cellulose EAPap has been reported as a combination of piezoelectric effect as well as ion migration effect.[11] When Li^+ and Cl^- ions are removed from the cellulose matrix, the ionic effect may be reduced, resulting in decreased bending displacement of cellulose EAPap. The elimination of ions is important to increase the piezoelectric effect in EAPap by decreasing the ion migration effect. Inves-
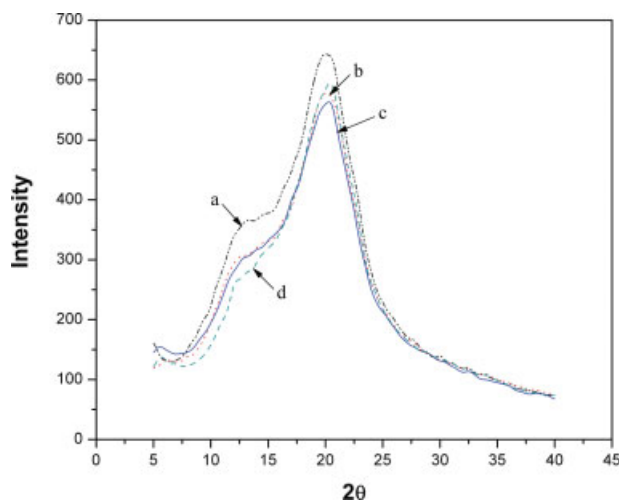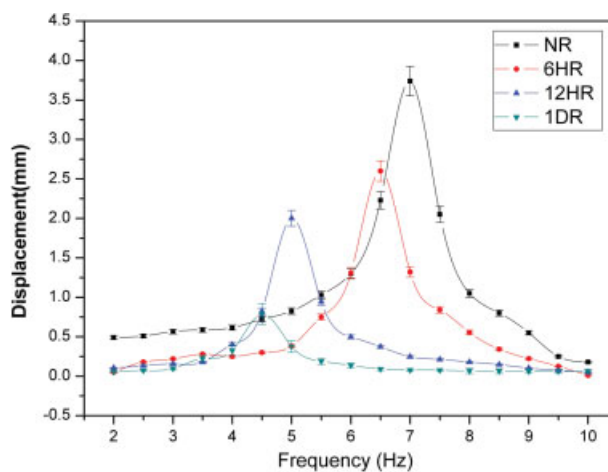

Figure 6 Actuation behavior of cellulose EAPap made by subjecting to different running water exposure time with frequency variation, tested at 70% humidity, 25°C, and 3 V_{PP}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tigation of piezoelectric effect on EAPap made with ion and solvent-free cellulose is on going. However, to increase the piezoelectric effect in EAPap, cellulose microfibers should be well aligned, which is another subject in this research.

CONCLUSIONS

In the present investigation, cellulose films were fabricated with varying Li^+ ions, and its effect on structure, properties, and actuation behavior was studied. ICP-MS and EDS analysis showed that both Li^+ and Cl^- ion contents were reduced from 4354.17 ppm and 10. 26% (atomic) to 10.26 ppm and 1.24 % (atomic), respectively, by exposing to running water. TG analysis showed the reduced thermal stability of the cellulose due to the elimination of Li^+ and Cl^- ions. Similarly, X-ray diffractograms of the samples indicated reduced crystallinity of cellulose upon exposure to running water. Young's modulus decreased, which coincides with the crystallinity result, but yield strength increased as the exposure time of running water increased. Bending displacement tests indicated that the resonant frequency shifted down, and the maximum bending displacement reduced with the running water exposure time. Adsorption of water to accessible cellulose hydroxyl groups increased the chain mobility by weakening intramolecular hydrogen bonds, and the reduced crystallinity may be attributed to the absence of interchain hydrogen bonds. The elimination of ions is important to increase the piezoelectric effect in EAPap by decreasing ion migration effect.

Figure 5 XRD patterns of samples: (a) washed with DI water: IPA mixture (60 : 40), (b) 6 h running water, (c) 12 h running water, (d) 1 day running water. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

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