Electromechanical properties of Electroactive Polythiophene/Elastomer Blend

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Abstract – The conductive polythiophene/dielectric elastomer blend was prepared in this research for used as electroactive actuator applications. The poly(dimethyl siloxane) (PDMS) dielectric elastomer was chosen as an elastomer matrix. Conductive polythiophene (PTh) was synthesized via oxidative polymerization in chloroform at 40 °C and then the blend was prepared by mechanical blending of fine PTh particles in PDMS fluid. The specified amount of crosslinking agent; tetraethyl orthosilicate, and catalyst; dibutyltin dilaurate, were added. After that, the electromechanical properties were measured by bending response testing. The effects of polythiophene particle concentration (0-15 vol. %) and electric field strength (0-1 kV/mm) with ratio of crosslinking agent:PDMS of 10, 15, 20 vol. % were studied. The results showed that pure PDMS and PTh/PDMS blends response well to an applied electric field. The bending angle response appears to increase with increasing of polythiophene particle concentration up to 5%v/v. and the bending angle increases stepwise under electric field strength. However, the bending angle decreases with increasing ratio of crosslinking agent:PDMS.

Keywords: Electromechanical, Conductive polymer, Dielectric elastomer, Polythiophene, PDMS
1. Introduction

Electroactive polymers (EAPs) are polymer materials that change their shape or size in response to electrical stimuli. This class of materials is therefore a good candidate for actuators in the field of medical devices, soft manipulators and biomimetics, since they mimic the behavior of biological muscles/insect-like actuators and robotic parts [1]. Various materials have been made as actuator: sharp memory alloys (SMA) and electroactive ceramics. However, these materials have limit in terms of weight and ability to change size or sharp. Dielectric elastomers are a type of electric-field-activated electroactive polymers that are capable of producing large strains, fast response, and high efficiency [2]. Currently, the combination of dielectric elastomer with conductive polymer has been interested in many applications such as poly(3-thiopheneacetic acid)/acrylonitrile-butadiene rubber blends [3] and polythiophene/polyisoprene elastomer blends for an artificial muscle application [4]. Conductive polymers are alternative to produce for actuators instead of a metallic material. The conductive polymers have many advantages over other materials such as low cost, relatively simple fabrication, light weight and combine the mechanical properties (flexibility, toughness, elasticity, malleability, etc.) of plastics with high electrical conductivities [5-7].

In this study, we interested to develop and testing the polythiophene/poly(dimethyl siloxane) blend towards electroactive actuator applications. The electromechanical properties of the blends are investigated in term of amount of crosslinking agent, polythiophene particle concentration and electric field strength.

2. Experimental

2.1. Materials

Thiophene, C₄H₄S (AR grade, Fluka) was used as the monomer. Iron (III) chloride anhydrous, FeCl₃ (AR grade, Carlo Erba) was used as the oxidant. Chloroform, CHCl₃ (AR grade, labscan Asia) and methanol, CH₃OH (AR grade, J.T. baker) were used as received. Hydroxyl terminated poly (dimethylsiloxane), OH-[Si(CH₃)₂O]ₙ-H (viscosity 3,500 cSt, Aldrich) was used as a elastomeric matrix. Tetraethyl orthosilicate (TEOS), Si (OC₂H₅)₄ (AR grade, Aldrich) and dibutyltin dilaurate (2EHSn), [CH₃ (CH₂)₃OCO]₂Sn[CH₂]₃CH₃]₂ (AR grade, Aldrich) were used as a crosslinking agent and a catalyst, respectively.

2.2. Synthesis of polythiophene (PTh)

Polythiophene was synthesized via chemical oxidative polymerization [8]. FeCl₃ anhydrous was added to chloroform and the mixture was stirred and heat at 40 °C. Thiophene monomer was added to chloroform and then added dropwise to the FeCl₃ solution with continuous stirring at room temperature for 3 hours. After all the thiophene monomer solution was added, the reaction mixture was continuity stirred at 40 °C for 9.5 hours and the reaction was stopped by adding methanol to the reaction mixture and stirred for 1.5 hour. Polythiophene particles were filtered and dried in vacuum oven at 27 °C for 24 hours. The synthesized polythiophene was grinded, screened and then characterized by via Fourier transform spectroscopy, scanning electron microscope (JEOL, JSM-5910LV) and particle size analyzer (Malvern, Masterizer).

2.3. Preparation of PTh/PDMS blend

The PTh/PDMS blend films were prepared according to the method of W. Wichiansee [2]. Polythiophene particles were mixed with PDMS, 2EHSn and TEOS the amount of TEOS was varied as 10, 15 and 20 vol.% (PDMS_10, PDMS_15 and PDMS_20). The mixture was poured in a mold and allowed to cure under vacuum for 24 hours. The volume fraction of polythiophene particle was varied as 5, 10 and 15 vol. % (5%PTh, 10%PTh, and 15%PTh).

2.4. Electromechanical properties measurement

The electromechanical properties of the PTh/PDMS blend were investigated in the way of the bending response. The experimental setup was showed in “Fig.1”. The samples were vertically immersed in silicon oil (viscosity=100 CSt) with a dc electric field applied between two copper electrodes (30 mm long, 30 mm wide, and 1.0 mm in thickness; the distance between the electrodes is 30 mm). All of experiments were recorded by video camera and the amount of deflection bending angle (θ) was calculated from the following equation,

\[ \theta = \arctan \left( \frac{A}{B} \right) \]  

where A and B are the measured deflection distance and the sample length, respectively which were detected by Engauge Digitizer (4.1) program.

![Fig. 1. Schematic diagram of the apparatus used to observe the bending response.](ms007-2)
3. Results and Discussion

3.1. Characterization of polythiophene

From the FTIR spectroscopy, the synthesized polythiophene shown characteristic peaks at 787, 1219, 1367 and 1739 cm⁻¹ which correspond to C-C bending vibration, C-C stretching vibration of α-coupled thiophene, C-H stretching vibration and C=C stretching vibration of thiophene ring, respectively. From “Fig. 2”, it was found that polythiophene particles had irregular shape. The average particle size of polythiophene particles was approximately 64.31 μm.

![Fig. 2](image)

**Fig. 2.** The SEM micrograph of polythiophene particles.

3.2. Appearance of PTh/PDMS blends

Polythiophene particles were mixed with poly(dimethyl siloxane) by mechanical mixing and then blend film was prepared by solution casting. “Fig. 3” shows the images of the appearance of PTh/PDMS blend films, diameter is 80 mm and thickness is approximately 0.8 mm, containing 5 vol.% PTh particles. It was found that the surface of pure PDMS film appears generally transparent, smooth and shiny while the PTh/PDMS blends showed dark and smooth surface. Moreover, the pure PDMS was found to be softer and more flexible than the PTh/PDMS blends. This may indicated that polythiophene particles act as reinforcing filler to PDMS matrix.

![Fig. 3](image)

**Fig. 3.** The PTh/PDMS blend samples at various PTh concentrations; (a) pure PDMS_10, (b) 5%PTh/PDMS_10, (c) 10%PTh/PDMS_10 and (d) 15%PTh/PDMS_10.

3.3. Bending response

The bending response or deflection of the PTh/PDMS blends samples were recorded using video camera and the bending response angle was calculated using equation (1). Under an application of electric field, the free lower end of the blends bend toward an anode electrode by an amount dependent on the studied variables; amount of crosslink agent, PTh particle concentration and electric field strength. In addition, the blends suddenly returned approximately to original position when the electric field is removed.

3.3.1 Effect of amount of crosslinking agent

The effect of crosslink on the bending response of the pure PDMS and PTh/PDMS blends were investigated. The amount of TEOS crosslink agent was varied as 10%, 15% and 20 vol% (PDMS_10, PDMS_15 and PDMS_20). The bending response and the bending angle of the PDMS and PTh/PDMS blends samples at electric field strength of 700 V/mm are shown in “Fig. 4” and “Fig. 5”, respectively. It can be observed that the pure PDMS responded to the applied electric field even without polythiophene addition. This because of the dipole moment is generated and leading to the electrostatic interaction between different strand segments of the PDMS [9]. In addition, it was found that the bending angle of the PDMS decreased with increasing the amount of crosslink agent, the bending angle of the PDMS_10, PDMS_15 and PDMS_20 were 23.08, 20.08 and 19.59, respectively. This may because of the increase of rigidity of the PDMS and the crosslinking agent prohibits the free movement of PDMS chains [4]. Moreover, the PTh/PDMS blends shown similar trend to the PDMS system, the bending angle decreased with the increase of the amount of crosslink agent.

![Fig. 4](image)

**Fig. 4.** Bending response pictures of PTh/PDMS blends at electric field strength of 700 V/mm.
3.3.2 Effect of PTh particle concentration

The effect of PTh particle concentration on the bending response of the PTh/PDMS blend was investigated by varying the polythiophene particle concentration as 5, 10 and 15 vol. % (5%PTh, 10%PTh, and 15%PTh). The bending response and the bending angle of the PDMS and PTh/PDMS blends samples at electric field strength of 400 V/mm are shown in “Fig. 6” and “Fig. 7”, respectively. From “Fig. 7”, it can be observed that the bending angle initially increased with increasing of PTh concentration up to 5 vol. % and beyond this concentration the bending angle appeared to decrease linearly. For the PTh/PDMS blend, both PDMS and polythiophene were polarized upon the application of electric field. Thus the generated dipole moment and the electrostatic interaction became stronger than the PDMS system which resulting in the increase of bending response. However, with higher polythiophene concentration, the bending response was obstructed due to the increase of rigidity and weight of the blend.

3.3.3 Effect of electric field strength

The bending response and the bending angle of the PDMS and PTh/PDMS blends samples under various electric field strengths are shown in “Fig. 8” and “Fig. 9”, respectively. From “Fig. 9”, the bending angle of the PDMS and PTh/PDMS blends obviously appeared to increase monotonically with electric field strength. As electric field was applied, electrical dipole moments were generated and lead to the attractive interaction between the applied field and the polarized polythiophene particles in the blend. With higher electric field strength, higher polarization and dipole interaction strongly effected to the increase of bending angle of the blend [10].
Conclusions

In this study, the bending response of PTh/PDMs blend was investigated by examining the effect of the amount of crosslink agent, polyythiophene particle concentration and electric field strength. It was found that both PDMS and PTh/PDMS systems responded well to the applied electric field because the poly(dimethyl siloxane) and polyythiophene particle were polarized and electrical dipole moments are generated. These lead to the attractive interaction between the applied field and the polarized polyythiophene particles in the blend. In pure PDMS system, the bending angle decreased with increasing crosslink ratio. The maximum bending angle was found to be 23.08 for the PDMS_10. For the blending response of the PTh/PDMS blends, it was found that the bending angle increased with increasing polyythiophene particle concentration up to 5 vol. % and then decreased linearly when the particle concentration higher than 5 vol.%. The bending angle increased stepwise under electric field strength. Moreover, the 5%PTh/PDMS_10 had highest bending response in which the bending angle was found to be 33.90 at the electric field strength of 700 V/mm.

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References