



## Preparation and Characterization of Novel Ionic Polymers to be Used as Artificial Muscles

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### Abstract

The muscle-like technology would be of enormous advantages for biomedical applications such as medical implants and human assist devices. Ionic polymer metal composites (IPMCs) are one kind of biomimetic actuators. An ionic polymer metal composite composed from an ionomer with high ion exchange capacity that packed between two thin metal layers. In the present study we focused on the preparation of a novel alternative polymeric ionomer to be used as artificial muscles. Sulfonated poly(ether ether ketone) (PEEK) have been synthesized as a new class of ionomeric membrane materials. PEEK was sulfonated at various degrees with sulfuric acid and N,N-Dimethylacetamide as a solvent. Fourier transfer infrared spectroscopy confirmed the quality of substitution reaction. Sulfonated samples showed O-H vibration at 3490 and S=O peaks at 1085 and 1100-1300  $\text{cm}^{-1}$ . By increasing degree of sulfonation to 80%, ion exchange capacity, water uptake and the number of water molecules per the fixed sulfone groups ( $\lambda$ ) were increased to about 2.4  $\text{meq.g}^{-1}$ , 75% and 19, respectively. After calculating the optimum degree of sulfonation, the applications of these ionomers as actuators are studied. Rigid microstructure of PEEK backbone causes to slow displacement. However, this inflexible backbone showed the acceptable tip force during its actuation. These IPMC are easy to prepare and much less expensive than the commercial per-fluorinated membranes such as Nafion<sup>®</sup>. The results approve the utilization of sulfonated aromatic for artificial muscles applications as novel strong muscles with low flexibility.

**Keywords:** Artificial muscles; Ionic polymer metal composites; sulfonated poly (ether ether ketone).

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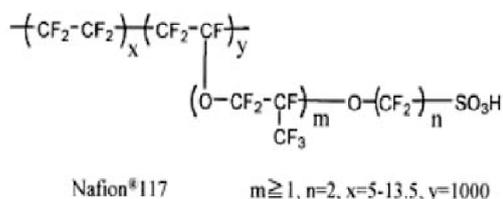
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### 1. Introduction

In recent years, there has been an intensive research effort for development of alternative synthetic materials that display biomimetic

properties. One class of biomimetic materials are those which show actuation behaviors. Electroactive polymers (EAPs) directly convert electrical energy to mechanical energy [1]. Ionic polymer metal composites (IPMCs) are one group of electroactive polymers. Comparing between properties of mammalian skeletal muscle and ionic polymer metal composites is exhibited [2-10]. IPMCs are active actuators that show large deformation in the presence of low applied voltage and exhibit low impedance. They operate best in a humid condition and can be made as self-contained encapsulated actuators to operate in dry environments as well. They have been modeled as both capacitive and resistive element actuators that behave like biological muscles and provide an attractive means of actuation as artificial muscles for biomechanics and biomimetics applications [11].

Essentially polyelectrolytes possess ionic groups on their molecular backbone. These ionic groups have the property of dissociating and attaining a net charge in a variety of solvent medium. These net ionic groups which are attached to networks of macromolecules are called polyions [12]. Thus, the essence of electromechanical deformation of such polyelectrolyte systems is their susceptibility to interactions with externally applied fields as well as their own internal field structure. In particular if the interstitial space of a polyelectrolyte network is filled with liquid containing ions, then the migration of such ions inside the structure thanks to an imposed electric field can also cause the macromolecular network

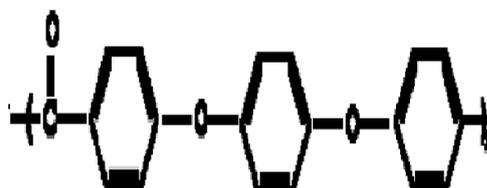


**Figure 1.** Molecular structure of perfluorinated ion exchange membrane, Nafion®.

to bend [13]. The most common IPMC muscle used in investigations is composed of a perfluorinated ion exchange membrane, Nafion®, which is chemically composited with a noble metal such as gold or platinum [8,9,14,15]. A typical chemical structure of the Nafion® is shown in Figure 1 [16, 17].

Deflection of the layered structure towards one of the electrodes occurs as a result of a field induced change in ion concentration, which attracts water molecules to one side of polymer. The non-uniform distribution of water produces swelling of one side of the actuator and contraction of the other, generating torque on the memberane and a bending motion [10,18]. The softness and flexibility of a muscle-like technology would be of enormous advantages for biomedical applications such as medical implants and human assist devices [19]. It is reported that the biological compatibility of the IPMC actuators is good [20] and, thus, it is suitable for detecting or actuating in the body of human. Nafion® is a well-known ionic polymer, which combines the mechanical strength and chemical/thermal stability with excellent charge conductivity. In recent years, there has been an intensive research effort for the development of alternative polymers to be used as an IPMC's matrix [21].

In the current study we focused on the synthesized a new alternative matrix for IPMC systems. Among the non-fluorinated hydrocarbon ionic polymers the membranes based on aromatic poly(ether ether ketone) (PEEK) selected because of their lower cost in comparison with Nafion®, good film



**Figure 2.** Molecular structure of sulfonated poly(ether ether ketone)

formation properties with the accompaniment of chemical, thermal and mechanical stabilities; more over their poor ionic conductivity, as a limiting property, is improved by sulfonation [22-24]. The chemical structure of PEEK is displayed in Figure 2. As a new alternative matrix material for IPMC systems, PEEK present an intriguing chemical structure composed of hydrophobic and hydrophilic regions. In the current research we synthesized and characterized partially sulfonated PEEK with various degree of sulfonation.

## 2. Experimental

### 2.1. Chemicals

Poly(ether ether ketone) was obtained from Poly Science, Inc. (Niles, IL, USA) in the form of extrudates. Sulfuric acid 95-97% (for sulfonation), N,N-dimethylacetamide (DMAc) as solvent, sodium hydroxide solution (for titration), hydrochloric acid and hydrogen peroxide were purchased from Merck (Darmstadt, Germany). Deionized water as diluent (purified with milipore™) was used in this work. Nafion® 117 (178 μm) membranes from Dupont™ (Wilmington, DE, USA) were used for comparing the data.

### 2.2. Sulfonation process

Sulfonation of PEEK with various degrees of sulfonation followed by the procedure reported in the literature [22,25,26]. PEEK

was dried at 100°C in a vacuum oven overnight. Dried polymer dissolved in concentrated sulfuric acid and stirred vigorously at room temperature for 20-120 h. The sulfonated polymer solution was added gradually to the large excess of ice-cold water under continues mechanical agitation for one hour until the polymer suspension was settled down after 12 h. The precipitated particles were filtered and washed several times with deionized water until the pH became neutral. Samples were dried in vacuum oven at 100 °C for 10 h.

### 2.3. Membrane preparation

Membranes were solvent casted, dried at ambient temperature, dissolved in N,N-dimethylacetamide (DMAc) with various degrees of sulfonation and stirred for 24 h. The resultant mixture was stirred for 8 h at 80 °C and concentrated in rotary evaporator. The viscose solution was casted on a clean glass plate, dried in several steps, at room temperature for one night, then stored at 70 °C for 8-10 h and 120 °C overnight. The sulfonated membranes and Nafion® 117 were modified by the modification procedure mentioned in below.

The membranes were boiled in 3 wt% hydrogen peroxide for 30 min., washed for several times and boiled for 1 h in deionized water. Membranes were boiled again in one

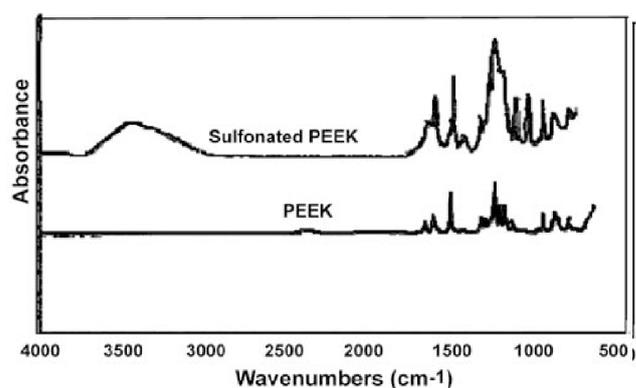


Figure 3. FT-IR spectra of PEEK and sulfonated PEEK.

**Table 1.** Comparing between mammalian skeletal muscle and Ionic polymer metal composites.

Property	Mammalian skeletal muscle		Ionic polemer metal composites		
	Typical	Maximum	Maximum	Typical	Minimum
Strain (%)	20	>40	-	303	0.5
Stress (MPa)	0.1 (sustainable)	0.35	15	3	0.23
Work density (kJ/m <sup>3</sup> )	8	40	-	-	5.5
Strain rate (%/s)	-	>50	-	-	3.3
Specific power (W/kg)	50	284	-	-	2.56
Efficiency (%)	-	40	-	1.5	2.9
Modulus (GPa)	10-60	-	0.1	0.05	-
Density (kg/m <sup>3</sup> )	1037	-	-	1500	-
Cycle life	-	> 109	-	-	-
References	2-5	-	6-10	-	-

molar sulfuric acid for 30 min., and washed three times with deionized water.

#### 2.4. Membrane electrode assembly.

The electrodes were prepared by catalyst decaling and painting methods and as same as of our previous reports [27,28]. Pt-black (purchased from Johnson-Matthey) was used as catalysts for the both of electerodes. It was mixed with a 5 wt% Nafion<sup>®</sup> solution (obtaned from Dupont<sup>™</sup>) in isopropanol and several drops of glycerol (obtained from Merck) as ionomeric coupling agent and suspension/painting agent, respectively. The suspension was brushed directly (4 mg.cm<sup>-2</sup>) onto dry membranes and then hot pressed to increase the contact area between the catalyst layer and membranes. The obtained membrane-electrode were boiled in a dilute solution of sulfuric acid, and washed several times with distilled water.

#### 2.5. Characterization methods

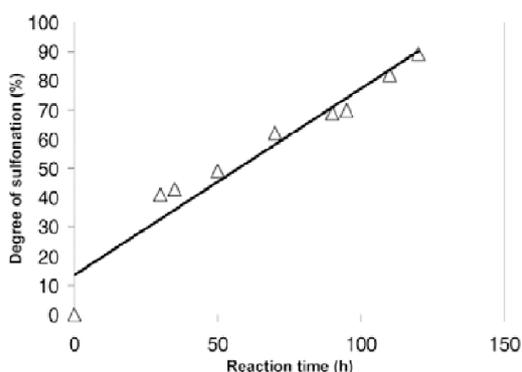
##### 2.5.1. Fourier transfer infrared

PEEK sulfonation was detected by FTIR spectroscopy (Nicolet-Magna 560). Scans for samples were recorded at a resolution of 2 cm<sup>-1</sup> over the wave number region 500-4000 cm<sup>-1</sup>. Samples were mixed with KBr grain spectroscopy grade and pressed into a disc by compaction.

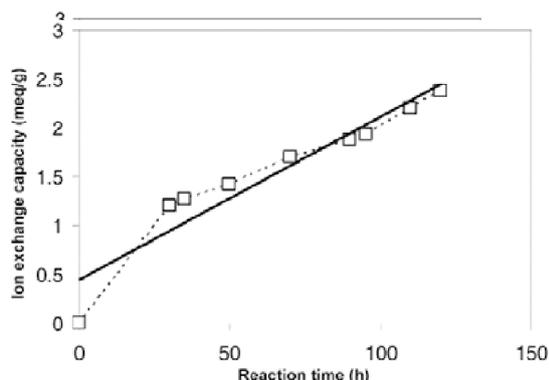
##### 2.5.2. Water uptake

Dried membranes were soaked in deionized water at room temperature, quickly weighed in different time intervals by carefully removing the excess water with filter papers and immersed back in the water tank. This process was repeated for several times until there was not any further weight gain. The water uptake was calculated from the following formula:

$$\text{Water uptake (\%)} = 100 \times (M_{\text{wet}} - M_{\text{dry}}) / M_{\text{dry}}$$



**Figure 4.** Degree of sulfonation as a function of reaction time.



**Figure 5.** Ion exchange capacity as a function of reaction time.

where  $M_{\text{wet}}$  and  $M_{\text{dry}}$  are the weight of wetted and dried membrane in grams.

### 2.5.3. Degree of sulfonation and ion exchange capacity

Dried samples were soaked in 50 ml of 0.01N sodium hydroxide solution for 12 h at room temperature. Ten ml of solution was titrated with 0.01N sulfuric acid. The samples were regenerated with 1M hydrochloric acid, washed with water and dried to a constant weight.

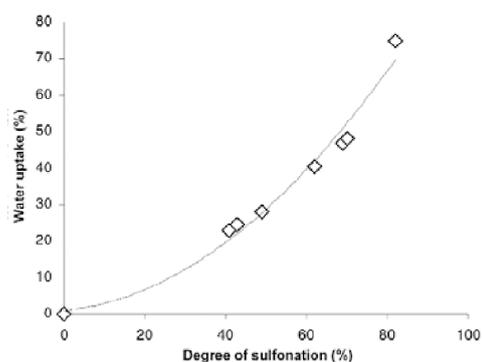
### 2.5.4. Actuation behavior

The bending behaviour of sulfonated PEEK membranes are characterized by applying a 0.1 Hz square wave at 4 volts electrical field. The collectors placed on the end of the actuators so the muscle has a one degree of freedom. The tip displacement of EAP is evaluated using a digital camera. The bending test performed at three times and the error bars are reported.

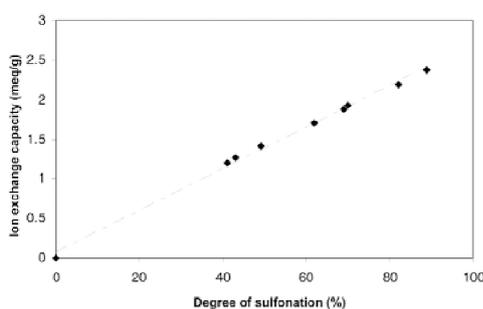
## 3. Results and discussion

The ionic polymers used in IPMC actuators are generally negatively charged, with this charge being balanced by unfixed ions. There are also pools of water, in which the mobile ions are dissolved. By applying an electric field to the control volume of actuator, the ions redistribute themselves, resulting in the

formation of two thin boundary layers a cation-poor layer on the anode side of the film and a cation-rich layer on the cathode side of it. The hydrated cations migrate to the cathode side of the IPMC and leading to the hydrophilic expansion. The strain in the cathode layer induces stresses in the rest of the polymer, resulting in a fast bending in direction of the anode [29]. After this immediate response, the hydrolytic pressure from the stretched macromolecular's chains causes water molecules to back diffuse from the cation rich regions, resulting in a time-consuming relaxation to the cathode side [29]. Reversing the applied potential inverts the bending and the subsequent relaxation. The degree of actuation exhibited is dependent on the type of polymer; the ion exchange capacity of polymer; the counter ion used, the thickness and the surface area of the polymer membrane; amount of absorbed water; the quality of electrodes and compatibility of electrodes with polymer surface [31]. Sulfonation is a common process for improvement of ion exchange capacity of polymers as well as water uptake. We have previously reported the procedure of PEEK sulfonation, the optimization of the sulfonation degree and the potential application of sulfonated PEEK as a proton exchange membrane for direct methanol fuel cells [22].



**Figure 6.** Water uptake of the membranes as a function of sulfonation degree.



**Figure 7.** Effect of degree of sulfonation on the ion-exchange capacity of sulfonated PEEK membranes.

FTIR spectra of the non-sulfonated and the sulfonated PEEK samples with 62% degree of substitution are shown in Figure 3. The reaction between benzene rings in PEEK and sulfuric acid molecules occurs through electrophilic aromatic substitution. The sulfonation process produces benzenesulfonic acid and water. The broad band in sulfonated PEEK samples is observed at  $3490\text{ cm}^{-1}$  which were assigned to O-H vibration from water molecules. Absorption band at  $1085$  and  $1100\text{-}1300\text{ cm}^{-1}$  (broad peak) in sulfonated PEEK was assigned to sulfur-oxygen S=O bonds [22].

As shown in Figures 4 and 5, by increasing reaction time with sulfuric acid, degree of sulfonation and ion-exchange capacity (IEC) are increasing to almost 90% and  $2.4\text{ (meq.g}^{-1}\text{)}$ , respectively. Introducing the sulfur groups in the PEEK structure reduce its crystallinity and increase its solubility. Degree of sulfonation of sulfur groups in PEEK alters its solubility from dissolution in hot DMAc (up to 40% sulfonation) to room temperature at up to 70% sulfonation. Above 70% sulfonation, PEEK degrades in hot water.

As seen in Figure 6, by increasing degree of sulfonation to 80%, water uptake is increasing to more than 75%. Water uptake or the ability of membrane to imbibe large amount of water enhance the ionic flow rate across the membranes.

The ratio of the mole number of water molecules to the fixed-charged sulfone groups, which is denoted as lambda ( $\lambda$ ), was obtained from following equation:

$$\lambda = \frac{\text{WU}}{\text{IEC} \times \text{M}_{\text{water}}}$$

where WU, IEC and  $\text{M}_{\text{water}}$  are the water uptake, ion exchange capacity and molecular weight of water for sulfonated PEEK, respectively. The average number of water molecules per fixed sulfonic acid ( $\lambda$ ) which shows that how many water molecules can be

bounded to the ionic side chain of sulfonated PEEK. The hydration of polyelectrolytes and the proton conduction in membranes are widely known as a critical issue and are often described as  $\lambda$ . Figure 7 shows the effect of degree of sulfonation on the ion-exchange capacity of sulfonated PEEK membranes. As shown,  $\lambda$  and IEC are increased by increasing the degree of sulfonation and reach to about 19 water molecules per sulfone group for PEEK with 82% of sulfonation. Sulfonation of PEEK samples opens up the hard to reach area of crystalline parts and thus accommodates more  $\text{H}_2\text{O}$  molecules [27]. By increasing concentration of sulfuric acid, sulfonation occurs more vigorously, and more water molecules form in the membrane. Cation mobility in the membranes is increasing with augmenting number of water molecules. The high  $\lambda$  as well as desirable ion exchange capacity at elevated sulfonation level, suggests that the water swollen in ionic domains of the membrane's pores is interconnected to form a network structure for rapid transportation of polar substrates. The lower actuation rate observed in the membranes with lower degree of sulfonation, may relate to the diffusion limitation caused by segregation in the ionic domains. When the sulfonation degree increased to a sufficient level, the ionic domains became more interconnected and simultaneously overcame the diffusion limitations and allowed the ionic diffusion to reach maximum value. According to these results sulfonated PEEK at 62% of sulfonation selected as an optimum degree of sulfonation because of good membrane processability and dimensional stability in aqueous environments. Membranes with greater degrees of sulfonation don't have good stability in aqueous environments for long periods of time.

After estimation the optimum degree of sulfonation, the actuation behavior of PEEK based artificial muscles at this composition is investigated. Figure 8 shows the tip displacement track of a sulfonated PEEK-

based IPMC actuating in response to a 0.1 Hz square wave at 4 volts. As seen in the displacement track, sulfonated PEEK-based IPMC has not rapid bending. But, the actuator moves in a linear fashion with displacement increasing by increasing the applied wave during the cycle. The slow displacement is may because of rigid microstructure of macromolecular backbone due to presence of aromatic rings. However, this stiff backbone showed the acceptable force during its actuation. Finally, we think that the aromatic based ionic polymers have great potentials as novel strong artificial muscles with low displacement for specific applications.

#### 4. Conclusion

In this paper the formation of a sulfonated poly(ether ether ketone) (PEEK) is described. Characterization of the sulfonated poly(ether ether ketone) shows that PEEK can be successfully modified using sulfuric acid with different degrees of sulfonation and the incorporated sulfonic acid functionalities aggregate during polymer modification. Afterward, the optimum degree of sulfonation determined according to processability, physical and chemical stability of membranes. The slow motion of this type of IPMC is may thanks to rigid microstructure of macromolecular backbone. However, this inflexible backbone showed the acceptable tip force during its actuation. These membranes are easy to prepare and much less expensive than the commercial per-fluorinated membranes such as Nafion<sup>®</sup>. Sulfonated PEEK membranes are suitable for IPMC's applications as novel strong muscles with low flexibility.

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