Preparation and Characterizing of PANI/PDMS Elastomer for Artificial Muscles

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Abstract. A dielectric elastomer has been synthesized using organic soluble PANI and PDMS through solution blending method for applications as artificial muscles. The dielectric constant of PANI/PDMS composite reached 4.82 with a filling amount of 0.8 wt.%, which was 2.24 times of pure silicone, due to the dipole polarization in matrix network and electron polarization in conductive polyaniline. The actuated strain of 0.8 wt. % PANI/PDMS was 16.57% compared to 8.52% of pure silicone at an electric field of 10V/μm, and can be applied as a soft actuator.

1. Introduction
Electrically Activated Polymers (EAPs), as a new type of flexible actuator, are being applied to electromechanical actuating and sensing fields. And among the EAPs, dielectric elastomers (DEs) are new rising material as energy harvester and actuating material [1-3]. They are attracting attentions for its large strain, fast response, light weight, low modulus, reliability and high energy density. As an electroactive polymer with the highest potential, DEs have been widely employed in artificial muscles, biomimetics, and micro-robotics as actuators, sensors, and generators [4, 5].

The key issue of dielectric elastomer is to obtain a large actuated strain under a low electric field. The vertical strain of DEAs can be approximated by:

\[ S_v = -P/Y = -\varepsilon_0 \varepsilon_r E^2 / Y \]  

Where P stands for Maxwell pressure on the material; Y represents Young’s modulus; \( \varepsilon_0 \) and \( \varepsilon_r \) stand for the vacuum permittivity and relative permittivity respectively. It is easy to infer that a reasonable solution to improve the actuated strain at a low electric field is to increase \( \varepsilon_r \) and decrease \( Y \) of DEs.

Numerous studies have been reported on various ways of improving the dielectric constant of DEs. Some works have been done by filling high permittivity ceramic particles such as barium titanate[6] and titanium dioxide[7] into elastomer matrix. The filling of ceramic particles can improve the dielectric constant of composites significantly, but the modulus of the material increases synchronously.

\[ \varepsilon(p) = \frac{\varepsilon_d}{|p-p_c|^s} \]  

This equation describes the greatly increasing permittivity of composite near percolation threshold [8]. Where \( \varepsilon(p) \) is the permittivity near critical percolation concentration \( p_c \), p is stand for the concentration and \( \varepsilon_d \) is the permittivity of matrix. We decided to make use of this phenomenon.

Polyaniline (PANI) is a kind of typical conductive polymers and can be used as fillers to synthesis conductive polymer. Compared to inorganic fillers, PANI have better compatibility with organic
matrix and less modulus so the composite would not lose flexibility. Some researchers prepared polymer with high dielectric constant using PANI as filler via a in situ polymerization or mechanical blending method, but the synthesis was complicated and filling amount was restricted[9,10]. Organic soluble PANIs [11] could be prepared in toluene solution. In this work, we present a dielectric elastomer using organic soluble PANI and PDMS through solution blending method.

2. Experimental

2.1. Materials
Aniline, ammonium persulfate(APS), toluene, dodecylbenzenesulfonic acid (DBSA), tetrahydrofuran, acetone were purchased from Sinopharm Chemical Reagent Co, Ltd. Polydimethysiloxane (PDMS, RTV-3483), curing agent (RTV-3083), electrically conductive Perfluoropolyether grease (Molykote HP-800 Grease) were provided by Dow corning corporation. All reagents were used as received except as noted.

2.2. Synthesis of Polyaniline-Dodecylbenzenesulfonic Acid in Toluene
5.59 g of aniline monomer was added into the emulsion prepared from 200 ml of water mixed with 36.28 g of DBSA and 50 ml of toluene in a cooling bath maintained at 2 ℃ for 1 h. 9.13 g of APS dissolved in 50 ml of water was dripped into the polymerization bath for a period of 1 h, and maintained stirring at 0-5 ℃ for 17 h. After polymerization was completed, 200 ml of toluene and 200g of acetone was poured into the emulsion and stirred for 1h. The solution was separated into 501.68 g of water layer and 198.36 g of oil layer after being left standing for 1h. The oil layer was vacuum filtrated to remove insoluble and obtained 196.25 g of clarified green oil layer, with a solid content of 4.38%.

2.3. Synthesis of PANI/PDMS Composite
Take an example of filling rate at 0.2 wt%, we mixedtured 0.15 g of dodecylbenzenesulfonic acid modified polyaniline in toluene solution, 3.3 g of PDMS and 0.17 g of curing agent for 20 mins, obtaining a homogeneous solution of PANI/PDMS, then poured the above solution into self-made Polytetrafluoroethylene mold and heated at 30 ℃ for 24h. After fully cured, the sample was removed from mold and PANI/PDMS composite with a thickness of 0.5mm was obtained.

2.4. Analyzing
Raman spectroscopy: DXR Raman spectrometer was provided by Thermo Electron Corporation. Varieties were analyzed after doping magnesium. Sample powders were poured on slides and compacted. Testing range was 4000-400 cm⁻¹, laser wavelength was 532 nm, and resolution was less than 2cm⁻¹.

Permittivity test: Permittivity of samples were tested by a broadband turnkey system Concept 80 provided by Novocontrol Technologies GmbH & Co. Samples were made into circle with diameter of 1 cm, while topper and lower surfaces were coated with conductive silver paste. Testing was progressed between two copper electrodes at frequency of 10-10⁶ Hz.

Electrostriction test: Electrically conductive Perfluoropolyether grease was evenly coated on both sides of dielectric elastomer. High voltage of 0-12V/μm was applied on electrodes by a high voltage power supply. The deformation of dielectric elastomer and scale under different voltages were both recorded by a digital camera. The image obtained was processed with image enhancement, tilt correction, edge extraction and position recognition in order to retrieve deformation displacement data of dielectric elastomer.

3. Result and Discussion
Fig.1 shows the Raman spectra of PANI-PDMS dielectric elastomer. The peak at 1590 cm⁻¹ shows the characteristic absorbing vibration of a quinone structure N=Q=N. As the filling amount of polyaniline increases, the quinone characteristic peaks are significantly enhanced. The peak at 1499 cm⁻¹ is caused by the characteristic absorbing vibration benzene structure N-B-N. The characteristic peak of quinone
structure and benzene structure in polyaniline are weakened after doping. The peaks at 1379 cm\(^{-1}\) and 1302 cm\(^{-1}\) are caused by aromatic amine Ar-N, and peaks at 830 cm\(^{-1}\) and 1161 cm\(^{-1}\) are bending vibration characteristic absorption band of outer and inner ring of benzene ring. From the result of Raman spectra, we assume that the PANI-PDMS composite was successfully synthesized.

![Raman spectra of PANI-PDMS](image1)

**Figure 1.** Raman spectra of PANI-PDMS

![Permittivity of pure silicone and PANI/PDMS](image2)

**Figure 2.** The permittivity of pure silicone and PANI/PDMS of different filling amount

Fig 2 is the permittivity of pure silicone and PANI/PDMS of different filling amount. As shown in the figure, the dielectric constants of composites increase at different levels. When the filling amount reaches 0.8 wt.%, the dielectric constant of PANI/PDMS composite is 4.82, which is 2.24 times of pure silicone. The reason of increasing dielectric constant of PANI/PDMS is due to the dipole polarization in matrix network and electron polarization in conductive polyaniline. According to the Maxwell-Wagner polarization theory, a great amount of charges accumulated on the surface between PANI and PDMS in an external electric field, forming numerous micro capacitors in parallel. Thence, interface polarization can enhance the permittivity of dielectric elastomer significantly. As the filling amount of conductive polyaniline increases, more micro capacitors formed in the system and dielectric properties of material are improved.
Fig. 3 shows the electrostriction strain curve of pure silicone and PANI/PDMS of different filling amount in electric field. The actuated strains of all samples are increasing as the electric field grew, and the actuated strains of PANI/PDMS composites are obviously larger than pure silicone. For example, the actuated strain of pure silicone at 10V/μm is 8.52%, and the actuated strain of 0.8 w.t % PANI/PDMS is 16.57% at the same electric field, the enhancement of dielectric constant is reflected intuitively through actuating property. The actuated strain was also compared with the CCTO@PANI-PDMS material fabricated by our group earlier [12], showing higher electrostriction at lower voltage (Fig.4). The PANI/PDMS dielectric elastomer showed a high actuating property in low electricity fields, and could be applied to fields with specialized requirements such as biological and medical science.

4. Conclusion
A dielectric elastomer has been synthesized using organic soluble PANI and PDMS through solution blending method. The dielectric constant of PANI/PDMS composite reached 4.82 with a filling amount of 0.8 wt.%, which was 2.24 times of pure silicone, due to the dipole polarization in matrix network and electron polarization in conductive polyaniline. The actuated strain of 0.8 w.t % PANI/PDMS was 16.57% compared to 8.52% of pure silicone at an electric field of 10V/μm, and
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6. References
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