Current Applied Physics 13 (2013) 1119–1127

Contents lists available at SciVerse ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Electrostrictive properties of thermoplastic polyurethane elastomer: Effects of urethane type and soft–hard segment composition

K. Petcharoen, A. Sirivat*

Conductive and Electroactive Polymers Research Unit, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form
25 February 2013
Accepted 5 March 2013
Available online 21 March 2013

Keywords:
Polyurethane
Electromechanical properties
Flexible actuators
Electrostriction
Dielectrophoresis force

ABSTRACT

The electromechanical behavior of thermoplastic elastomer polyurethane (TPE-PU) is investigated under the effects of urethane type (ester and ether-types) and soft–hard segments at various electric field strengths and temperatures. The highest dielectric constant, electrical breakdown strength, and specific conductivity belong to the ester-type polyurethane (LPR matrix), while the lowest values are obtained from the ether-type polyurethane composing predominantly with the soft-segment (E 80A matrix). Under the electric field strength in the range between 0 and 2 kV/mm, the LPR matrix attains the storage modulus sensitivity ($\Delta G'/G'_0$) up to 2 at 2 kV/mm. For the temporal response, the polyurethanes behave with good reproductively (number of cycles $>10^5$ times) and with very good recoverability. The steady state behavior can be attained at the first actuation and at the electric field strength of 1 kV/mm. Furthermore, the storage modulus (G') shows linearly negative responses with increasing temperature. In the deflection experiments, the deflection distance and the dielectrophoresis force increase monotonically with increasing electric field strength. All of the TPE-PU possesses very fast response times for activation (<10 s.) and deactivation (<5 s.). TPE-PU material is systematically shown here to be a potentially good actuator material with high efficiency based on the electrostrictive performance data obtained.

1. Introduction

The smart materials generally tend to respond with any external stimuli such as pH [1], temperature [2], electric field [3] and etc, by changing shapes and or dimensions. Electroactive polymers (EAPs) belong to one sub-group of the smart materials in which the mechanical response can be induced by electric field [4]; as these materials can be utilized in the actuator and transducer applications [5]. There are many required properties: lightweight, good mechanical flexibility, high resilience, good processability and short response time [6–8]. Oshiki et al. (1975) reported that most EAPs are based on either the piezoelectric mechanism or the electrostrictive interaction in which can be described by following general equation:

$$T = G^E S + eE + \gamma E^2, \tag{1}$$

where T is the stress, G^E is the elastic coefficient, S is the strain, e is the piezoelectric stress coefficient, E is the electric field, and γ is the electrostriction coefficient [9]. The equation can be interpreted as the linear relation associated with the piezoelectricity and the quadratic response for the electrostriction behavior under an applied electric field. Thus, it is generally useful to classify a material and its behavior by using the stress response under electric field.

In the recent years, the EAPs such as poly(vinylidene fluoride) [10], acrylic elastomers [11], silicon [12], and urethane [13] are the most common smart materials providing high ability to convert electrical energy into strain response [14]. Nevertheless, high flexural endurance, high shape recoverability, and large deformation are attained only by the polyurethane [15,16]. Due to the polyurethane performances under an electric field, many attempts have been made to enhance the actuation behavior through electromechanical properties. Ueda et al. (1997) studied the actuation mechanism of polyurethane elastomers and they suggested that the deformation of the specimen under electric field was induced by the dipole orientation within the materials [17]. Guillot et al., (2003) investigated the electrostrictive properties in a polyurethane and found that up to 85% of the electromechanical activity came from the electrostrictive effect due to a phase separation in the polyurethane. The minor factor (less than 15%) was attributed to the Maxwell stress, due to the electrostatic

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* Corresponding author. Tel.: +66 2 218 4131; fax: +66 2 611 7221.
E-mail address: anuvat.s@chula.ac.th (A. Sirivat).

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http://dx.doi.org/10.1016/j.cap.2013.03.005

attraction under applied electric field [18]. Generally, the effect of electrostriction on the strain response mainly depends on the chemical composition, the physical structure, the dielectric constant, the Young's elastic modulus, and the electrostrictive coefficient of material [19].

The thermoplastic elastomer polyurethane (TPE-PU) can be regarded as a linear block copolymer consisting of three segment structures: polyol, diisocyanate, and a chain extender. These segments can influence their properties over a wide range, such as elasticity due to the soft–hard segment composition [20]. The TPE-PU properties are directly related to their chemical structure (ether or ester types) and segmented flexibility which can dictate various electrostrictive behaviors under electric field [21].

The aim of our investigation is to determine the influence of the TPE-PU structure, in terms of the urethane type and the soft–hard segment composition on the electrostrictive behavior. In particular, the stress (storage modulus; G′) and the strain responses under the influence of an electric field strength and temperature are investigated, compared with others, and reported here.

2. Experimental

2.1. Materials

Thermoplastic Poly(ether-urethane), Elastollan® 1180A; (E80A) and 1195A; (E95A), BASF, and Thermoplastic Poly(ester-urethane), LPR®4525; (LPR), Behnmeyer were used as the electroactive polymers. The polyurethane consists of butanediol as the chain extender, diphenylmethane diisocyanate as the hard segment, and the different soft segment are tetramethylene glycol and adipate ester for the ether-type and ester-type polyurethanes, respectively, as shown in Fig. 1. All of the TPE-PU pellets were dried at 80 °C for 24 h prior to use for evaporation of moisture content. Poly(dimethylsiloxane), (PDMS 100 cSt, Sigma–Aldrich), was used as a liquid medium in the bending experiment.

2.2. Preparation of the TPE-PU films

All TPE-PU films were prepared by using a compression molding technique (Wabash, Model 9354) at 225 °C for 10 min with a pressure of 15 tons. The compression mold was a spherical shape with a diameter of 25 mm and a thickness of 1 mm for electromechanical testing. For the bending experiment, the mold had a rectangular shape with a thickness of 0.2 mm.

2.3. Characterization and testing

2.3.1. Fourier transform infrared spectrometer

The TPE-PU films were first characterized for the functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) in the absorption mode with 32 scans and a resolution of ±4 cm^{-1}, a wave-number range of 4000–400 cm^{-1} with a deuterated triglycine sulfate as a detector. For the ATR-FTIR technique, air was used as the background material.

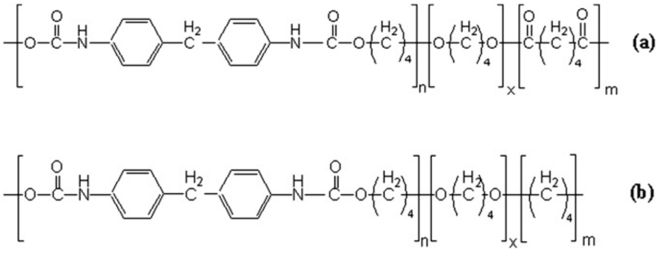

Fig. 1. TPE-PU structures: Ester-type (a); Ether-type (b).

2.3.2. Viscosity measurement

The average molecular weight was calculated from the Mark–Houwink equation:

$$[\eta] = KM^a, \tag{2}$$

where $[\eta]$ is the intrinsic viscosity, M is the viscosity-average molecular weight, the constant parameters K and a for polyurethane are $K = 6.80 \times 10^{-5}$ dL/g and $a = 0.86$. The intrinsic viscosity of polymer solutions in DMF was measured at 30 °C by using the Ubbelohde I capillary viscometer [22].

2.3.3. Thermal analysis

A thermogravimetric analyzer (Perkin Elmer, TGA7) was used to determine the degradation temperature of the TPE-PU. The experiment was carried out by weighting a sample of 5 mg and loaded into a platinum pan. The mass change under the temperature scan from 30 to 600 °C with a heating rate of 10 °C/min and under a nitrogen flow was monitored. A differential scanning calorimeter (Metter-Toledo, DSC-822e) was employed to obtain the melting temperature of the TPE-PU. The sample of about 5 mg was heated at a rate of 10 °C/min from 30 to 250 °C.

2.3.4. Electrical conductivity

The electrical conductivity measurement (Keithley, Model 8009) was performed at room temperature. The resistivity test fixture connected with the power source (Keithley, Model 6517A) to supply the voltage and to read the resultant current. The applied voltage and the current were used to determine the electrical conductivity by the following equation:

$$\sigma = \frac{1}{\rho} = \frac{t \times I}{22.9 \times V}, \tag{3}$$

where σ is the specific conductivity (S/cm), ρ is the specific resistivity (Ω cm), t is the specimen thickness (cm), I is the measured current (A), V is the applied voltage (V), and 22.9 is constant factor of the test fixture.

2.3.5. Electrical breakdown strength

The electric puncture tester (MFG Yaduda Seiki) was used to measure the electrical breakdown strength of the TPE-PU. The sample films were placed between the parallel electrodes and electric field was applied until it reached the breakdown voltage.

2.3.6. Dielectric constants

The LCR meter (HP, model 4284A) connected with the melt rheometer (Rheometric Scientific, ARES), parallel plate fixture with diameter of 25 mm, were used to measure the dielectric constants. The AC voltage of 10 V was applied through the specimens at temperature range of 300–360 K. Before testing, the specimens were coated with a silver paint.

2.3.7. Electromechanical behavior

The melt rheometer (Rheometric Scientific, ARES) was used to study the electromechanical properties of the films. The specimens were fitted with copper parallel plate fixture (diameter of 25 mm) and the DC voltage (Instek, GFG 8216A) was applied through the specimen. At first, the strain sweep test was carried out to