Ionic Polymer-Metal Composites Made from Radiation Grafted FEP-*g*-Styrene-SO_3H Membranes

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ABSTRACT: Ionic polymer-metal composites have been made from radiation grafted fluorinated ethylene propylene (FEP) membranes. Membranes have been synthesized by grafting of styrene on FEP films followed by sulfonation. These membranes were then used to fabricate IPMCs. Chemical plating of silver has been done to form the microelectrodes. Influence of degree of grafting on actuation, surface resistance, and tensile properties of the IPMC have been evaluated. It has been observed that on increasing the degree of grafting surface resistance, tensile strength, and elongation of IPMC decrease while degree of actuation and modulus increase. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2041–2046, 2008

Key words: ion exchange membrane; grafting; actuation

INTRODUCTION

Recent years have witnessed the development of electro-active polymers for various bio-medical and space applications.[1–3] Ionic polymer metal composite is one such electro-active polymer which has gained recognition as an actuator because of its excellent power to weight ratio and large relative displacement at a very low applied voltage ($\leq$5 V).[4–7] IPMCs have been called as "Soft actuators-sensors" or "Artificial muscles" by some researchers due to their long strain characteristics and electro-chemical-mechanical muscle like behavior.[8] A typical IPMC consists of a thin ion exchange membrane with metal electrodes (usually 5–10 μm thick) plated on both surfaces.

The basic mechanism of actuation of IPMC is well established.[4,8]When an IPMC in the solvated state (i.e., hydrated) is stimulated by a potential (1–5 V), mobile counter ions along with water molecules move towards the cathode due to electrostatic force. As a result the composite undergoes an initial fast bending. This is followed by slow relaxation, either in the same or in the opposite direction because the material strain is not maintained within the actuator. This depends on the composition of the backbone polymer and nature of the counter cation.[9,10]

The most popular ion exchange membrane used for manufacturing an IPMC is Nafion,[9,11] because the large fluorinated polymer backbone provides mechanical strength whereas the short side chains help in ion transport. Shahinpoor and Kim[9] has done a detailed analysis of IPMC using Nafion membranes. They reported excellent performance of these IPMCs and have demonstrated several applications for the same.[12] Several other commercial ion exchange membranes which are used include Flemion^{TM} from Ashai glass (Japan), Aciplex^{TM} from Ashai chemicals, and Neosepta^{TM} from Tokuyama.[9,10,13] Also some studies suggest the use of radiation grafted ion exchange membranes for manufacturing IPMCs.[14]

The electrode layer is made by electrochemical plating of noble metals like platinum, gold, silver, palladium etc.[9] The process of electrochemical plating involves two steps: (1) initial compositing process where the metal to be deposited is first allowed to exchange with the membrane and then reduced using a strong reducing agent like sodium borohydride or lithium borohydride; (2) surface electroding process is to grow the metal on top of the initial coated layer to reduce the surface resistance.

IPMCs made from Nafion and Flemion membranes have been studied elaborately.[4,8–10] Influence of various parameters like anisotropic roughening, number of coating cycles concerning actuation has been studied extensively.[15] Jho and coworkers[14] reported the fabrication of IPMC using radiation grafted membranes. This study was carried out to explore new possibilities for IPMC development with controlled displacement and speed of actuation. They have reported grafting of styrene on different fluoropolymers (PVDF-*co*-HFP, PE-*co*-TFE and). It was found that IPMCs made from PVDF-*co*-HFP and PE-*co*-TFE exhibit better displacement when

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compared with those made from PTFE-*co*-TFE. This has been explained based on the structure of the fluoropolymers. According to their study grafting onto PTFE-*co*-TFE is not uniform because of lower crystallinity. But in our earlier study on fluorinated ethylene propylene (FEP) membranes, we have found that a uniform distribution of grafted and sulfonated chains throughout the entire membrane is achieved at a grafting level of about 23%.[16] Also the effect of degree of grafting on actuation has not been reported. Hence, we have taken up this study to determine the effect of degree of grafting on factors governing the actuation of IPMC. The membranes were anisotropically roughened, and secondary coating of silver was carried out to achieve better actuation.

EXPERIMENTAL

Materials

FEP film with 125 μm thickness was purchased from DuPont. It was washed with acetone and dried in oven at 50°C before irradiation. Styrene (Fluka) was washed with 5% NaOH to remove inhibitor (4-*tert*-butylcatechol) and finally with distilled water. Styrene was then distilled at 60°C under reduced pressure. Chlorosulfonic acid (AR grade) obtained from S.D fine chemicals (India) was used as a sulfonating agent to sulfonate the grafted films.

Silver nitrate ($AgNO_3$), hydroxylamine hydrochloride, and hydrazine hydrate were purchased from Qualigens (India). Ammonia solution used for forming the silver complex was purchased from RANKEM (India). Sodium boro hydride ($NaBH_4$) was purchased from Merck-schuchardt, Germany.

Grafting procedure

Simultaneous radiation grafting was used in this case. Procedure for grafting and sulfonation has been mentioned elsewhere.[17]

Fabrication of Ipmc

Anisotropic roughening across the length of the IPMC film was done using 600-silicone carbide paper. This kind of roughening was done to create a preferred bending response. A detailed study on directional roughening was carried out by Stoimenov et al.[15] They report that anisotropic roughening across the length improves the bending response of the actuator by a factor of 2.1.

The roughened membranes were washed by boiling in 2.5*M* aqueous HCl for about 1/2 an hour. Further, they were boiled in deionized water till free from acid. These pretreated membranes were then immersed in a 0.05*M* Ag $(NH_3)_2Cl_2$ solution. Ion exchange process was carried out at 60°C with constant stirring. The process time is generally 60–90 min. The membranes were then taken out from the complex solution and immersed in 100-mL deionized water. To this 5% aqueous sodium borohydride solution was added drop wise at 60°C with constant stirring. A black layer of silver metal deposited on the surface of the membrane. The final step involves growing of silver metal on top of the initial silver layer. The primary coated membrane was placed in the Ag complex solution under stirring at 40°C. To this, 6-mL hydroxylamine hydrochloride and 3 mL of the hydrazine hydrate solution are added at an interval of 30 min. The temperature was increased gradually up to 60°C over a period of 4 h. Finally, a small amount of the solution was withdrawn and boiled with sodium borohydride ($NaBH_4$) solution to check the end point. This method of coating is adopted from the process developed by Shahinpoor and Kim.[9] The membranes obtained had a thickness of about 200–240 μm. Then the membranes were kept in 5% solution of lithium chloride for exchange and finally in deionized water for hydration.

Scanning electron microscopy analysis (SEM)

The surface topography and depth profile of the IPMC samples was studied by using scanning electron microscope LEO 1450 scanning electron microscopy analysis (SEM) instrument. The deposition of silver on to the surface of the membrane and the thickness of the silver layer was investigated. The beam was operated at 10 kV. The working distance was kept at 15 mm and the analysis was carried out using RBSD (Robinson back scattered detector) with atomic number constant feature.

Surface resistance measurement

The surface resistance of membranes was measured along the length (in plane direction) of the membranes by using Keihtley digital multimeter. Two leads connected to this multimeter were placed one-centimeter apart on the surface of the membrane, and the resistance was measured.

Modulus measurement

Tensile modulus was measured using Hounsfield 50-KS universal testing machine. The test samples were cut into strips of length 10 cm and width 1 cm with a standard die. Before the test, membranes were kept in deionized water for complete hydration. Although mounting the sample in the clamp, the surface of the IPMC films was wiped with absorbent paper. The measurements were done in atmospheric condition. The gauge length was 30 mm with a load range of 500 N. The tensile modulus was calculated from stress–strain curve.

Actuation

IPMC samples prepared from membranes with varying degree of grafting were chosen and actuation of these samples was studied. Strips of size 5 cm × 1cm were placed between two platinum electrodes and potential ranging from 0.3 V to 1 V was applied using Autolab PGSTAT30 in GPES mode. The angle of actuation was determined using a protractor placed behind the sample as shown in Figure 1.

RESULTS AND DISCUSSION

In the present study, we have developed IPMCs using radiation grafted FEP membranes. Three different membranes have been used for IPMC fabrication, with degree of grafting of 11, 23, and 47%. The corresponding sulfonated membranes have ion exchange capacity (IEC) of 1.2, 1.7, and 2.3 meq/g, respectively. The method of determination of IEC has been reported in our earlier studies.[17] The sulfonated membranes have been coated with silver by electrochemical deposition method. Resultant IPMCs have been characterized in terms of surface resistance, tensile properties, and actuation.

Scanning electron microscopy analysis

One of the important parameters governing the actuation of IPMC is the thickness and uniformity of the electrode layer. These parameters can be studied by observing the cross-sectional micrographs of IPMC.

Our earlier SEM study on FEP-*g*-styrene-*co*-acrylic acid membranes[16] has shown that the process of grafting follows the "front mechanism" where grafting starts at the surface and slowly progresses inwards. Thus at lower degree of grafting, the inner core of the membrane remains ungrafted. We have found that through–through grafting can be achieved at a grafting level of almost 18–20%. This strongly reflects on the performance of the IPMC as will be explained later.

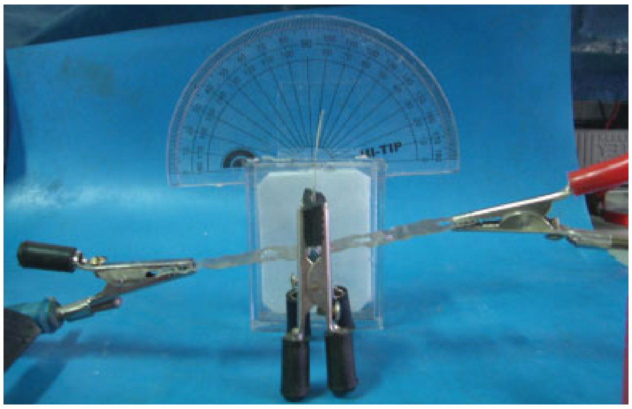


Figure 1 Experimental setup to measure degree of actuation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

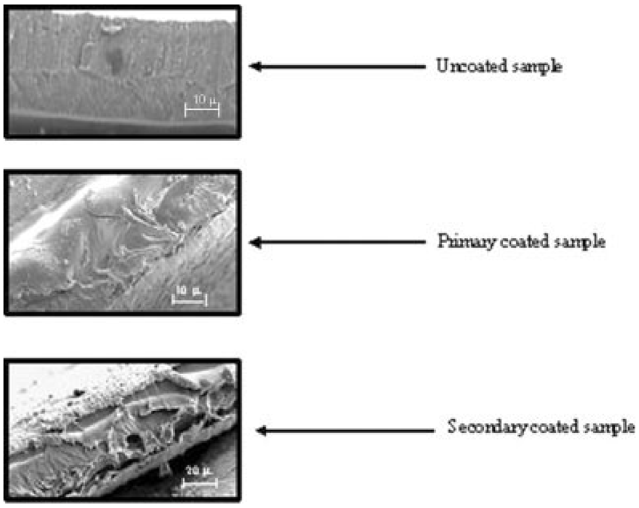


Figure 2 SEM micrographs of uncoated, primary coated, and secondary coated samples.

SEM micrographs of sulfonated FEP-*g*-Sty uncoated, primary coated with Ag and secondary coated with Ag membranes are shown in Figure 2. From Figure 2, it is seen that a uniform layer of silver metal is present on either side of the membrane. Furthermore, the thickness of the electrode deposited was found to be influenced by the degree of grafting. The thickness of the primary electrode layer varied monotonously from 5 to 7.2 μ whereas that of the secondary layer was 10–13 μ as the degree of grafting increases from 11 to 47%. This is due to the increase in number of ionic sites at higher degree of grafting, which are available for exchange during deposition of metal electrode layer.

Surface resistance measurements

Surface resistance is one of the key parameters, which influences the performance of IPMC. IPMC with low surface resistance exhibits large bending displacement.[18] Surface resistance can be decreased by increasing the number of coating cycles during the manufacture of IPMC.[9,11]

In the present study, secondary coating of silver has been carried out to decrease the surface resistance. Surface resistance of primary coated and secondary coated sulfonated FEP-*g*-ST membranes with various degrees of grafting samples has been measured using digital multimeter. The variation of surface resistance of primary and secondary coated films with degree of grafting is shown in Figure 3.

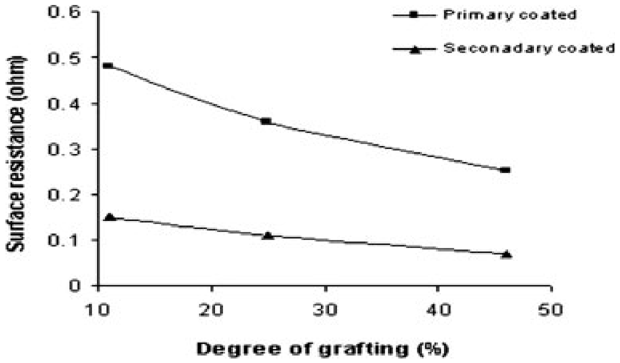


Figure 3 Plot of surface resistance versus degree of grafting.

It is seen from the figure that on secondary coating, the surface resistance decreases to 1/4th of the value for primary coating. This is because, on secondary coating more amount of silver gets deposited on top of the initial silver layer, leading to reduction in the surface resistance. This is evident from the SEM photographs of the primary and secondary coated samples. This can be seen from Figure 4 that the percentage of micro-cracks that are present on the primary coated electrode reduce on secondary coating, leading to decrease in surface resistance. Similar observations have been reported by many researchers for the other systems.[9,19]

Also surface resistance for the coated films decreases with increasing the degree of grafting. This is attributed to the fact that as the degree of grafting increases the number of ionic sites available for exchange with the metal during initial compositing process increase, resulting in more amount of silver coating on the surface of the membrane.

Tensile properties

The tensile properties of uncoated and coated sulfonated FEP-*g*-styrene membranes with different degree of grafting were determined. All the samples were tested under wet conditions because the final application involves use of IPMC in hydrated state.

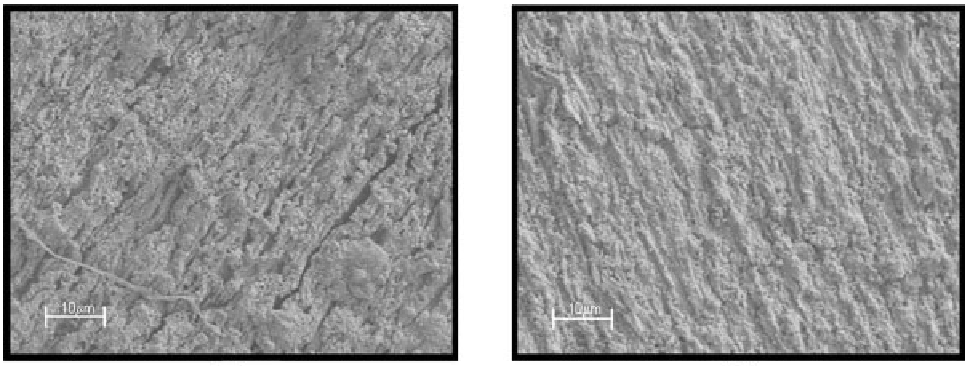
The modulus, tensile strength, and percent of elongation values are provided in Table I. It is seen from the Table I that on coating the ion exchange membrane, the modulus increases whereas the tensile strength and elongation decrease. Increase in modulus on coating is due to the introduction of stiffer metallic layer on the polymer membrane. Shahinpoor and Kim report similar observation for IPMC made from Nafion membranes.[9] Further, introduction of amorphous polystyrene into the base polymer matrix results in decrease in crystallinity leading to decrease in tensile strength. This also reduces interchain interaction leading to decrease in tensile strength and elongation. This decrease is further pronounced as the degree of grafting increases due to increase in the amount of grafted chains.

Also it is seen from the table that as the degree of grafting increases the stiffness decreases. This is because of increase in water uptake with increase in number of styrene sulfonated moieties in the membrane. However, because the membrane has a phase separated morphology due to the presence of sulfonated styrene domains, the increase in water uptake does not lead to increase in elongation at break. Sia and Zamani.[13] also report decrease in stiffness with increase in volume uptake of water and ethylene glycol for IPMC made from Nafion and Flemion membranes.

Stiffness of IPMCs depends on the thickness of metal coating. IPMC with higher stiffness requires greater force for actuation. Thus it is necessary to optimize the thickness of the coated metal layer to obtain an IPMC with better actuation.

Actuation

The most significant property of an IPMC is its actuation behavior under low electrical step



(a) (b)

Figure 4 SEM micrographs of (a) primary coated (b) secondary coated samples.

TABLE I
Tensile Strength, Modulus and Percent of Elongation Values of Sulfonated FEP-*g*-ST Uncoated, Coated Membranes

Degree of grafting (%)	Tensile strength (MPa)		Modulus (MPa)		Elongation (%)	
FEP film	20		482		350	
	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated
11	12.4	10.6	139.8	171.5	71.4	44.1
25	10.3	7.8	104	152	66	38.4
32	8.5	5.7	85	146	61	33.1
46	7.5	3.65	55.3	138.4	54	28.3

voltages. Actuation of IPMC mainly depends upon the type of ion exchange membrane used, the thickness of electrode, the type of counter ion, surface resistance etc. In this article, we discuss the actuation of IPMC with lithium as the counter ion.

When voltage was applied across the IPMC film, bending was observed towards anode. The angle of displacement increases from 10° to 90° with increase in voltage from 0.3 V to 1 V. A plot of initiation voltage verses degree of grafting in presented in Figure 5. The initiation of actuation has been observed at a voltage as low as 0.3 V for membrane with 46% degree of grafting while that for 11% degree of grating the initiation voltage required is 0.9 V. IPMC made from membranes with higher degree of grafting exhibit greater displacement because the ionic groups are uniformly distributed through out the matrix of the membrane. Although at lower degree of grafting, the distribution of ionic groups throughout the polymer matrix is not uniform and less number of groups are available for the transport of hydrated ions. Thus greater force is required to bend such IPMCs. However, the maximum voltage required to actuate these IPMCs is not more than 1 V, which is lower than the voltage for electrolysis of water.

Response time and average velocity of IPMC actuation to achieve a deflection of 50° for each sample is shown in Table II. It is clearly seen that as the degree of grafting increases the time required to bend the sample under an applied DC electric field decreases. This is again explained in terms of number and distribution of ionic groups present in the polymer matrix.

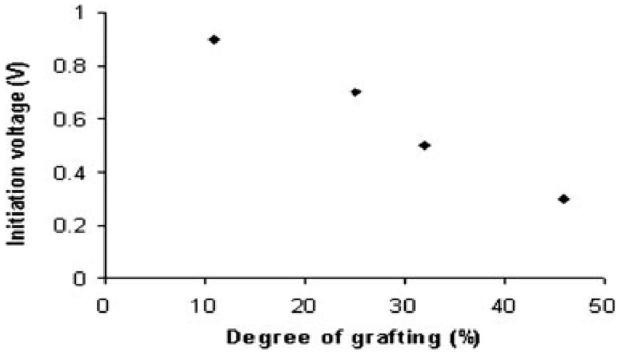


Figure 5 Plot of initiation voltage versus degree of grafting.

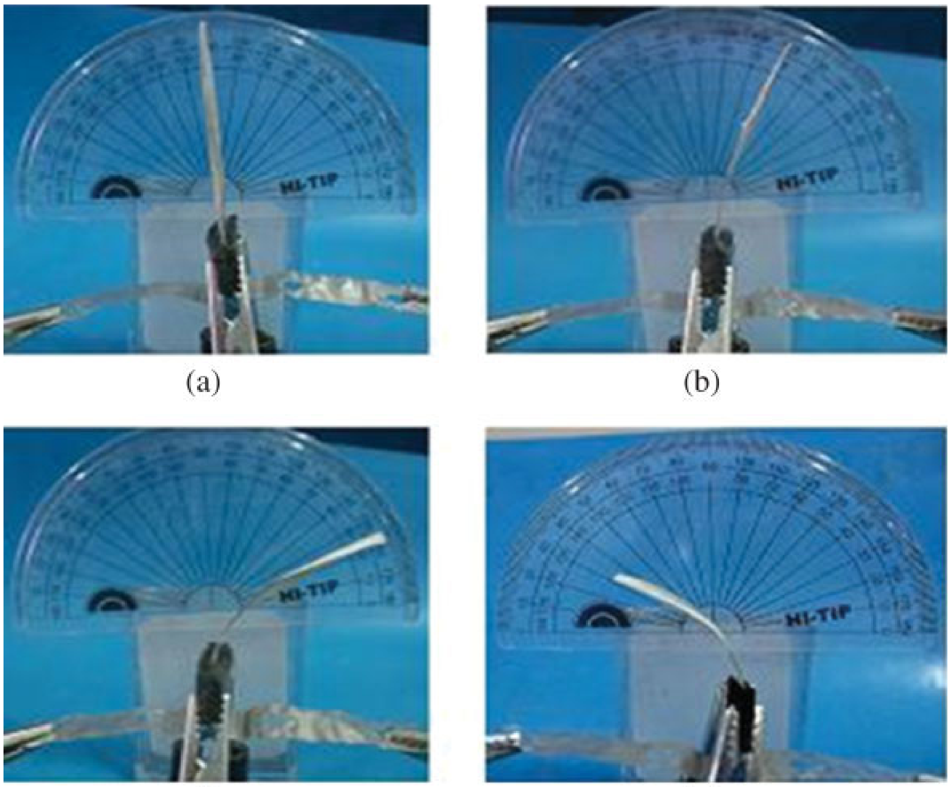
Figure 6 shows the actuation of IPMC made from membrane with 32% degree of grafting. The bending response of sulfonated FEP-*g*-ST IPMC initially starts with slow motion towards the anode. As the time increases the IPMC bends further towards the anode until a saturation level is reached (angle of displacement 70°). Upon removal of the electric field the IPMC slowly retracts back to a steady state position. This takes place because as the IPMC bends towards the anode, concentration and pressure gradients are setup within the polymer membrane. On removal of the electric field these gradients facilitate the movement of water molecules and free cations back towards their neutral positions, causing relaxation.

CONCLUSIONS

IPMCs were manufactured from radiation grafted membranes by the chemical plating method. The results suggest that the actuation of IPMC is strongly dependent on the degree of grafting of the base membranes, surface resistance of the electrode layer, and mechanical properties. From this study, it can be seen that IPMC made from radiation grafted membranes operate at lower voltages (0.3–1 V). IPMC made from 46% grafted membrane exhibits actuation at 0.3 V. Thus by optimizing the degree of grafting and the surface electroplating process, IPMC with tailor made

TABLE II
Response Time and Average Velocity of IPMCs with Different Degree of Grafting

Degree of grafting (%)	Response time (s)	Avg. velocity (bending) (°/s)	Avg. velocity (relaxation) (°/s)
11	11	4.55	3.1
25	8	6.25	5
32	5	10	7.6
46	3	16.7	12



(a) (b)

(c) (d)

Figure 6 Actuation of 32% grafted membranes. (a) IPMC before application of voltage, (b) Initial bending on application of low voltage, (c) Saturation level of bending reached, (d) Response on reversing the polarity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

properties can be achieved. They can be designed to be used for a variety of applications such as mechanical grippers, biomedical devices, artificial fingers, etc. Because they exhibit better performance when compared with conventional membranes.

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