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Electroactive artificial muscle based on crosslinked PVA/SPTES

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ABSTRACT

Based on a crosslinked ionic networking membrane of sulfonated poly(arylenethioethersulfone) copolymer (SPTES) and poly(vinyl alcohol) (PVA), a novel biomimetic artificial muscle with electrically driven bending deformation was developed. Sulfonated endcapped poly(arylenethioethersulfone) copolymer (SPTES) was synthesized through direct copolymerization of sulfonated monomers and poly(vinyl alcohol) (PVA) was crosslinked with SPTES by the dehydration method. The crosslinking reaction and molecular interactions between PVA and SPTES were observed in the FT-IR spectra of the PVA/SPTES ionic networking membrane. In comparison with the Nafion membrane, the crosslinked PVA/SPTES membrane shows much higher proton conductivity and ionic exchangeable capacity that are main factors influencing the actuation performance. Electroactive PVA/SPTES actuators show much larger bending deformation under step inputs without straightening-back relaxation and harmonic responses under sinusoidal excitations in a wide frequency band.

1. Introduction

In last decades, a variety of electroactive polymers that exhibit substantial deformations in responses to electrical inputs voltage have been emerged. The performance of the developed polymer actuators exceeds that of natural muscle in many respects, making them particularly attractive for biomedical devices, medical prostheses, biomimetic robots, entertainment toys, and micro/nano electromechanical systems [1]. Among the electroactive polymers (EAP), ionic polymer-metal composite (IPMC) is one of electrically driven bending actuators [2,3]. The sandwiched structure of IPMC actuators consists of an ionic exchangeable polymer core and platinum electrode facesheets through electroless plating [4]. When an electric field is prescribed through the thickness of an IPMC, cations inside the membrane carry solvent molecules toward the cathode and the ion movement creates bending deformation providing the source of actuation force [5]. In EAPs, the polymer membrane is one of the most critical components. At present, Nafion-H based on a perfluorinated ionomer is the only commercially available, state-of-the art membrane used in IPMC actuators [6]. Although it has good chemical and physical properties for ionic IPMC actuator applications, it has severe performance limitations at temperatures higher than 80 °C and at low humidity. At these conditions, proton conductivity drops considerably due to membrane dehydration [7]. In addition, the cost of Nafion is extremely high because of the complex and extensive chemistry required for synthesis. Nafion-based IPMC actuators show relaxation-back phenomena in step responses, low blocking force and limited actuation bandwidth. Among candidates to substitute the Nafion, hydrocarbon polymers containing polar groups that retain large amounts of water over a wide temperature range are particularly attractive and relatively much cheaper to synthesize than perfluorinated polymers [8]. Wang and Oh developed several electroactive artificial muscles based on hydrocarbon polymers with poly(styrene-ran-ethylene) [9,10] and poly(styrene-b-[ethylene/butylene]-b-styrene) [5,11]. Also, the radical copolymerization of fluoroalkyl acrylate (DuPont Zonyl TAN, FA) and acrylic acid (AA) resulted in novel ionic polymer transducer membranes [12,13]. Long and Leo [14] presented a review paper on the ionic polymer membranes which can be used in the polymer actuators.

There are two strategies to prepare sulfonated hydrocarbon polymers. The first one is post-sulfonation of prepared polymers by different sulfonation agents such as concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, trimethylsilyl chlorosulfonate, and sulfur trioxide–triethyl phosphate complex. The other method is direct polymerization of designed sulfonated monomers. In the post-sulfonation reactions, aromatic electrophilic substitution by the sulfonic acid groups is usually restricted to the activated position ortho to the aromatic ether bond, which might

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deteriorate the chemical stability of the polymer because of the cleavage of the ether linkage. In addition, the sulfonic acid groups are relatively easy to eliminate from the activated aromatic ring via desulfonation. Moreover, the degree of sulfonation is difficult to control, and extremely high degrees of sulfonation often cause the functionalized polymers to become soluble in water. Finally, post-sulfonation might also cause the partial degradation and cross-linking of the polymers especially when strong sulfonation agents such as chlorosulfonic acid are employed. In direct polymerization, monomers with the sulfonic acid groups attached to the deactivated aromatic rings are used to prepare the sulfonated polymers. It is expected that the attachment of the sulfonic acid groups to the deactivated ring positions might provide chemical stability and enhance the acidity of the resulting polymer structure, resulting in more facile proton transport [15]. Much effort has been expended in the development of new proton conducting polymers by direct polymerization. These developments include the attachment of the sulfonic acid groups onto highly stable aromatic polymers, such as poly(ether ether ketone) [16], polyethersulfone [17,18], polyimide [19], and poly(phenylene sulfide) [20]. These polymers generally exhibit good thermal and chemical stabilities and high proton conductivities. Bai reported the synthesis of endcapped poly(arylenethioethersulfone) copolymer (SPTES) by direct polymerization employing sulfolane as the polar aprotic solvent. His studies indicated that the SPTES copolymers have good film-forming capabilities and exhibit hydrophilicity. The hydrated SPTES membranes showed high proton conductivity. These properties imply the potential usefulness of the SPTES copolymer membranes as ionic polymer actuators as well as fuel cell membranes.

Although SPTES copolymer has good proton conductivity and thermal stability, it is very difficult to improve its molecular weight to satisfy the requirement of mechanical stiffness for the electroactive polymer actuator. Blending or crosslinking it with other polymers may overcome the problem. Poly(vinyl alcohol) (PVA) is known to have good chemical stability, good film-forming and mechanical properties, and also a cheap price. PVA has been used in the polyelectrolyte fields by blending it with alkaline, Nafion and sulfosuccinic acid, or poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) [21–24]. There are two crosslinking mechanisms that are the bases for the function of the PVA: one is the physically crosslinked network by hydrogen bonding such as in PVA and poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA) compounds and the other is the chemically crosslinked network such as by carboxylate (–OH in PVA reacts with –COOH) and glutaraldehyde (–OH in PVA reacts with –CHO) [22,25,26]. Recently, Gu reported a direct covalent crosslinking of sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK) and poly(vinyl alcohol) (PVA) prepared through a post-heating process [27]. Crosslinked SPPESK with PVA membranes was prepared through direct covalent crosslinking by condensation of –SO_3H in SPPESK with –OH in PVA. PVA is a crosslinker candidate for sulfonated polymer due to a lot of –OHs existing in its main chain.

In this study, the crosslinked PVA/SPTES ionic exchangeable membrane was synthesized with direct copolymerization and post-heating method for a novel electro-active polymer actuator. Through electroless plating and ion-exchange processes, the electroactive PVA/SPTES actuator was finally obtained. For the confirmation of the crosslinking structure, FT-IR and water solubility of the membrane were studied. The mechanical, electrical, thermal properties and the water uptake of the PVA/SPTES membrane were also studied. The electromechanical performances of the PVA/SPTES actuator under DC and AC excitations were investigated in comparison with those of the Nafion actuator for the first time.

2. Experimental

2.1. Fabrication of PVA/SPTES membrane

The 4,4′-thiobisbenzenethiol, anhydrous potassium carbonate, and 4-fluorophenylsulfone were obtained from Aldrich and used as-received. PVA (solid, $M_w = 61{,}000$) was purchased from Fluka. N,N-dimethylacetamide (DMAc, anhydrous, 99%, Sigma–Aldrich Co.) was used as received. Other chemicals were of analytical grade and used as received unless otherwise mentioned. SPTES-60 copolymers that the composition of sulfonated repeating unit is 60% were prepared by the method described in the literatures [8].

The SPTES membrane was prepared by dissolving the sodium-form SPTES-60 copolymer in dimethylacetamide (DMAc) to obtain 5–10 wt.% transparent solution. The solution was then filtered using a 0.45 μm Teflon syringe filter to remove contaminants and cast directly onto clean glass substrates. The sodium-form membranes were carefully dried in vacuum at 60 °C over 24 h. The SPTES-60 copolymer sodium-form membranes were converted into acid-form by the acidification procedure. This involved immersion of membranes for 24 h in 2.0 M sulfuric acid at room temperature, followed by soaking for 2–4 h in deionized water, washing with deionized water for 2 h, and vacuum drying at 80 °C for 24 h.

Solid PVA ($M_w = 61,000$) and the dried SPTES in the acid form were weighed respectively and then dissolved under agitation in dimethyl sulfoxide (DMSO) to make a 10 wt.% pre-membrane solution. Membranes were prepared by spreading the polymer solution into a PTFE mold and evaporating the solvent in a vacuum oven at 80 °C under nitrogen atmosphere for 48 h. The membranes were then heat treated at 120 °C for 1 h, immersed in deionized water and peeled off the PTFE mold for the subsequent experiments.

2.2. Characterization of ionic membranes

The ion exchange capacity (IEC, mmol/g) of the membranes was determined titrimetrically, as described in the literature [19]. The IEC is defined as the milli-equivalent of sulfonic acid groups per gram of dried samples.

Proton conductivities of the hydrated membranes were measured using a complex impedance analyzer (Solartron SI1287 electrochemical interface) over a frequency range of 1–100 kHz. Ionic membranes were sandwiched between two stainless steel electrodes, and an ac perturbation of 10 mV was applied to the cell. The membranes were immersed in deionized water at least 3 h for adequate swelling before being measured. Measurements were carried out at the room temperature, and the proton conductivity (σ) was obtained using the following relation:

$$\sigma = \frac{L}{R \times A} \quad (1)$$

where σ is the proton conductivity (S/cm), L the measured thickness of the polymer membrane (cm), R the measured impedance of the membrane (Ω), and A is the cross-sectional area of the membrane (cm^2). The measurements with an error margin of 5% were done in duplicate.

The membranes were soaked for over 24 h in deionized water and weighed to determine the uptake contents. The soaked membrane was dried overnight in vacuum at 50 °C, and the weight of a dried membrane was measured. The uptake content was calculated by:

$$\text{uptake content (\%)} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \times 100 \quad (2)$$

where w_{dry} is the mass of the dried membrane and w_{wet} is the mass of wet membrane, respectively. All the measurement data in this