Dry and Durable Electro-Active Paper Actuator Based on Natural Biodegradable Polymer

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ABSTRACT: This article describes a dry and durable electro-active paper (EAPap) actuator based on natural biodegradable polymer: cellulose and chitosan. To fabricate this actuator, cellulose and chitosan were dissolved in trifluoroacetic acid. The solution was cast to form a film followed by depositing thin gold electrode on both sides of the film. The actuator was actuated under AC voltage at an ambient condition by changing the actuation voltage, frequency, and time. The actuator revealed a large bending displacement under low voltage, electrical power consumption at low humidity condition. This cellulose–chitosan blended EAPap actuator is suitable for dry and durable actuator. Details about the fabrication, durability, electrical power consumption, and characteristics as well as morphology of the actuator are explained. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2044–2049, 2010

Key words: electro-active polymer; cellulose; chitosan; biomimetic actuator; biodegradable

INTRODUCTION

Lightweight and comfortable electro-active actuators stimulated by acceptably low electric fields are required for emerging technologies ranging from micro air vehicles, flat-panel speakers, active video displays, micro-robotics to responsive prosthetics.[1] Some of the key characteristics required in the development of actuator materials include high strain, high fatigue resistance, and reliability.[2] Several classes of materials including single-crystal piezoelectric ceramics[3] and single-walled carbon nanotubes[4] have been considered as suitable candidates for actuator, but they exhibit relatively low displacement in the presence of an electric field. In last 10 years, electro-active polymers (EAPs) have received much attention due to the development of new EAP material that exhibits a large displacement output. Generally, EAPs are divided into two major categories based on their activation mechanism: electronic (driven by electric field) or ionic (involving mobility or diffusion of ions). The electronic polymers, such as electro-active, electrostatic, piezoelectric, and ferroelectric require high activation field close to the breakdown level. In contrast, ionic EAP materials, such as gels, polymer-metal composites, conductive polymer, and carbon nanotubes require low driving voltage. However, there is a need to maintain their wetness.[5–9]

Cellulose, as an environmentally friendly and renewable biomaterial, constitutes around 1.5 × 10^{12} tons of the total annual biomass production. Cellulose has basic molecular unit of $C_6H_{10}O_5$ and is linked in the form of β-1,4-glucan. Numerous new applications of cellulose take advantage of its biocompatibility and chirality for the immobilization of proteins and antibodies for the separation of enantiomeric molecules as well as the formation of cellulose composite with synthetic polymers and biopolymer.[10,11] As one of new applications, cellulose paper has been discovered as a smart material that can be used as sensors and actuators.[12] This smart material is termed as Electro-Active Paper (EAPap).[13] Cellulose EAPap has merits as a smart material in terms of lightweight, dryness, biodegradability, abundance, low price, large displacement output, and low actuation voltage. Possible application areas of this material are micro-insect robots, flying objects, flying magic paper, flower-robots, smart wallpaper, e-papers, and microelectromechanical systems sensors. However, this material is sensitive to humidity, its maximum actuator performance is shown at high humidity condition, and the actuator performance tends to degrade with time.[14]

As an attempt to improve the performance of EAPap actuator, polypyrrole and polyaniline

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conductive polymers have been coated on cellulose EAPap.[15,16] The conductive polymer-coated EAPap actuator exhibited a large displacement output, but it was still sensitive to humidity and the actuator performance degradation was not improved. Another attempt is to mix carbon nanotubes (CNT) with cellulose to improve the performance of EAPap as a bending actuator.[17–19] This CNT-mixed cellulose EAPap can increase the mechanical power output and the resonance frequency, but it is also still sensitive to humidity. So, preparing cellulose EAPap actuator with high performance in ambient humidity condition is a challenging work to make this smart material useful in practical application.

Cellulose–chitosan laminated films have been used as EAPap actuator.[20] The results showed the maximum bending displacement at 60% relative humidity, which is promising to reduce the humidity sensitiveness. Cellulose–chitosan blended film has been used for EAPap actuator.[21] As the molecular structures of cellulose and chitosan are very similar, it is expected to give high compatibility between cellulose and chitosan. Chitosan and cellulose blending ratio and humidity effect on the actuator performance were investigated. When cellulose–chitosan was blended at 60 : 40 ratios, the maximum bending displacement was obtained at 50% relative humidity condition. The actuation principle of cellulose–chitosan blend EAPap actuator has been known to be an ion migration effect associated with Cl^- mobile anions and ($-^+NH_3$) fixed cations.

In this study, we further investigate its durability, electrical power consumption, and characteristics of the cellulose–chitosan blended EAPap actuator. Detailed fabrication process and characterization of the cellulose and chitosan blend EAPap is delineated. The durability of the cellulose–chitosan blend EAPap actuator is evaluated in terms of free bending displacement with respect to time in an ambient condition. Its characteristics are investigated by taking scanning electron microscope (SEM) and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

Cotton cellulose (MVE, DPw 7450) was donated from Buckeye Technologies Co., (USA). Chitosan, medium molecular weight, Brookfield viscosity 200,000 cps, was purchased from Aldrich. Hydrochloric acid (36.5–38%) was purchased from Sigma-Aldrich (St. Louis, MO). Trifluoroacetic acid (>99%) was purchased from Daejung Chemical and Metals Co. Sodium hydroxide (bead, 98%) was purchased from Samchun Pure Chemical Co.

Preparation of cellulose–chitosan blend EAPap actuator

The cellulose–chitosan EAPap actuator was prepared according to the following process. Cotton cellulose pulp (1.2 g) was mixed with chitosan powder (0.8 g) and dissolved in trifluoroacetic acid (100 mL) at room temperature. The clear mixture solution was spin-coated on wafer and cured at room temperature for 12 h. To ensure complete elimination of the solvent, the films were then dried at 60°C for 6 h. Transparent films can be obtained by peeling them off from the wafer. After that, the films were soaked in 0.1*N* NaOH at room temperature for certain time to remove the acids. They were then washed with running tap water, and then immersed in deionized water. As sodium ions were entirely removed by water, its concentration in the film was negligible. After that, the films were immersed in hydrogen chloride aqueous solution (the concentration of hydrogen chloride is 1%) for 2 h, and washed with tap water and deionized water to eliminate little ionic molecules. And then, the wet films were laid in the air for 24 h. To make an EAPap actuator, gold electrodes were deposited on both sides of the film using a physical vapor deposition system. The size of the sample was 10 mm × 40 mm. The configuration of the cellulose–chitosan blend EAPap actuator is shown in Figure 1.

Characterization

SEM images of the actuator were taken with a microscope (Hitachi S-4200, Japan) to study the surface and cross-sectional morphologies of the cellulose–chitosan blend EAPap actuators. The surface and cross-section of the actuator were sputtered with gold, and then SEM images were observed. XRD patterns were recorded on an X-ray diffractometer (D/MAX-2500, Rigaku), by using Cu Kα radiation at 40 kV and 30 mA. The diffraction angle was ranged from 5° to 40°.

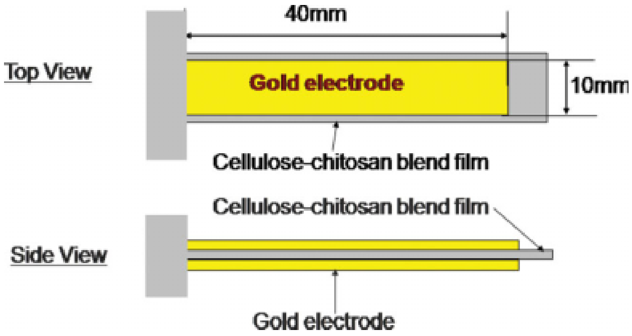

Figure 1 Configuration of cellulose–chitosan blend EAPap actuator. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

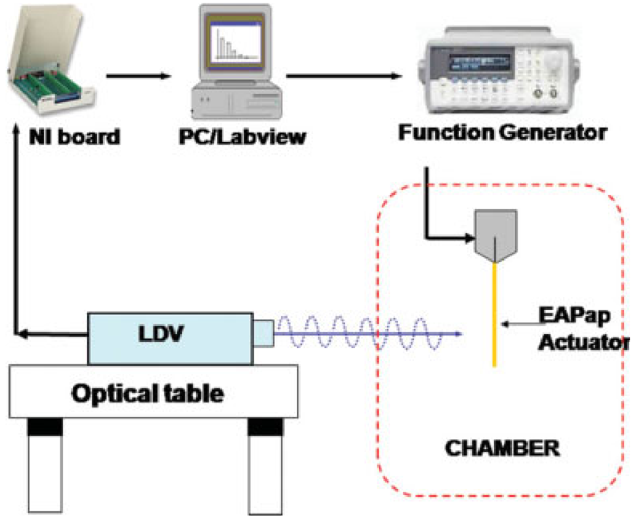

Figure 2 Computerized setup for bending displacement measurement of EAPap actuator. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Bending displacement measurement

The actuator performance of the cellulose–chitosan blend EAPap actuator was evaluated in terms of bending displacement with respect to the actuation frequencies, voltages, and time variations. The bending displacement measurement system consists of a high precision laser doppler vibrometer (LDV) (Ometron VS100), an environmental chamber (KMS, CTH3-2S), optical table, NI board (SCB68), Labview software on a personal computer and a function generator (Agilent, 33,220A) (Fig. 2). An EAPap actuator is supported vertically in air. Function generator controlled by computer sends out the excitation AC voltage and it is applied to the EAPap actuator, resulting in a bending displacement on it. The bending displacement of the EAPap sample is measured by the high precision LDV mounted on an optical table and the LDV signal is converted to the displacement through the Labview software.

RESULTS AND DISCUSSION

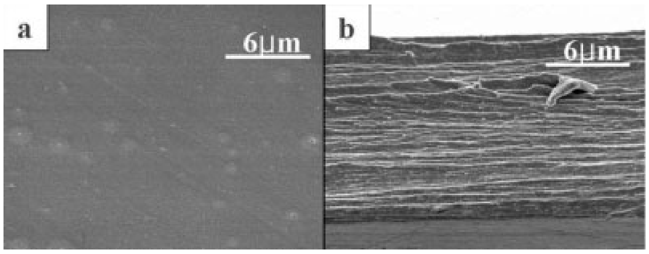

Figure 3 SEM images of cellulose–chitosan blend EAPap actuator: (**a** surface, **b** cross-section).

Cellulose and chitosan blend EAPap was made using solution casting. Figure 3 shows the surface and cross-section morphologies of the actuator before actuation. As the gold layer was so thin, it can be assumed that the surface SEM images can represent the true surface morphology. According to the SEM images, the surface is rather smooth and no phase separation can be observed. A lamination structure can be observed from the cross-section images. This kind of structure has been reported previously as nematic ordered cellulose.[22] No obviously phase separation can be observed. All these results indicate that cellulose and chitosan were blended well. This would be explained by the chemical structure similarity of the cellulose and chitosan. Also, this good miscibility makes a guarantee for the uniformity and stability of the EAPap actuator performance.

The actuator performance under AC voltage was evaluated in terms of bending displacement with voltage, frequency, and time. Figure 4 shows the bending displacement of the actuator measured with respect to the frequency at different actuation voltages (peak to peak) at the ambient condition. The maximum bending displacement was shown at the resonance frequency, 4 Hz. The resonance frequency is related with the mechanical properties of the actuator, for example, thickness, Young's modulus, and density.[23,24] As Young's modulus increases, the resonance frequency increases. On the other hand, as mass of the actuator material increases, the resonance frequency decreases. The maximum displacement increases as the voltage increase from 3 to 6 V. With the voltage increasing, the anions, such as Cl^-, move to positive electrode quickly, resulting in the

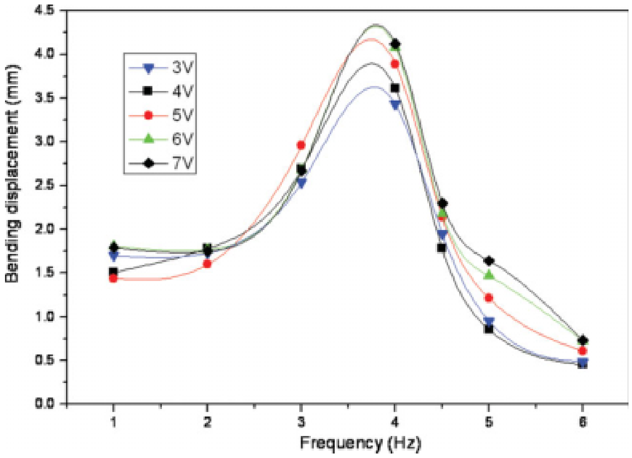

Figure 4 Bending displacement with respect to voltage and frequency variations at the ambient condition. (25 ± 0.5°C, 30 ± 2% RH). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

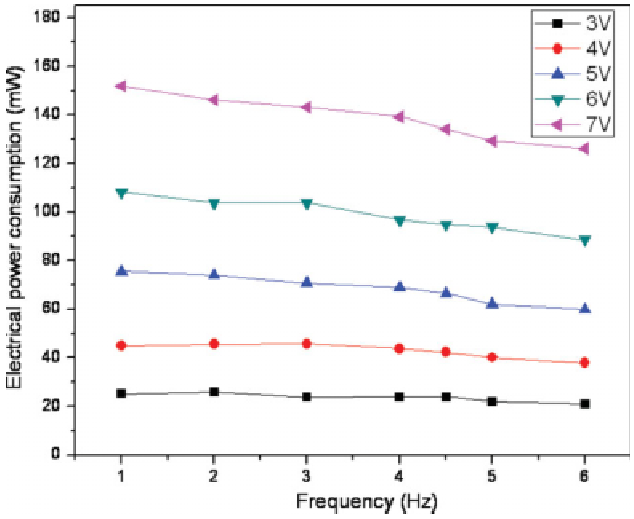

Figure 5 Electrical power consumption of cellulose–chitosan blend EAPap actuator at the ambient condition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increased repulsive force between the anions on the positive electrode so as to increase the bending displacement. The maximum bending displacement of 4.1 mm was obtained at 6 V and 4 Hz. Over 6 V, the bending displacement was saturated. Note that the maximum bending displacement of the cellulose–chitosan blend EAPap actuator achieved at the ambient humidity condition is almost same as that of cellulose EAPap actuator achieved at 90% RH.[18]

The actuation mechanism of chitosan–cellulose blend is more likely based on ion migration effect. As the chitosan molecules can make cations ($^{+}NH_3$) fixed on the molecular chain while anions (Cl^{-}) can move freely. These are all factors that make the ion migration effect play a dominant role in the cellulose–chitosan blend EAPap actuator. The solid presence of cations as fixed ions can improve the actuator performance, which can work in room humidity condition. The thickness of present actuator is about 13 μm [Fig 3(b)], whereas it was 30 μm for the cellulose EAPap case.[18] As the thickness is different even the actuation voltage is same, the voltage should be represented as electrical field strength. By comparing the bending displacement with respect to the electric field strength, the cellulose–chitosan blended EAPap is 75 mm·(V/μm)$^{-1}$, whereas the cellulose EAPap is 18.3 mm·(V/μm)$^{-1}$. In summary, the cellulose–chitosan blend EAPap actuator exhibited excellent actuator performance in dry condition. The value of bending displacement with respect to the electric field strength is far higher than our previous results.[13–15,18–20]

Figure 5 shows the electrical power consumption of the actuator at the ambient condition. With electrical field increasing from 3 to 7V, the electrical power consumption level was increased from around 20–150 mW. Under the same electrical field, the electrical power consumption with the variation of frequency was very low. The electrical power consumption of cellulose–chitosan blend EAPap was 96 and 68 mW when it was excited with electric field 6V and 5V at resonance frequency. This value is higher than that of DMAc cellulose, which was about 55 mW. The increased electrical power consumption might be due to the increased amount of ions and ions mobility of cellulose film associated with blended chitosan. Although the electrical power consumption of the cellulose–chitosan blend EAPap actuator was higher than our previous results, the net electrical power consumption calculated by diving by electrode area is about 24 and 17 mW/cm^{-2} for electric field 6 and 5 V. These values are close to the microwave power limit that does not damage living organs.

The durability is one of key characteristics of actuator. For cellulose EAPap actuator, beyond requiring a high humidity level, another problem was its performance degradation with time.[20,25] This problem was found to be associated with solvent residues, electrolytic gas or ion chains broken. To evaluate the durability of this new cellulose–chitosan blend EAPap actuator, it was actuated for 9 h at 5 V and 4 Hz, at the ambient condition. During the initial 2 h, the bending displacement was measured every 30 sec, and 10 min after that. The durability test result is presented in Figure 6. The initial bending displacement was about 3.6 mm and then drops very quickly to 2.3 mm in few minutes. After that, the bending displacement increased slowly and stably saturated to its maximum value after about 2 h.

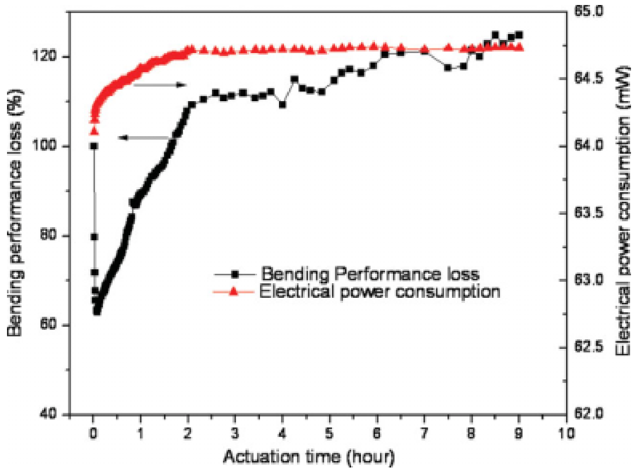

Figure 6 Durability test of cellulose–chitosan blend EAPap actuator at the ambient condition and its electrical power consumption. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

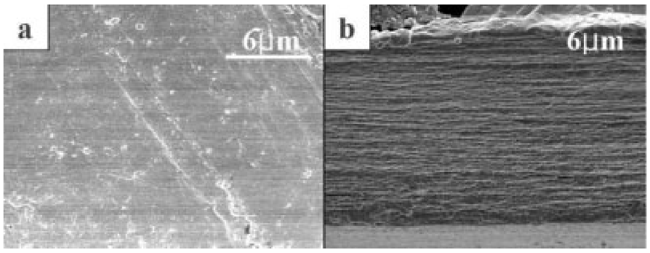

Figure 7 SEM images of cellulose–chitosan blend EAPap actuator after the durability test: (**a:** surface; **b:** cross-section).

For next 7 h, the bending displacement was kept very stable. The durability test was repeated three times and the results were almost same. The initial drop of the bending displacement might be associated with initialization of the material for the electrical actuation. This cellulose–chitosan blend EAPap actuator shows a much better life time and reliability than our previous results.[20,25] The electrical power consumption variations during the durability test was also measured and shown in Figure 6. On the fixed electric field (5 V) and frequency (4 Hz), the variation was very small, less than 1 mW during 9 h. It almost can be ignorable and also indicated the stability of the new cellulose–chitosan blend EAPap actuator.

As we known, the performance degradation of actuator usually is related with the electrode damage and structural changes. To further investigate the durability and reliability of this new cellulose–chitosan blend EAPap actuator, the surface, cross-section morphology, and crystalline structure of the actuator were investigated before and after the durability test. Figure 7 shows the surface and cross-section SEM images of cellulose–chitosan blend EAPap actuator after 9 h test. The surface morphology became a bit rough and uneven after the test. In some surface area, small holes were appeared, which indicate slight electrode damage. However, any significant electrode damage was not seen.

From cross-section images shown in Figure 7(b), we can see that the lamination represented nematic ordered cellulose become loose and irregular in some area. This might be associated with the structural change. Regarding the crystalline structure of cellulose fibers, it is known to be classified into four crystallization types, viz. cellulose I, II, III, and IV, and their crystalline structure can be transformed form one type to another. Figure 8 shows XRD patterns of regenerated cellulose (A), cellulose–chitosan blend EAPap actuator before the durability test (B), and after the durability test (C). The regenerated cellulose belongs to cellulose II. Cellulose II is well known to be a thermodynamically stable crystalline cellulose allomorph. Originally, XRD peaks of cellulose II appear at 12.1°, 19.8°, and 22° assigned to (1 1 0), (1 $\bar{1}$ 0), and (2 0 0). As shown in Figure 8(A), these peaks are located at 9.6°, 20.2°, and 21.2° that represent cellulose II crystalline structure. With the introduction of chitosan, the (1 1 0) peak became much smaller, and the (1 $\bar{1}$ 0) peak at $2\theta = 20.5^\circ$ and the (2 0 0) peak at $2\theta = 21.6^\circ$ were combined, forming a new peak at $2\theta = 19.8^\circ$. Compared with (1 $\bar{1}$ 0) peak and (2 0 0) peak, this new peak was changed to blunt with decreased intensity. This means that some structural changes of cellulose might be happened by blending with chitosan. After actuation for 9 h, the (1 1 0) peak disappeared and the diffraction intensity slightly decreased. But, compared with XRD patterns of cellulose–chitosan blend EAPap before and after the durability test, the main crystalline structure is still remained. The crystalline structure of cellulose–chitosan blend EAPap did not change so much during the long time actuation.

Based on these results, we believe that this cellulose–chitosan blend EAPap actuator must have much longer life time than 9 h. This excellent bending actuator performance along with long durability behavior proves that the cellulose–chitosan blend EAPap can be a robust actuator in dry condition.

CONCLUSION

A novel cellulose–chitosan blend EAPap actuator was prepared by dissolving the polymers in trifluoroacetic acid as a cosolvent, and its characteristics and actuator performance were evaluated. When the EAPap actuator was activated with AC voltage in an ambient condition, the bending displacement increased with the increase in voltage, and its maximum bending displacement of 4.1 mm was achieved at 6 V and 4 Hz, which is almost same as the

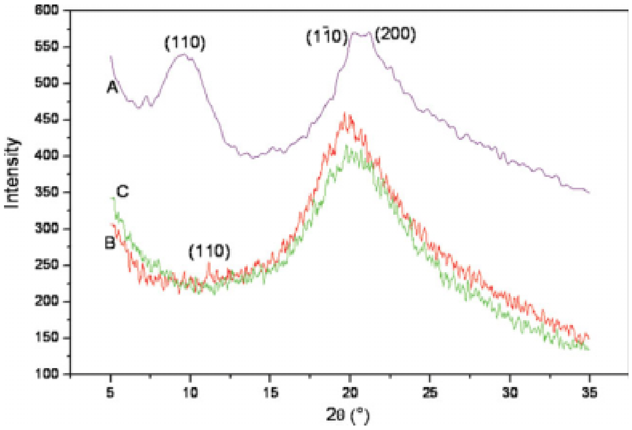

Figure 8 X-ray diffraction patterns of regenerated cellulose (A) and cellulose–chitosan blend EAPap actuator, before actuation (B), and after actuation (C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cellulose based EAPap actuator at 90% RH. The durability test result showed that this cellulose–chitosan can be actuated stably for more than 9 h. The electrical power consumption during the durability test was 17 mW/cm^{-2} with very stable condition. The SEM images and XRD patterns of this cellulose–chitosan EAPap actuator did not show any significant damage of electrode surfaces after 9 h actuation. All these results indicate that the cellulose–chitosan EAPap actuator can be used as a dry and durable biomimetic actuator, which is promising for applications including flapping wings for flying objects, micro-insect robots, and smart shape control devices.

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