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Electro-Active Polymer Actuator Based on Aligned Cellulose Nanofibrous Membrane

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We report cellulose-based electro-active paper (EAPap) actuator formed by electrospinning. Cellulose is one of the most abundant natural polymers and has become an attractive smart material. To prepare electrospun nanofibrous cellulose membrane, the LiCl/N,N-dimethylacetamide (DMAc) solvent system was used. The presence of residual LiCl in electrospun membrane was confirmed by elemental analysis using energy dispersive X-ray spectroscopy. To induce orientation, the cellulose membrane was mechanically aligned in simple extension. FE-SEM was used to observe the morphology of the oriented electrospun membranes. The orientation and crystallinity of the cellulose membrane were examined by WAXD. The electro-active characteristic of the electrospun cellulose membrane was measured by the cyclic bending displacement test under different voltages. Aligning of the electrospun membrane was found necessary to render electro-active characteristic.

Keywords: actuator; cellulose; electro-active paper; electro-active polymer; electrospinning

INTRODUCTION

Electro-active polymers, which behave similar to biological muscles, have been studied for biomimetics applications due to its large displacement output, quick response and low working input signal. Currently, many electro-active polymeric materials are under investigation,

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and some of them are almost ready for commercialization; ionic polymer metal composites (IPMC), gel polymers, conductive polymers, grafted elastomers, and electron-irradiated poly(vinylidene fluoride-trifluoroethylene) (P(VDF TrFE)) [1–5].

Electro-active paper (EAPap) based on cellulose has been studied as an attractive smart material thanks to its unique characteristics including lightweight, biodegradability, low cost, large bending displacement, low power consumption and piezoelectricity [6]. However, because electro-active paper is relatively a new material, detailed investigation of its characteristics such as actuating and material properties is necessary. Recently, mechanical and electrical properties of several types of cellophane were studied to explore their applicability as EAPap [7]. In order for cellulose fibers to exhibit piezoelectricity, they have to be aligned. However, it is very difficult to align properly the conventional cast-films, and also it is difficult to cast cellulose films with uniform thicknesses. Electrospinning can provide polymeric nanofibrous membranes, and a number of approaches have been demonstrated to produce uniaxially aligned nanofibers [8–10].

The electrospinning method has attracted a great deal of attention as a means of producing non-woven membranes of polymeric nanofibers [11]. In fact, electrostatic generation of the ultrafine fibers has been known since the 1930s [12,13]. When an electrical force at a polymer droplet overcomes the surface tension force, a charged jet is ejected. As the liquid jet is continuously elongated and the solvent is evaporated, the fibers of submicron size in diameter are formed, and the final product consists of randomly interconnected webs of fibers. Electrospun membranes are porous, light-weight, flexible and of large surface area. Therefore, the electrospun membranes are widely applicable to the fields of sensors, filters and reinforcements in composites.

In this study, nanofibrous cellulose membrane was produced by electrospinning and their applicability as electro-active paper actuator was investigated. Uniaxially orientation was induced to the electrospun cellulose membrane by mechanically simple stretching. The effect of alignment on the crystallinity and the bending displacement was investigated.

EXPERIMENTAL

Preparation of Cellulose Solution

The pulp cellulose (Buckeye Technologies Inc., grade MVE) was washed in distilled water at room temperature. After cellulose were dried under vacuum at 60°C, cellulose solution was prepared by

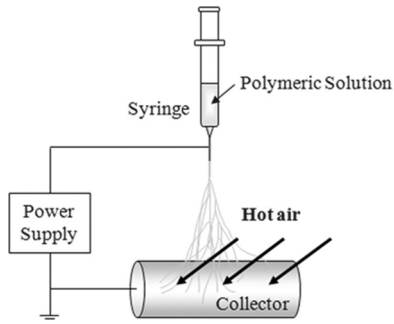
dissolving cellulose fibrils in lithium chloride (LiCl) and *N,N*-dimethylacetamide (DMAc) (both from Aldrich) at 150°C. The concentration of LiCl in DMAc was 8 wt%. After the initial mixing, the temperature of the solution was lowered to 50 ~ 60°C. The cellulose solution was stirred continuously until it became transparent. The final cellulose concentration in the solution was 2 wt%.

Electrospinning

A schematic diagram of the electrospinning set-up used in this study is shown in Scheme 1. Electric field strength was 2 kV/cm, and the spinneret-to-the collector distance was 15 cm. The feed rate of the cellulose solution was kept at 20 μL/min. A rotating drum was used as collector instead of the conventional plate. To remove residual solvents and moisture more effectively, hot air was blown to the rotating drum. Then, the membrane was washed in DI water so as to remove the LiCl residue on the electrospun fibers. In order to induce fiber orientation of electrospun cellulose fibrous membrane, the membrane was uniaxially aligned by the mechanical extension method. Mechanical stretching was employed not only to enhance fiber orientation of cellulose membrane but also to increase the crystallinity of cellulose fibers. Cellulose membrane was stretched up to 10% strain by using Instron machine.

Characterization

FE-SEM (S-4200, Hitachi, Japan) was used to observe the morphology of the electrospun cellulose membranes at an accelerating voltage of 15 kV. Elemental analysis of the cellulose fiber was carried out by the energy dispersive spectrometer (EMAX, Horiba, Japan). The effect



SCHEME 1 Schematic diagram of electrospinning set-up.

of the orientation on the crystallinity of the cellulose was examined by WAXD (X'pert MRD, Philips, Netherlands) with a reflection geometry and CuKα_1 radiation (wavelength $\lambda = 1.0406$ Å) operated at 40 kV and 30 mA. Data were collected within the scattering angles (2θ) of $5 \sim 40^\circ$.

Evaluating the Performance of EAPap

To evaluate the performance of the electrospun cellulose membrane as an EAPap actuator, very thin gold electrodes were deposited on both side of the membrane so that electric field can be applied to the cellulose. Because electrospun cellulose membrane was very porous, the electrodes were connected to each other through the pores. Then, the sample just became a conductor and could not function as an EAPap. Therefore, pores in the cellulose membrane had to be filled with cellulose solution before deposition of gold electrodes. The size of each EAPap was 40×10 mm and the average thickness was 120 nm.

In order to measure induced in-plane strain, sample was fixed in an environmental chamber. An electrical excitation signal was generated by the function generator (Agilent, 33220A) and applied the EAPap sample across the electrodes. To detect in-plane strain, laser displacement sensor (Keyence, LK-G15) was vertically installed at the bottom of the sample. The tests were conducted at $17 \sim 22^\circ$C and $18 \sim 24\%$ relative humidity.

RESULTS AND DISCUSSION

LiCl/DMAc is regarded as one of the most effective solvent systems to dissolve cellulose. The addition of LiCl in DMAc has been proven to be necessary to bridge the electrostatic interaction between DMAc and cellulose [14]. In the electrospinning process, the vapor pressure and the boiling point of the solvent are important because the fibers are formed as a result of the solvent evaporation. To enhance the evaporation rate of DMAc that has a low vapor pressure (2 mmHg at 25°C) and a high boiling point (165°C), the electrospun fiber was dried by hot air at about 80°C while being collected on the rotating drum. LiCl is known to have a strong tendency to absorb moisture in the atmosphere. Therefore, we examined the presence or absence of the LiCl on the electrospun membrane by the elemental analysis using EDS. Figure 1 compares the energy dispersive X-ray spectra of the as-spun cellulose membrane and that of the cellulose membrane after washing in water. In Figure 1(a) distinct chlorine peaks at 2.5–3.0 keV were observed for the as-spun membrane. After the membrane was washed

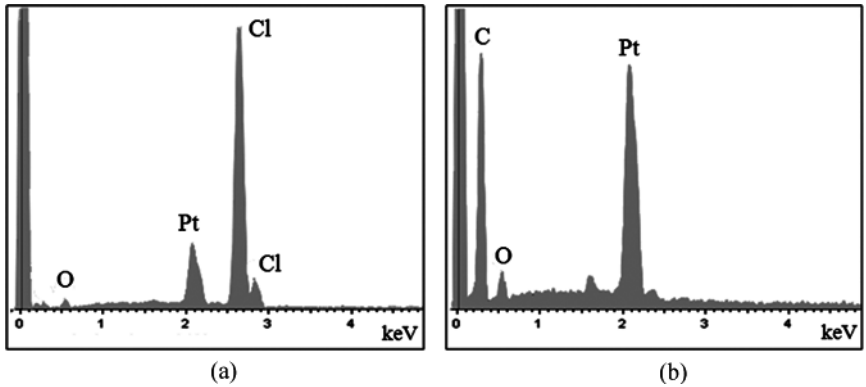


FIGURE 1 Energy-dispersive X-ray spectra of (a) as-spun cellulose membrane, (b) electrospun cellulose membrane washed with water.

with water, the Cl emission peaks completely disappeared (Fig. 1(b)). The fact that the remove of LiCl was essential to yielding optimum membrane was also confirmed by the SEM observation. As shown in Figure 2(a), electrospun fibers containing LiCl had beads or clusters

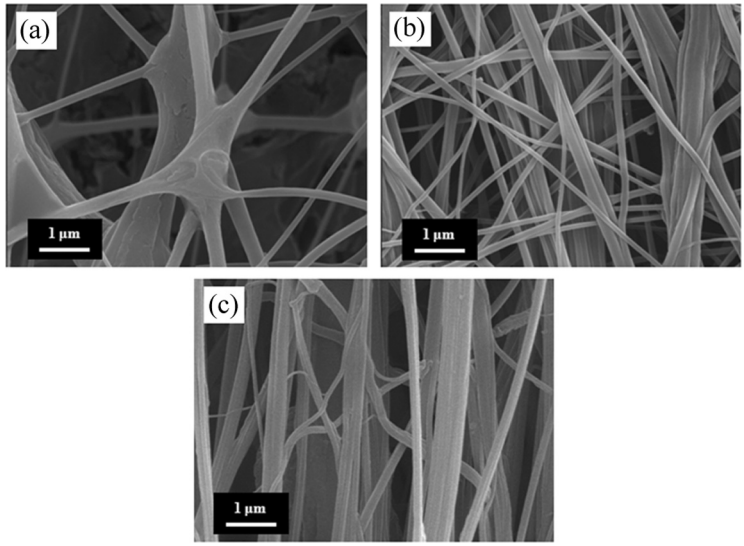


FIGURE 2 FE-SEM images of (a) as-spun cellulose membrane, (b) electrospun cellulose membrane washed with water and (c) mechanically aligned cellulose membrane.

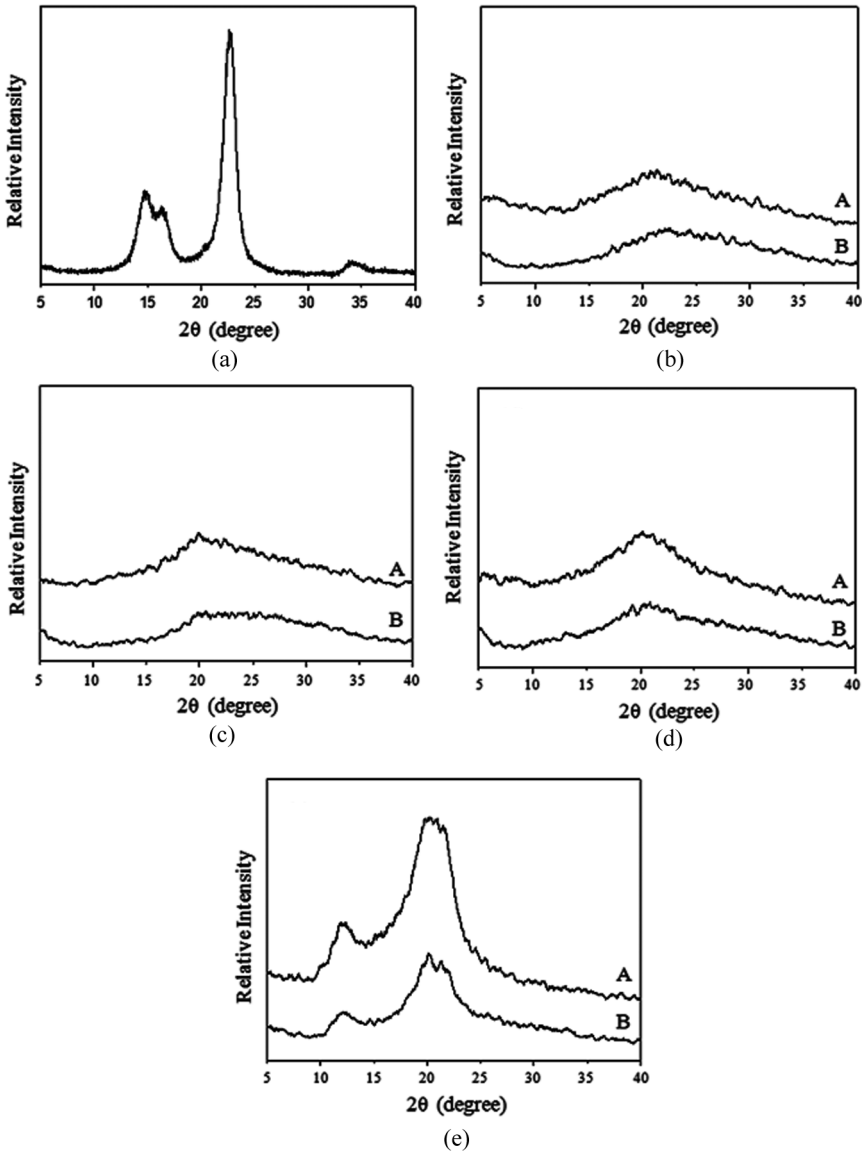


FIGURE 3 XRD patterns of (a) neat pulp cellulose, (b) cast cellulose film, (c) stretched cast cellulose film, (d) unaligned electrospun cellulose membrane, and (e) aligned electrospun cellulose membrane. (A: along the fiber axis, B: perpendicular to the fiber axis).

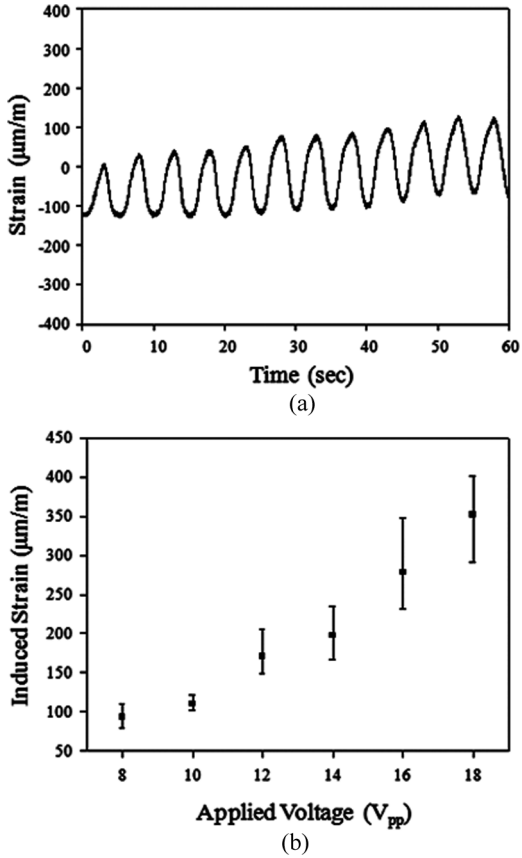


FIGURE 4 Bending displacement test result of the aligned electrospun cellulose membrane: (a) induced strain as a function of time (applied voltage = 6 V), (b) induced strain as a function of applied voltage.

at the intersection of the fibers. When the electrospun membrane was washed with water, it showed randomly oriented, non-woven fibrous morphology (Fig. 2(b)). On the other hand, the uniaxially stretched membrane showed fibers mostly aligned along the stretching direction (Fig. 2(c)).

The effect of stretching was clearly seen in the X-ray diffraction patterns in Figure 3 as well. In Figure 3(a) three prominent peaks were observed in the neat pulp cellulose at 14.8°, 16.3°, and 22.6°, which is characteristic of the crystalline cellulose I [15]. On the other hand, the X-ray diffraction profiles of the cast fiber (Figs. 3(b) and 3(c))

and the unaligned electrospun cellulose membrane (Fig. 3(d)) were quite different. Indeed, they all showed broad patterns that represent the amorphous structure. Because of the random nature of their internal structure, X-ray patterns were independent of the direction. However, the aligned electrospun cellulose membrane showed dramatically different patterns, as seen in Figure 3(e). Sharp peaks at 12.1°, 19.8° and 22.0° appeared which were known to be characteristic of the crystalline cellulose II [15]. Thus, the amorphous cellulose membrane was transformed to the crystalline cellulose as a result of mechanical extension. Also, the X-ray diffraction intensity was strongly influenced by the stretching direction. It is interesting to note that the X-ray intensity of the cast cellulose film, when stretched, independent of the direction.

The performance of the electrospun cellulose membrane as the EAPap was evaluated by measuring the induced strain in a cyclic bending displacement test at a constant frequency of 0.2 Hz. Figure 4(a) is the plot of the induced strain of the aligned electrospun cellulose membrane under the applied voltage of 6 V. The induced strain of the aligned electrospun cellulose membrane was improved with an increase in the applied voltage, as shown in Figure 4(b). However, in the case of the stretched cast cellulose film the increase in the induced strain upon the increase in the applied voltage was insignificant. It could be concluded that aligning of the membrane was very effective in enhancing the electro-active property of the electrospun cellulose membrane.

CONCLUSION

Pulp cellulose was completely dissolved in LiCl/DMAc at a concentration of 2 wt%, and fibrous cellulose membrane was produced by electrospinning. Hot air blowing method was found to be effective in evaporating the solvent during the electrospinning process. After the residual LiCl in the electrospun membrane was washed with water, a clear electrospun membrane was obtained. The uniaxially stretched electrospun cellulose membrane showed fibers aligned along the stretching direction. Upon electrospinning the type I cellulose structure was changed to amorphous, and then to type II cellulose crystal after the uniaxial stretching. The bending displacement characteristic of the aligned cellulose membrane was far better than that of the cast cellulose film. Alignment of the electrospun membrane was found to be effective in enhancing the electro-active property.

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