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Electroactive bio-composite actuators based on cellulose acetate nanofibers with specially chopped polyaniline nanoparticles through electrospinning

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ABSTRACT

A dry type electro-active biopolymer actuator was newly developed with electrospun cellulose–polyaniline bio-composite membranes. Through electrospinning with the mixture of cellulose acetate and polyaniline solutions, well-defined cellulose acetate nanofibers reinforced with chopped polyaniline nanoparticles were obtained and extracellular nano-porous bio-composite membranes with a good biocompatibility were fabricated. The electro-active bio-composite actuator based on cellulose acetate nanofibers with specially chopped polyaniline nanoparticles through electrospinning shows much larger electromechanical deformations than a pure cellulose acetate actuator.

1. Introduction

Electrically responsive polymer actuators [1–5] showing similar responses to natural muscles have received great attention as an important topic in biomimetic engineering, because of their potential applications to biomimetic robots and biomedical devices. In particular, electro-active biopolymer actuators that can be biodegradable and biocompatible have been developed for biomedical applications. Until now, a few biopolymers [6–10] such as plant cellulose, bacterial cellulose, cellulose acetate (CA) and chitosan, have been used for piezoelectric and ionic actuators. They exhibit drastic dimensional changes upon application of an electrical field. The actuation of biopolymer actuators can exhibit mechanical deformations and displacements under electric stimuli due to the piezoelectric and ionic migration effects as well as the subsequent interaction with the polarized particles in the biopolymer. Clearly, it has been reported that the actuation performance of some biopolymers critically depends on the crystallization and ionic migration properties of the membranes.

Cellulose is the most abundant renewable natural polymer material that is an inexhaustible resource. Cellulose derived from a renewable natural resource; therefore, as regards sustainability and environmental protection, they can participate in the natural ecological cycle. Moreover, because of its biocompatibility, cellulose can be used in vivo as a good biological material. Cellulose-based actuators have received increasing interest because the piezoelectric activity can be easily tuned by controlling their size, shape, and composition [11,12]. Nevertheless; some developed biopolymer actuators have limitations to real applications due to low actuation performances in comparison with synthetic polymeric actuators. Most recently, much attention has been focused on the cellulose-based hybrid actuators, since the complex interaction between cellulose and additional materials could enhance the ion-migration and piezoelectric efficiency of the cellulose actuator, leading to increased potential for many real applications [11–18]. However, it is very difficult to obtain well-dispersed composite membranes reinforced with nanoparticles and to explain the influence of nanoparticles on the actuation performance of cellulose-based composite actuators. Also, reliable and reproducible production methods should be pursued to overcome the irregular and uncontrollable performance of the nano-composite actuators.

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Electrospinning was developed long ago, and from the 1990s, it began to be widely used in the preparation of nano-composites. Electrospinning uses an electrical charge to draw very fine fibers, typically on the micro or nanoscale, from a liquid state of molten precursors without solvent. In the preparation of nano-composites, electrospinning is an extremely practical and effective way to disperse nanoparticles into polymeric fibers and membranes, as it results in relatively uniform distribution, and obtains desired nanoscale fibers. The electrospinning method has been proven to be an effective way of constructing a series of well dispersed nano-composites with controllable and repeatable productions [19–22]. Based on recent progress in electrospun cellulose–fullerene actuators, [11] we further attempt to make high-performance electro-active bio-composite actuator based on cellulose acetate nanofibers reinforced with polyaniline (PANI) nanoparticles through electrospinning process. Until now, polyaniline nanoparticles have not been used as nano-fillers to produce the electroactive polymer membranes, because conductive polymer particles could not be uniformly dispersed into polymer membranes.

In our electrospinning experiments with the mixture of cellulose acetate and PANI conducting polymer, it was surprisingly and unexpectedly observed that chopped PANI particles were embedded into the electrospun cellulose acetate fibers. Our original purpose of electrospinning was to make mixed cellulose acetate fibers integrated with PANI conducting polymer fibers that can play a role in electrical wires. But, the PANI conducting polymer nanoparticles were formed and embedded into the cellulose acetate nanofibers through electrospinning process. Only a small amount of chopped polyaniline nanoparticles, resulting in well dispersed nano-composites, can enhance the actuation performance of cellulose-based biopolymer actuators. Therefore, we developed a high-performance electro-active bio-composite actuator by using cellulose acetate biopolymer matrix and polyaniline as a nano-additive. The PANI nanoparticles were used as structure-directing cores for controlled actuation of PANI/CA actuators. By controlling the loading level of the PANI conducting polymer, we are able to obtain well-defined bio-composite nanostructures via the electrospinning method that are greatly beneficial for producing regular membranes repeatedly with well dispersed PANI nanoparticles in the cellulose acetate nanofibers. The electrospinning method can produce reliable electrospun membranes with controlled weight ratio between PANI and CA, unlike conventional casting methods that are not good for repeatability and dispersion in constructing the nano-composites. The overall morphology can be further manipulated by changing concentration ratio between cellulose acetate and polyaniline. These highly adjustable nanostructures can enrich the types of particle-fiber structure and greatly enhance the actuation performances of the electro-active cellulose-based bio-composite actuators.

2. Materials and methods

Cellulose acetate (CA; white powder; Mn$\sim$30,000 by GPC, 39.8 wt% acetyl groups) was purchased from Sigma–Aldrich. N,N-Dimethylacetamide (DMAc; Assay:99.0%) and PANI were purchased from Sigma–Aldrich and used as received. DMAc and acetone were used as the solvent for cellulose acetate and PANI. Cellulose acetate was dissolved in DMAc/Acetone (2:1 v/v)[23] and stirred vigorously at room temperature until a transparent solution (20 wt/v%) was obtained. To this, 0.1 wt.% and 0.5 wt.% PANI were added respectively, and the solution was homogenized in an ultrasonic bath. Fig. 1 shows the schematic diagram for the fabrication procedure of PANI/CA bio-composite actuators. First, CA and PANI were dissolved with co-solvent, and then, the prepared membrane was electrospun, and finally it was coated with gold to make an electroactive bio-composite actuator. In the electrospun PANI/CA bio-composite, the hydroxyl groups of cellulose acetate could interact physically with the secondary amine groups of polyaniline to form weak hydrogen bonds that ensure the well invasion of chopped polyaniline nanoparticles into cellulose acetate matrix.

The electrospinning apparatus was composed of several components: a high voltage supplier (Gamma High Voltage Research, E3 30P-5W, USA), a capillary tube with a stainless steel needle (16 gage), a syringe pump (Hardvard Apparatus, USA), and a stainless steel collecting screen (diameter $\approx$ 10 cm). A high electric field from the high voltage supplier is generated between the needle and the collection plate. As it reaches a certain voltage difference, the electrical charge passing through the polymer solution overcomes the surface tension of the polymer solution droplet that is formed at the tip of the needle. Electrospinning was carried out using a syringe with a 1.2 mm diameter spinneret at an applied voltage difference of 20 kV over the distance of 20 cm ($E = 1$ kV/cm). The syringe pump was set to deliver the solution at a flow rate of 3.0 ml/h using a 5 mL syringe. A syringe pump was used to squeeze out the solution at a speed of 2 ml/h through a needle with an inner diameter of 0.21 mm. Thus, membranes with a thickness of 100 μm were obtained. The membranes were immersed overnight in 1.5 N aqueous solution of lithium chloride. The PANI/CA bio-composite actuators were fabricated by depositing very thin gold electrodes on both sides of the as-fabricated cellulose acetate by using a physical deposition system (108 auto sputter coater, Cressington). Length, width and thickness of the prepared actuators were 10 mm, 40 mm, and 0.1 mm, respectively.

Electromechanical actuation tests including harmonic responses, and current–voltage tests were conducted. The tip displacements of the actuators were measured with a laser displacement sensor (LK031, Keyence) and a National Instruments data acquisition system (PXI 6252). The LabVIEW program was used with an industrial computer to acquire and control the data.

X-ray diffraction (XRD) results of the composites were obtained with a DMAX-Ultima III X-ray diffractometer in the range from 5° to 60°. Scanning electron microscopy (SEM) images were recorded using a cold field emission scanning electron microscope (S-4700, Hitachi, Japan). The experimental setup for the actuation measurement consisted of a charged couple device (CCD) camera (XC-HR50), a laser displacement sensor for sensing displacement and motion, and an NI-PXI system and a current amplifier (UPM1504) for signal generation and actuation of the electrospun cellulose acetate actuator, respectively. TEM pictures of electrospun nanofibers were taken from an in situ TEM system operating at 150 kV.

3. Results and discussion

The SEM images of the prepared PANI/CA membranes are shown in Figs 2a–c. As seen in the SEM images, similar nano-fibrous textures in the membrane surfaces were observed with different PANI contents. The various kinds of nonwovens are made up of crimped fibers. As an additive, the PANI conducting polymer does not make remarkable difference between electrospun membranes and well-defined nano-porous structures in the electrospun membranes are obtained. As the loading level of the PANI conducting polymer increases up to 0.5 wt%, the diameter of electrospun nanofibers decreases, resulting in well-defined nanoporous networking structures. As we know, ion migration as well as piezoelectricity in cellulose actuators is an important parameter for high-performance actuation and the high porosity observed in electrospun membranes can play a beneficial role in the ion migration. SEM images observed in Fig. 2a–c shows a high degree of porosity in the 0.5 wt% PANI/CA membrane which can be advantageous for actuator applications [24].