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LETTER

Investigation on thermo-mechanical behaviors of artificial muscle films

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Introduction

A recently presented model by de Gennes et al. [1] described the underlying principle of electro-thermo-dynamics in ionic polymers based on internal transport phenomena and electrophoresis. Ionic polymer metal composites (IPMCs) show a great potential as soft robotic actuators, artificial muscles, and dynamic sensors in the micro-to-macro scale [2]. Its performance is expected to greatly exceed the conventional actuators such as shape memory alloys and piezoelectrics. However, practical gel actuators have not been developed yet primarily because most of hydrogels matrix stiffness is quite weak [3] and their shape or volume change sensitivity to applied voltage is so low. Although a polyvinyl alcohol gel swollen with dimethyl sulfoxide has a relatively stiff matrix and exhibits a fast shape changing upon applied voltage, the improvement of its matrix stiffness is still necessary and higher voltage bearing-capacity than several hundred volts is also required [4]. Nafion, which has a relatively stiff matrix, was found to exhibit a fast self-bending upon a small applied voltage around 1 V or less. Investigations have been performed to develop practical actuators made by such ionic polymer-metal composite [5, 6]. Extensive works have been done on Nafion-based IPMC, including optimization of its mechanical properties and working stability [7, 8], some excellent results on modeling of IPMC with water have also been reported [9–12]. However, few works have been done on another important application such as an artificial muscle or artificial skin as well as biosensor etc. In this work, the precise measured mechanical properties and coefficients of thermal expansion (CTEs) for two typical films, matrix-Nafion117 film and $[Pt(NH_3)_4]^+$-added matrix-Nafion117 film, were reported.

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Materials

The Nafion117 film as a matrix used in this work came from DuPont Company. The Nafion117 film was soaked in $[Pt(NH_3)_4]Cl_2$ solution then chemically reduced to ionic polymer metal composite by a $NaBH_4$ to obtain more metal Pt particles on its surface. Then a new ionic polymer-metal composite (IPMC) film was obtained [2]. The measurement and analysis of the thermo-mechanical properties of these films were carried out.

Experimental methods

All the samples of films were kept in water prior to uniaxial tensile tests. Therefore, all samples have a relative humidity during the uniaxial tensile tests. The uniaxial tensile tests were carried out by the shape and size of 80 × 5×0.2 mm, which is based on the ASTME8M-006 criterion. The effective tests were that the fractures of films occurred near the middle part of sample. The measurement of deformation was calculated based on the digital image correlation (DIC) method under different stresses [13–16]. DIC is a technique for measuring surface displacements or deformations value based on the matching pixel gray level values between two digital images, which were taken at the different loadings. This is accomplished by capturing two digitized images of a random speckle pattern representing two different deformed states. For the randomization of the speckles, subsets comprising a wide variation in gray levels are more uniquely identifiable than individual pixels. According to the statistical principle of the correlation, measurements of each pixel deformation on the surface as shown in Fig. 1a and b can be accomplished by virtue of determining the movement of the central point of subset. These pixel distributions responded to the different deforming extents of film surface. At the same time, the change extent of pixel lines in Fig. 1b is larger that in Fig. 1a, especially in Y direction, which is defined as the vertical loading direction. This phenomenon hints that there may be a difference between the Poisson's ratios of these two typical films. The uniaxial tensile rate is 2 mm min^{-1}.

Simultaneous thermal analyzer was performed using ZRY-2P with 30 mL min^{-1} nitrogen flow at a heating rate of 10 °C min^{-1}, uncovered Al_2O_3 crucible was used as sample container. Thermal expansion data were collected on film's surface by thermal mechanical analysis (TMA Q400, TA-Instruments) using a macro-expansion quartz probe. These data were collected with a heating rate of 3 °C min^{-1} from room temperature to 300 °C when the film was under tensile stress about 0.1 MPa. Calibration of the instrument was performed using an aluminum standard.

Results and discussions

Mechanical properties

Compared with the deformation data within applied stress of 3–6 MPa as shown in Fig. 1a and b, the deformation degree of Nafin117 is greater than that of typical IPMC so that the stiffness of IPMC has been improved. Figure 2 shows the normal stress versus displacement curves of two films. These curves indicated that the elastic deformation of two typical films was in the range 3–6 MPa and the fracture toughness of matrix-Nafion117 film is obviously higher than that of IPMC. This is because Pt particles deposited on the matrix-Nafion117 film's surface strongly restricted the surface deformation of ionic polymer (Nafion117) and formed a sandwich structure section in micro scale, in which the stiffness in metal layer is higher than that in the meat of IPMC [17–19]. The metal layer microstructure and size of IPMC is similar to the result reported in reference [2] based on the SEM and TEM measurements, where the surface is characterized by the grains approximately 50 nm. This granular nano-roughness

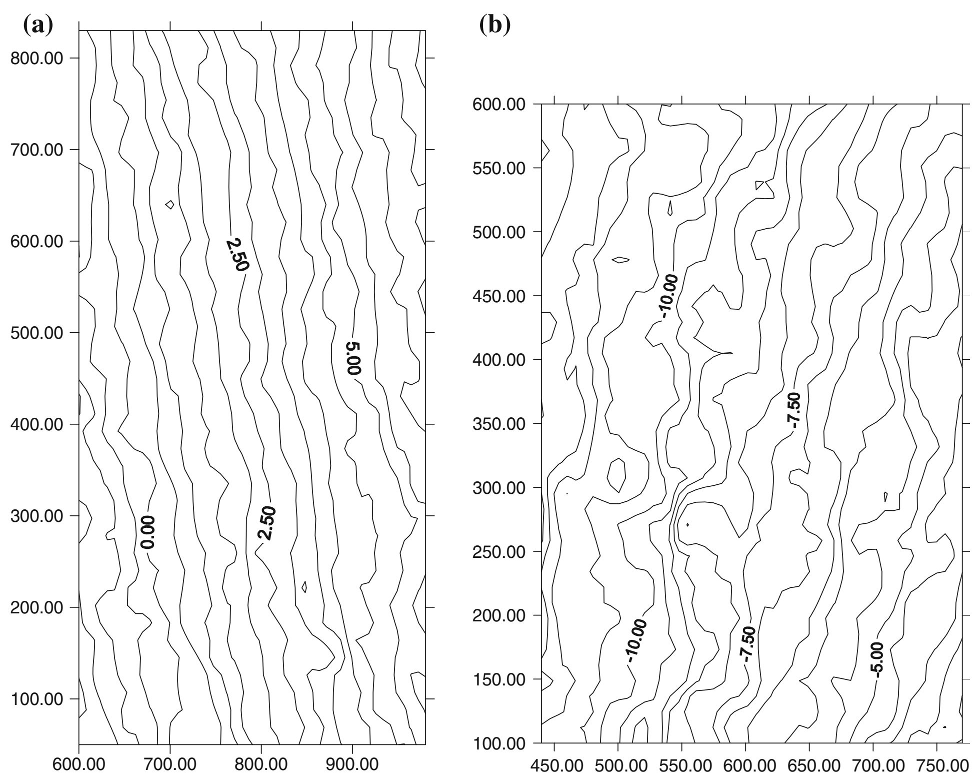

Fig. 1 Pixels distribution diagrams at different stress states in 2D. (**a**) $\sigma = 6$ MPa, $[Pt(NH_3)_4]^+$-added Nafion117 film; (**b**) $\sigma = 3$ MPa, Nafion117 film

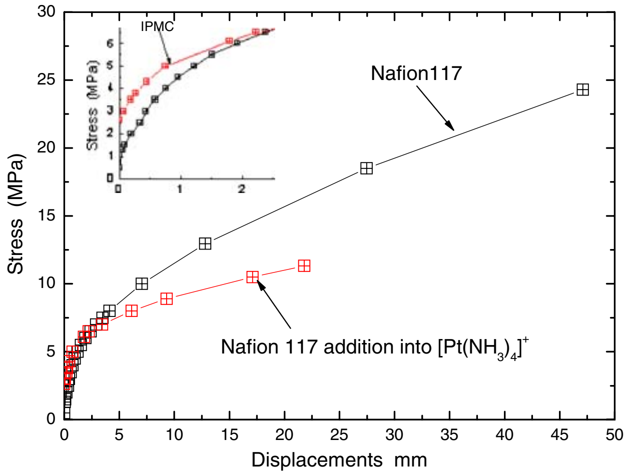

Fig. 2 Stress versus displacement curves of two typical films

is responsible for producing a high level of electric resistance, yet provides a porous layer that allows water to move in and out of the membrane. However, these strength results of two typical films (both stiffness and the modulus of elasticity) are different from the reported results in reference [2]. The reason causing the difference is mainly dependent on the effects of different measurement methods of deformation and loading types. The present work directly measured the deformation of the films under the uniaxial tension. However, the results in reference [2] were based on the estimated radius of curvature and bending moment. The harder out-layer related to the meat of IPMC plays an important role during bending deformation when the thickness of film is less than 0.2 mm. Therefore, the strength data in this work are more reliable than the data reported in the previous work [2].

Figure 3 summarized the curves of both modulus of elasticity E and Poisson's ratio μ compared with the two films. The Young's modulus is defined as the slope of the curves as shown in Fig. 3a. When the $[Pt(NH_3)_4]^+$ is added into matrix-Nafion117 film, the modulus of elasticity can be improved from 166 MPa to 232 MPa. Another important mechanical property of the film, such as Poisson's ratio μ, indicates the linear elastic deformation ratio of the lateral strain to longitudinal strain of this film. The effect of addition of $[Pt(NH_3)^4]^+$ into matrix-Nafion117 on the difference of Poisson's ratio is relatively small in the two typical films as shown in Fig. 3b, in which the slopes of curves are 0.163 and 0.181, respectively. For either modulus of elasticity or Poisson's ratio of these films, these differences indicate the effects of addition of $[Pt(NH_3)^4]^+$ into matrix-Nafion117 on their stiffness in mechanics view. In addition, an addition of $[Pt(NH_3)^4]^+$ into matrix-Nafion117 could induce the nonlinear characteristics of electromechanical properties of the IPMC. These features will be discussed in detail in upcoming review papers.

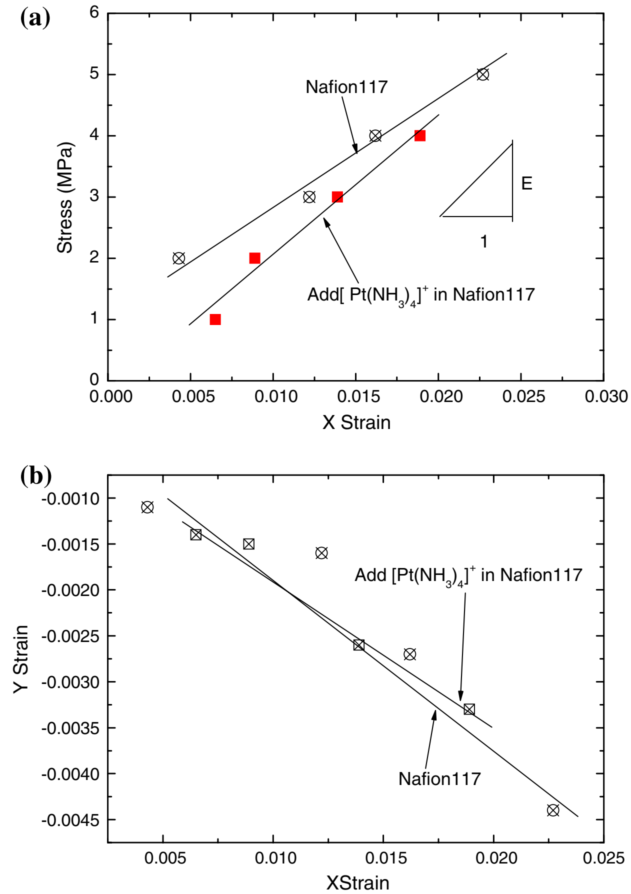

Fig. 3 Elastic modulus and Poisson's ratio curves of two typical films. (**a**) Elastic modulus curves, (**b**) Poisson's ratio curves

Thermal properties

Figure 4 shows the CTEs of two typical films, which are the IPMC film and the matrix-Nafion117 film, respectively. The addition of $[Pt(NH_3)_4]^+$ influences not only the mechanical properties but also the CTE of the polymer film. The measured results of CTEs indicate that there are two flat values of CTE from room temperature to 300 °C for IPMC film, which are the steady values of -100×10^{-5} °C^{-1} and 40×10^{-5} °C^{-1}, respectively. It is interesting to find that the CTEs show a negative value from 50 °C to 100 °C and a positive value from 160 °C to 250 °C, respectively. It is a precarious range from 100 °C to 150 °C. Compared with the CTEs of IPMC film at different temperatures, they have the fully opposite thermal response. As the artificial muscles IPMC film in actual application, it fully exhibits biomaterial property responding to temperature such that it will shrink when the temperature is lower than 100 °C, and it will be scalded by the sudden expansion when the temperature is over 100 °C, especially over 160 °C. In addition, the moisture in the surface IPMC film will be vaporized if the temperature is

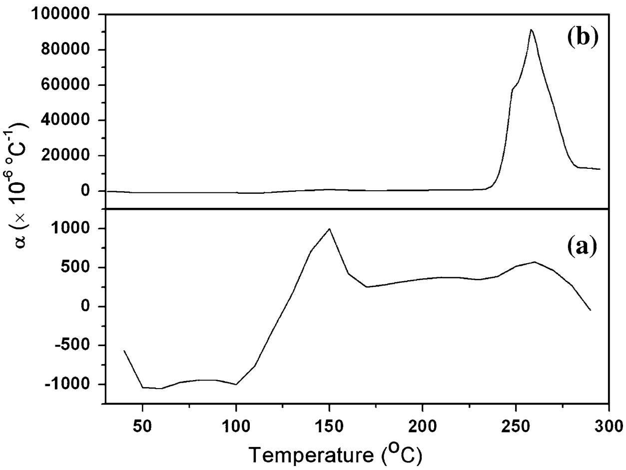

Fig. 4 CTE (α) curves of two typical films. (**a**) α vs. *T* curve of IPMC film, (**b**) α vs. *T* curve of Nafion117 film

over 100 °C so that the main contribution of out-layer $[Pt(NH_3)_4]^+$ will be weaken when the temperature is over 100 °C. Therefore, the CTE over 100 °C can be as a result of damage threshold value. At the same time, the thermal expansion property could result in the bending deformation after applied lower voltage in the previously reported works [2, 4, 7, 10–12]. And the bending deformation was induced by shrinking of the film. The CTE is higher than some traditional polymers such as carbon-graphite fiber-reinforced polymer [20–23]. Therefore, their shape or volume change sensitivity to applied voltage exhibits differences. However, the CTE of matrix film (Nafion117) is similar to that of some traditional polymer film from room temperature to 100 °C (or 240 °C), which is about 200×10^{-5} °C^{-1}. And the CTE of IPMC film depends strongly on the temperature range. Therefore, according to the positive and negative values of CTEs at different temperatures, the deformation mode of IPMC film can be predicated. However, even now, the effects of temperature on the linear thermal expansion mechanism of IPMC film and the effective factors/terms are still not clear. It might refer to the electrochemistry and electromechanical coupled effects.

Conclusions

In this work, the CTEs and mechanical properties of two typical polymer films, which are the matrix film of Nafion117 and $[Pt(NH_3)_4]^+$-added matrix film, were investigated. The following conclusions were obtained:

1. The mechanical properties of two typical films indicate that the addition of $[Pt(NH_3)_4]^+$ into Nafion117 matrix can greatly enhance the stiffness of the film and slightly reduce its lateral deformation capability. The main reason could be the effect of the nonlinear characteristics of electromechanical properties of the IPMC.
2. Compared with the modulus of elasticity reported in previous works, the effect of loading types cannot be ignored. The reason could be that the out-layer of addition metal into matrix formed a sandwich structure of film in microscopic view. This sandwich structure could induce the stress gradient in the bending loading, but have no or less effect in uniaxial tension. Therefore, considering the mechanical properties of material and structure, the mechanical properties of IPMC film should be determined by the uniaxial/biaxial tensile tests.
3. The CTE indicates that the parameter of IPMC depends strongly on the temperature. When the temperature is less than 100 °C, the CTE of IPMC is a negative value, while it is a positive value if the temperature is over 100 °C. Hence, the IPMC can be used as an artificial muscle or skin material. In addition, according to the positive and negative values of CTE at different temperatures, the deformation mode of IPMC film can be predicated when it is used in soft robotic actuators and dynamic sensors.

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