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New polyester dielectric elastomer with large actuated strain at low electric field

Dan Yang [a], Ming Tian [a,b], Hailan Kang [a], Yingchao Dong [a], Haoliang Liu [a], Yingchun Yu [a], Liqun Zhang [a,b,*]

[a] *Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *State Key Laboratory for Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China*

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ABSTRACT

A new polyester dielectric elastomer aiming at large actuated strains driven by low electric fields was synthesized from five monomers through melt polycondensation. The polyester dielectric elastomer displays not only high dielectric constant but also low glass transition temperature. The effect of crosslink density on the elastic modulus, dielectric properties, and actuated strain of this elastomer was investigated. The sample with the lowest crosslink density showed high actuated strain (11.9%) at low electric field strength (just 15.6 kV/mm) without any prestrain. Moreover, this elastomer presented good cell compatibility. This research might help to establish a new route for electroactive polymers.

1. Introduction

Electroactive polymers (EAPs) are of particular interest since they are soft and flexible, and can convert electrical energy to mechanical energy. They are considered as potential materials for artificial muscles, sensors, micro air vehicles, flat-panel speakers, microrobotics and responsive prosthetics [1–5]. Among the different electric field activated EAPs, dielectric elastomer actuators (DEAs) demonstrate potential advantages on excellent EAP properties such as large strain, fast response, high energy density, wide range of applications, and simple working principle [6,7]. So during the past decades, DEAs have attracted more and more attention. However, one severe drawback of these DEAs is that they generally require a high actuated voltage (as high as 100 kV/mm) to obtain a satisfactory actuated strain [2,8,9]. The requirement largely limits their applications, especially in the biological and medical fields [8–10]. In order to improve electromechanical performance, high prestrain is applied on dielectric elastomers, but the high prestrain will bring several negative aspects into applications and complicate the design of the devices [11,12].

Theoretically, based on the assumptions that a dielectric elastomer (DE) film is an ideal elastomer and electric field-induced strains are small strains with free boundary conditions, the thickness strain S_z can be approximated by

$$s_Z = \varepsilon\varepsilon_0 E^2/Y \tag{1}$$

where ε and ε_0 are the relative permittivity (dielectric constant) of the dielectric elastomer and the permittivity of free space, respectively; E is the applied electric field strength and Y is the elastic modulus of the dielectric elastomer [1,13]. Eq. (1) indicates that an ideal dielectric elastomer should have a low elastic modulus and high dielectric constant to overcome the disadvantage of high applied electric field strength, and thus obtain an excellent electromechanical actuation [13–15]. However, traditional dielectric elastomers usually do not have both a low elastic modulus and a high dielectric constant. Consequently, developing a new structured polymer material from molecular design becomes more and more important for researchers to achieve high performance DEAs.

In this study, a new polyester elastomer that contains a large amount of polar ester groups in the main chains was reported. The original goal of preparing this kind of polyester elastomer is to create high strength elastomers for engineering application [16]. The ester groups, which have excellent internal rotation capacity, could contribute to a low glass transition temperature (Tg) and a corresponding low elastic modulus, and high polarizing capability of ester groups could be in favor of a high dielectric constant. This new dielectric elastomer was made from five monomers (two kinds of acids and three kinds of alcohols) through polycondensation, as illustrated simply in Scheme 1. Such a polymer construction is to suppress the crystallization of polyester. A small amount of double bonds from itaconic acid in the chains can be used to tune the elastic modulus of the elastomer through peroxide induced curing reaction. Additionally, all the monomers are available from biomass feedstock, so this elastomer is more environment-friendly than other dielectric elastomers. The biocompatibility of elastomer was preliminarily checked. Some very valuable results were obtained and demonstrated.

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* Corresponding author at: Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China. Fax: +86 10 64433964.
E-mail address: zhanglq@mail.buct.edu.cn (L. Zhang).

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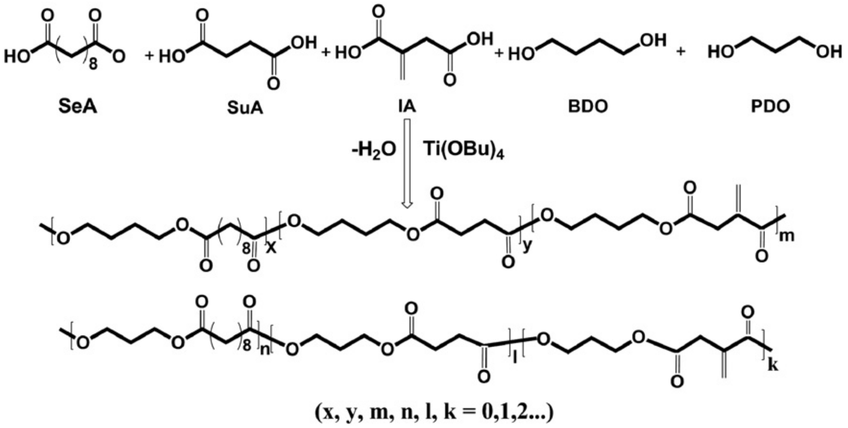

Scheme 1. Chemical reaction for formation of polyester elastomer.

2. Experimental

2.1. Preparation of polyester

By varying feed ratios, catalyst type and reaction conditions, we obtained a polyester elastomer with good overall properties. First, the five monomers 1,4-butanediol (0.165 mol), 1,3-propanediol (0.165 mol), sebacic acid (0.1275 mol), succinic acid (0.1275 mol), and itaconic acid (0.03 mol) and the inhibitors hydroquinone and orthophosphoric acid at 0.04 wt.% and 0.01 wt.% of the total monomers mass, respectively, were allowed to react at 180 °C under nitrogen for 2 h. Secondly, the catalyst $Ti(OBu)_4$ (0.05 wt.%) was added into the reaction mixture. The temperature was gradually increased to 220 °C and the pressure reduced to 300 Pa. The copolyester obtained was dissolved in chloroform and precipitated with ice-cold methanol. The precipitate was then dried at 40 °C in a vacuum oven for 24 h.

2.2. Characterization

The uncured polyester elastomer and different amounts (0.02 g to 0.16 g per 100 g elastomer) of dicumyl peroxide (DCP) were blended in a Haake Remix (Remix 600p, Thermal Electron Co., USA) at 50 rpm for 30 min at 60 °C. Then the cured elastomers were obtained through hot press. A swelling test was carried out in toluene at 30 °C for 72 h for measuring the crosslink density of the specimens [17]. The elastic modulus was determined by the slope at 5% strain of the stress–strain curves obtained on a CMT4104 tensile apparatus (Shenzhen, China) at a rate of 100 mm/min at 25 °C. The dielectric properties of the samples were measured by an HP 4294A impedance analyzer (Agilent, U.S.A). We measured the area actuated strains of the dielectric elastomer which perpendicular to a high voltage supplied by an intelligent high voltage DC generator (Wuhan Dotek Electric Co., Ltd, China).

3. Results and discussion

By varying the reaction conditions and monomer feed ratios, we obtained a polyester elastomer with good overall properties. The Fourier transform infrared (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy were used to confirm the molecular structure of the polyester elastomer (see Supplementary Material). The Tg is very low (close to −57 °C), according to differential scanning calorimetry (DSC) result (see Supplementary Material). The low Tg promotes high segmental movement and leads to a low elastic modulus of the elastomer, which gives a high actuated strain according to Eq. (1). The number-average molecular weight (Mn) of the elastomer is about 33000 and the polydispersity index (PDI = Mw/Mn) is 3.70, according to gel permeation chromatography (GPC) results. The molecular weight is sufficiently high to ensure a high elasticity of the elastomer after crosslinking. Though the PDI is relatively high, we can get almost the same date of the average molecular weight, PDI and Nuclear Magnetic Resonance spectrum for each repeated synthesis.

Chemical crosslinking is prerequisite for most elastomers to obtain a three dimensional network to further increase the elasticity and mechanical performance. Generally, increasing crosslink density will bring a rapid increase of modulus, roughly according to the following equation:

$$E = 3NkT \tag{2}$$

where E is Young's modulus, N is the crosslink density, k is the Boltzmann constant, and T is the absolute temperature. The increase of modulus of dielectric elastomer adversely affects the actuated strain driven by an applied voltage.

Fig. 1(a) shows that the elastic modulus of the polyester elastomer increases almost linearly with increasing crosslink density. The elastic modulus at a crosslink density of 3.28×10^{-5} mol/cm^3 is just 0.097 MPa, however, the elastomer with this crosslink density still presents satisfactory elasticity, because the tensile permanent deformation of polyester elastomer with crosslink density of 3.28×10^{-5} mol/cm^3 is just 4%. The modulus of crosslinked polyester elastomers are at the same order of magnitude with two common dielectric elastomers, i.e. VHB 4910 (produced by 3 M company, about 0.1 MPa according to our measurements) and Dow Corning SILASTIC 3481(DC 3481, about 0.35 MPa) [18], which also means that polyester dielectric elastomer may can load stress as same as these two dielectric elastomers.

Fig. 1(b) shows the dielectric constant and its evolution with crosslink density of this elastomer. As there are a great quantity of ester groups and terminal hydroxyl or carboxyl groups of high polarity in the polyester chains, the polyester elastomers exhibit high dielectric constants (from 5.6 to 7.8 at 1 kHz), which are higher than those of two commercial dielectric elastomers: silicone elastomer DC 3481 (about 3.25–3.65) [18] and acrylic rubber VHB 4910 (3 M) (about 4.7) [19]. Generally, the larger the amount of polar groups in the polymer chains, the higher the dielectric constant of the polymer. However, the introduction of polar groups into the polymer chains usually leads to an obvious decrease of segmental movements because of the increase of chain–chain interaction and the decrease of internal rotation capability, all of which corresponds to an increase of modulus. The ester group is special in that it doesn't strongly affect the segmental movement of polymer chains as a result of its excellent internal rotation capability. Although its polarity is not as high as that of the –CN group; however, the amount of ester groups in polymer chains has to be controlled to guarantee a high elasticity. Besides,