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High electromechanical performance of modified electrostrictive polyurethane three-phase composites

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ABSTRACT

In order to enhance the electrostrictive polymer, the polyurethane has been modified with conductive fillers that are promising for actuator applications, energy conversion, and sensors. The polyurethane (PU) matrix and the conductive fillers such as graphene nanosheets (GRN) and polyaniline nanopowder (PANI) were prepared to gain films by solution casting method. The morphology, structure and thermal behavior of PU three-phase composite were observed by SEM imaging, FTIR, and DSC techniques. In addition, the electrical and mechanical properties of polyurethane filled with both composites were investigated by an LCR meter and strain gauge setup. In order to study the electrostriction behavior, the electric field induced strain of PU three-phase composite films was monitored via lock-in amplifier at a low frequency of 1 Hz. A greater electrostriction effect of the PU three-phase composites at low electric field significantly related with contribute to conduction and interfacial polarization base on space charges distribution, filler-filler network and microstructure on crystallinity in the HS domain of PU matrix. Therefore, electrostriction behavior in the PU three-phase composites has been discussion. It was known that why the three-phase composites can provide high electromechanical performance for actuator applications.

1. Introduction

Over the last decade, much interest on current technology has been devoted to the polymers due to the limited performance of conventional materials for instance metals, ceramics, and alloys. Electroactive polymers (EAPs) are smart materials which have the capability to convert energy from mechanical energy to electrical energy and vice versa. It has been greatly studied for energy harvesting, sensor and actuator applications [1]. Compared to other materials, the EAPs, especially the dielectric elastomers (DEs), have various advantages such as flexibility, large dimensional change, easy processing, light weight, and low cost [2–4]. EAPs can be categorized into electromagnetic, dielectric elastomers, electrostatic, electrostrictive, and piezoelectric. Electrostrictive polymers and dielectric elastomers are promising candidates for high-strain actuator due to their quadratic strain in the electric field. They can be found in every dielectric material. Moreover, previous work mainly focused on piezoelectric materials. In comparison to the electrostrictive polymers, the piezoelectric materials have brittleness, heavy, large stress and depolarization problems in long-term operation. Therefore, new smart electrostrictive polymers have been suggested as great promising materials for energy harvesting, actuator application, artificial muscles, et cetera [5].

Recently, the enhancement electrostrictive coefficient has been studied based on polyurethane composites [6]. As an electrostrictive polymer, polyurethane is of great interest for a wide range of actuator and transducer applications because of it is large deformations, high specific energy, and short response time. The dielectric permittivity and Young's modulus are the key factors to enhance the electrostrictive abilities of polyurethane. The last results showed that polyurethane enhanced the dielectric permittivity because of a strong polarization to be induced under an electric field. Increasing the dielectric constant leads to enhancing electrostrictive coefficient. Based on Eq. (1) the enhancement strain deformation (S_{33}) depends on the dielectric permittivity through

$$S_{33} = Q.{\varepsilon_0}^2.(\varepsilon_r - 1)^2.E_3^2 \tag{1}$$

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where ε_r is the real part of the relative dielectric permittivity, ε_0 is permittivity of free space, Q is the intrinsic electrostrictive coefficient, and E is electric field. Hence, the relationship with the electrostrictive coefficient (M) might be defined as

$$M_{33} = \varepsilon_0{}^2.(\varepsilon_r - 1)^2.Q_{33}^2 \tag{2}$$

So the electrostrictive coefficient from (1) and (2) equals

$$M_{33} \propto \frac{\varepsilon_0(\varepsilon_r - 1)^2}{\varepsilon_r Y} \tag{3}$$

Thus the electrostrictive coefficient (M_{33}) is proportional to the dielectric constant (ε_r) and inversely proportional to Young's modulus (Y) [6]. It is clearly understood that the dielectric permittivity is one of the key factors for affecting electromechanical properties as shown in Eq. (3).

Several papers presented in order to enhance the electromechanical properties of electroactive polymers with incorporated of conductive fillers based on carbon family such as carbon black (CB), carbon nanotubes (CNTs), and graphene nanosheet (GRN) [7–10]. Recently, Ning et al. proposed that the electromechanical properties of thermoplastic polyurethane filled with graphene oxide (GO) and polyethylene glycol (PEG) [9]. They presented that the large dielectric constant of TPU composites was observed due to synergistic effect of PEG and GO fillers. This effect was explained that the increase in dipole polarizability of TPU chains caused by the disruption of hydrogen bonds and the increase in interfacial polarizability caused by the favorable electron transfer from partially reduced GO coated by PEG to TPU. Moreover, the elastic modulus (Y) of the TPU/PEG/rGO composites largely decreased because of the plasticizing effect of PEG and the separation of GO from TPU. Besides, the different of filler dimensionality, zero dimensional CB and one-dimensional CNTs conductive fillers, were studied on the strain responsibility in polydimethylsiloxane (PDMS) matrix [10]. It was reported that the percolation threshold of CB/PDMS is much higher than that of CNTs/PDMS, explained by the instinct structure and geometry of fillers. Compared to one-dimensional CNTs, which can form conductive network by the filler entanglement, higher content CB particles are needed for the construction of interlinked carbon networks due to their low aspect ratio. In fact, the larger aspect ratio of GRN lattice corresponded to the high number of micro-capacitor and leads to great electrical conductivity, hence the GRN has been considered to be a good candidate for high dielectric permittivity filler [11]. A different type of filler such as polyaniline has been proposed to influence the electrostrictive effect [12]. As great interfacial polarization, the addition of 2 wt% polyaniline in PU matrix with dielectric permittivity of 23.75 was found to enhance the electrostrictive coefficient up to 6.12×10^{-16} m^2/V^2 in electric field under 2 MV/m [13]. The latest article proposes the effect of hybrid blend where graphene coupled with the variation of carbon for instance carbon black (CB) and multi-walled carbon nanotube (MWCNT). However, the incorporation of higher amounts of MWCNTs reduce the nanocomposites maximum elongation, due to the increase of the crosslinking density with the addition of the filler to polymer matrix [14]. The effect of hybrid blend improved the electrical conductivity and mechanical properties on account of good dispersion and high interaction with the elastomer matrix [15]. Therefore, the three-phase composites including the polymer matrix, the conductive carbon, and conductive polymer are of great interest due to their high electromechanical performance.

Having considered from the previous mentions in several papers, therefore in this work, the two-phase composites and three-phase composites were prepared with two different types of filler. Graphene nanosheets (GRN) and polyaniline (PANI) in corporated with PU matrix. All composites were prepared via solution casting method. In order to minimize variations, all samples were prepared with the same thickness of 100 µm. The morphological structure, chemical bonds, and phase structure were assessed by using SEM, FTIR, and DSC, respectively. The dielectric coefficient was determined as functions of filler content and frequency with the range of 10^0–10^5 Hz, while Young's modulus was determined as well. In addition, the strain deformation was assessed as a function of DC electric field and the electrostrictive coefficient was calculated and compared to each other to gain new understanding.

2. Materials and methods

2.1. Materials preparation

Thermoplastic polyurethane elastomers (DP 9370A) were supplied from Covestro AG (Germany). This PU was used as a matrix based on MDI (4,4 methylene bis(phenyl isocyanate) BDO (1,4–butanediol) as the hard segment and PTMO (poly (tetramethylene oxide)) as the soft segment. Graphene nanosheets and polyaniline powders used as fillers were provided by Sigma Aldric. The conductivity and particle size of graphene was about 4–6 S/cm and 2–3 µm. The 1–Methyl–2–pyrrolidone (NMP, 99% purity, M79603, Sigma Aldrich) with the 99% purity as a solvent was purchased from Sigma Aldrich.

First, the PU granules were dried at 80 °C for 24 h. Then PU granules were dissolved in NMP under mixing at 80 °C for 45 min to obtain a homogeneous solution. Graphene and polyaniline were added into the NMP and dispersed for 20 min by using ultrasonic. Then graphene and polyaniline solutions were added into PU matrix and continuously mixed at 80 °C for 3 h until gaining a homogeneous solution. The final solution was cast onto a glass surface at 60 °C by casting method and dried in the oven for 24 h to remove the solvent. Finally, the PU/GRN-PANI film was taken off from the glass surface and annealed at 125 °C for 3 h to remove remaining solvent and the final thickness of the films was 100 µm.

2.2. Characterization methods

2.2.1. Structure and morphology

The PU three-phase composites were characterized in the matter of their morphology and dispersion of the fillers by scanning electron microscopy (SEM, FEI Quanta 400, USA). In order to observe the cross-section, the specimens were sliced using liquid nitrogen, whereas the magnification and the high voltage was conducted in the specimen of 5000× and 20 kV, respectively.

2.2.2. FTIR characterization

By using Fourier Transform Infrared Spectroscopy (FTIR, Bruker EQUINOX 55), the infrared spectra were recorded in the region of 800–4000 cm^{-1}. The FTIR was used to determine the different aspect of functional groups in the PU composites. The curve-fitting results of the specimen were divided into two region where the first region was the amine region of 2700–3500 cm^{-1} and the second region was carboxyl region of 1000–1800 cm^{-1}.

2.2.3. Thermal analysis

A Differential Scanning Calorimeter (DSC, Perkin Elmer DSC7, USA) was used to investigate the thermal stability, including the glass temperature (T_g), the melting transition temperature (T_m) and the enthalpy changes (ΔH) of the composites. The specimen of 10 mg was sealed in the hermetically aluminum crucible, and then with the help of liquid nitrogen, the DSC cell was maintained in an equilibrated atmosphere. The specimen was cooled by using liquid