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Materials Science and Engineering A 454–455 (2007) 453–460

MATERIALS SCIENCE & ENGINEERING A

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Poly(*p*-phenylene) and acrylic elastomer blends for electroactive application

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Received 21 July 2006; received in revised form 8 November 2006; accepted 8 December 2006

Abstract

Polymer blends between poly(*p*-phenylene) PPP and an acrylic rubber (Nipol AR71) were fabricated in order to tailor their electromechanical properties towards electroactive applications. Experiments were carried under the oscillatory shear mode and with applied electric field strength varying from 0 to 2 kV/mm. The dynamic moduli, G' and G'', of the pure AR71 depend on the temperature and electric field strength; the storage modulus (G') monotonically increase with increasing electric field. The storage modulus sensitivity ($\Delta G'/G'_0$) increases with electric field strength and attains maximum values of 62% at the $E = 2$ kV/mm. For the polymer blends with the undoped particle concentrations of 5, 10, 20, 25, 30 and 40 vol.%, the dynamic moduli, G' and G'' of each blend, are higher than those of pure AR71. Their storage modulus sensitivity ($\Delta G'/G'_0$) increases with electric field strength; it attains a maximum value about 97% at $E = 2$ kV/mm. The effect of temperature, on electrorheological properties of pure AR71 and polymer blends, is studied between 27 and 77 °C. The storage modulus increases linearly with temperature with the slope proportional to the effective strand density.

Keywords: Electroactive polymer; Poly(*p*-phenylene); Acrylic elastomer; Dynamic moduli

1. Introduction

Electroactive materials have been continuously developed for a variety of applications such as muscle/insect-like actuators, robotics, drug release, etc. One type of electroactive materials is the electroactive polymer [1]. Electroactive polymers (EAPs) offer promising and novel characters: lightweight, high energy density, and high flexibility; they are material candidates for muscle-like actuators. Dielectric elastomers belong to a type of electric-field-activated electroactive polymers that are capable of producing large strains, fast response, and relatively high efficiency [2]. In particular, an acrylic elastomer is a dielectric material which has many advantageous characters over other dielectric polymers: inexpensiveness, flexibility, low swelling in water, high tensile strength, good resilience, and high respond under electric field [3]. These characteristics are desirable properties required to induce large actuation strains when subjecting a material to an electric field.

Recently, incorporation of a conductive polymer into a dielectric elastomer forming a composite has been of interest. Shiga [4] studied the electroviscoelastic effect of the polymer blends between poly(*p*-phenylene) and a silicone elastomer. They mixed the poly(*p*-phenylene) particles in silicone elastomer solution and altered the morphology of the dispersed phase by applying the electric field. The storage and loss modulus sensitivities ($\Delta G'$ and $\Delta G''$) increased linearly with the poly(*p*-phenylene) volume fraction. Shiga and coworkers also studied the effect of morphology of the dispersed phase. In the case of the random dispersion, the storage modulus increased linearly with increasing electric field, but this relation did not hold in the case of the pre-aligned structure. The effect of temperature on the electroviscoelastic response was also studied; the storage modulus response increased from 50 °C and attained maxima at 110 °C. From the results obtained by Shiga, we can expect that conductive polymers may alter electrorheological properties to the host elastomer through many other factors: variable conductivity, improved thermal stability, and mechanical properties. Examples are a polyanilene–polyisoprene composite for biosensor application [5], a polyanilene-EPDM composite [6], and TiO_2 embedded in PDMS gels for actuator application [7].

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doi:10.1016/j.msea.2006.12.033

In our work, we are interested in poly(*p*-phenylene)/Nipol AR71 elastomer blends as candidates for artificial muscles or actuators. The thermal properties, electrical properties, and electrorheological properties were investigated in terms of poly(*p*-phenylene) particle concentration, temperature, and electric field strength.

2. Experimental

2.1. Materials

Benzene solution (AR grade, Thai aromatic Co. Ltd.) was used as the monomer. Aluminum chloride, $AlCl_3$ (AR grade, Riedel-delHean) was used as the oxidant. Cupric chloride, $CuCl_2$ (AR grade, Fluka-Aldrich) was used as the catalyst. The sulphuric acid dopant, H_2SO_4 (AR grade, Fluka-Aldrich) was used as received. Acrylic elastomers Nipol AR71 (Commercial grade, Zeon Polymix Advance Co. Ltd.) were used as the polymer matrices.

2.2. Synthesis poly(p-phenylene) and preparation of polymer blend

We followed the poly(*p*-phenylene) synthesis procedure of Kovacic [8] using benzene, $AlCl_3$, and $CuCl_2$. The reaction was carried out under nitrogen in a 3-neck flask equipped with a panddle stirrer. After the dropwise addition of benzene (1 mol) and aluminum chloride (0.5 mol), cupric chloride (0.5 mol) was introduced into the solution. Temperature was raised up to 35–37 °C, and the reaction was allowed to proceed for 3 h. Then the solution was cooled to 5 °C and filtered with 18% HCl solution. The obtained poly(*p*-phenylene) powder was washed with boiling 18% HCl solutions until the washing solutions were colorless. The poly(*p*-phenylene) powder was finally washed with hot water until the washings had a pH of 7.0. After drying at 27 °C under vacuum for 12 h, the final obtained product was in the form of a finely divided, light brown solid powder. Great care was taken to avoid contamination from moisture [9–11]. We followed the doping procedure of poly(*p*-phenylene) from previous work [12]. A suspension of dried poly(*p*-phenylene) powder in sulphuric acid was prepared in a sealed flask. The mole of sulphuric acid (N_{acid}) was varied versus the mole of monomer (N_{monomer}). N_{acid}:N_{monomer} values chosen were 1:100, 1:10, 1:1, 10:1 and 100:1. The mixture was stirred for 2 h, at temperature of 5 °C, under nitrogen atmosphere. The doped poly(*p*-phenylene) was filtered out by a funnel. After drying at 27 °C under vacuum for 12 h, the obtained products were dark brown powders whose color depended on the degree of doping.

The blends were prepared by mechanical blending of poly(*p*-phenylene) with an acrylic elastomer. We dissolved 7 cm^3 of acrylic elastomer (Nipol AR71) in 70 cm^3 of acetone and stirred for about 10 h. Then we added PPP powder and stirred the mixture overnight. The dispersion of particle is randomly. Concentrations of PPP in AR71 prepared were 5, 10, 15, 20, 25, 30, and 40 vol.%. We cast the sheets in a mold and left them in a vacuum oven to remove bubbles at 27 °C for 24 h.

2.3. Characterization and testing

The undoped and doped poly(*p*-phenylene) (PPP) were characterized by a FT-IR spectrometer in order to identify their functional groups. The FT-IR spectrometer (Thermo Nicolet, Nexus 670) was operated in the absorption mode with 32 scans and a resolution of $\pm 4\,\text{cm}^{-1}$, covering a wavenumber range between 400 and 4000 cm^{-1}, using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PPP was intimately mixed with dried KBr at a ratio of PPP:KBr = 1:20.

The UV–vis spectra of undoped and doped poly(*p*-phenylene) were recorded with a UV–vis absorption spectrometer (Perkin-Elmer, Lambda 10). Measurements were taken in the reflectance mode in the wavelength range between 200 and 900 nm. Synthesized PPP was grinded into a fine powder and put into a sample holder. The scan speed was 100 mm/min, and a slit width of 5.0 nm using a deuterium lamp as the light source.

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to determine the amount of moisture content and the decomposition temperatures of undoped and doped poly(*p*-phenyene) at various mole ratios of dopant to poly(*p*-phenylene) with the temperature scan from 30 to 900 °C, and with a heating rate of 10 °C/min. The samples were weighted in the range of 5–10 mg and loaded into a platinum pan, and then heated it under a nitrogen gas flow.

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, model JSM-5200) to determine the morphology of poly(*p*-phenylene) in powder forms and PPP/AR71 blends at various particle concentrations. The scanning electron micrographs of poly(*p*-phenylene) and polymer blends were obtained by using an acceleration voltage of 15 kV with magnifications of 350 and 1500 times.

X-ray diffraction patterns as recorded by a diffractometer (Phillips PW 1830/00 No. DF 1241) between angles of 5° and 35° were used to study the atomic arrangements and the degree of crystallinity of undoped poly(*p*-phenylene) and doped poly(*p*-phenylene). Samples were prepared in a pellet form from the compression.

Particle sizes of poly(*p*-phenylene) were determined by using a particle size analyzer (Malvern Instruments Ltd., Masterizer X Version 2.15). The lenses used in this experiment were 30 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the standard size distribution.

Electrical conductivity was measured by a meter which consists of two probes making contact on a surface of film sample. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage and the current change in the linear Ohmic regime were converted to the electrical conductivity of polymer using Eq. (1) as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s t} = \frac{I}{KVt} \tag{1}$$

where σ is the specific conductivity (S/cm), ρ the specific resistivity (Ω cm), R_s the sheet resistivity (Ω), I the measured current