Materials Science and Engineering C 31 (2011) 206–214

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Electroactive polydiphenylamine/poly(styrene-block-isoprene-block-styrene) (SIS) blends: Effects of particle concentration and electric field

K. Thongsak [a], R. Kunanuruksapong [a], A. Sirivat [a,c,*], W. Lerdwijitjarud [b,c]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, 10330, Thailand
[b] Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
[c] Center of Petroleum, Petrochemical, and Advanced Materials, Chalalongkorn University, Bangkok, 10330, Thailand

ARTICLE INFO

Article history:
Received 31 March 2010
Received in revised form 8 July 2010
Accepted 17 August 2010
Available online 20 September 2010

Keywords:
Electrorheological properties
Poly(strene-block-isoprene-block-styrene) block copolymer
Polydiphenylamine
Morphology
Dynamic moduli

ABSTRACT

Polymer blends between dedoped-polydiphenylamine (De_PDPA) and poly(strene-block-isoprene-block-styrene) triblock copolymer with 19%wt PS (D1114P, Kraton) were prepared to investigate electrorheological (ER) properties. Polydiphenylamine was synthesized by the interfacial oxidative polymerization and dedoped with ammonium hydroxide aqueous solution. ER properties were measured under an oscillatory shear mode in the frequency range of 0.1–100 rad/s, at various electric field strengths between 0 and 2 kV/mm. At 27 °C and 1 rad/s, the storage modulus sensitivities ($\frac{\Delta G'}{G'_0}$) of the blends with 0, and 5%v/v are small, but dramatically increase at concentration above 5%v/v, consistent with the increase in the dielectric constant. The sensitivities are reduced when the particle volume fraction is above 20%v/v (2 kV/mm) or 10%v/v (1 kV/mm). The storage moduli (G') of 20 and 30%v/v blends are nearly independent of temperature up to 370 K but decrease beyond that. For the 0, 5, and 10%vv blends, the storage moduli increase with increasing temperature up to 370 K and decrease at higher temperature. The softening of the blends at 370 K coincides with the polystyrene glass transition temperature. At the lower concentrations, the blends still behave as elastomeric materials in which the elasticity is entropic in origin. In the deflection experiments, the deflection response increases with increasing particle volume fraction up to 10%v/v, and it decreases at higher concentration.

1. Introduction

Electroactive materials are utilized in many forms such as artificial muscles, muscle/insect-like actuators, and robotics [1]. They have recently received much attention and continuously developed since these materials can convert electrical energy into mechanical energy. Electroactive polymers, belonging to a type of electroactive materials, offer novel characteristics such as light weight, flexibility, and high energy density. Elastomer, a dielectric material, is one type of electric-field-activated electroactive polymers. It is capable of producing fast response, large strains, and relatively high efficiency [2].

Therefore, several elastomers have been used as the electroactive dielectric elastomer. Polyisoprene has many advantageous characteristics such as flexibility, low swelling in water, high tensile strength, good resilience, well behaved hysteresis, and etc. Crosslinking is necessary in order to access these polyisoprene properties [3]. With these characteristics, it is possible to obtain large actuation strains when subjected to an electric field. Thus, a poly(strene-block-isoprene-block-styrene) triblock copolymer (SIS) is an interesting and alternative material. SIS is a thermoplastic elastomer, a blend between two immiscible polymers. It has a hard and glassy domain of styrene acting as the reinforcing phase within the soft and rubbery isoprene matrix; therefore the storage modulus and the yield strength can be increased relative to those of the pristine polyisoprene. Moreover, SIS has elastomeric properties of a crosslinked rubber that can easily be processed by conventional processing such as melting or solvent casting [4].

Recently, the blending of a dielectric elastomer with a conductive polymer has been investigated in many applications. For instances, the polyaniline–polyisoprene blended film for selective determination of H_2O_2 detection biosensor [5], the blending of polyaniline/EPDM elastomer to improve thermal and chemical stability [6], a solid state actuator based on the PEDOT/NBR system [7], and the blended polythiophene/polyisoprene elastomer for the electroactive actuator application [3] are just a few. There are many possible conductive polymers that can be used. Polydiphenylamine is one interesting conductive polymer as it has a molecular structure similar to polyaniline. It also can be easily synthesized by an oxidative polymerization and easily doped with the acid solution of pH below 6.

In our work, we are interested in developing and testing polydiphenylamine/SIS thermoplastic elastomer blends towards electroactive actuator applications. The mechanical properties, viscoelastic

---

* Corresponding author. The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, 10330, Thailand. Tel.: +66 2 218 4131; fax: +66 2 611 7221.
E-mail address: anuvat.s@chula.ac.th (A. Sirivat).

0928-4931/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2010.08.022

properties, and electrical properties will be investigated in terms of polydiphenylamine particle concentration and electric field strength.

2. Experimental

2.1. Materials

Diphenylamine, DPA (AR grade, Fluka), was used as a monomer. Hydrochloric acid, HCl (AR grade, Lab Scan), was used as an oxidant. Ammonium persulfate, $(NH_4)_2S_2O_8$ (AR grade, Riedel-de Haën), was used as an initiator. Toluene, C_7H_8 (Lab Scan, AR grade), was used as a solvent. Ammonium hydroxide solution, NH_4OH, (AR grade, Panreac), was used as dedopant. Poly(strene-block-isoprene-block-styrene) triblock copolymer, SIS (D1114P (19%wt PS), Kraton), was used as a polymer matrix.

2.2. Synthesis and doping of polydiphenylamine (PDPA)

Polydiphenylamine (PDPA) was synthesized through the interfacial polymerization according to Orlov et al. (2005) method [8]. A 0.2 M solution of diphenylamine in toluene, a monomer solution, a 0.25 M solution of ammonium persulfate, and a 1 M solution of HCl were prepared. The solutions were first cooled to −2–0 °C and then mixed momentarily. The reaction was carried out under intense stirring and temperature was kept at −2–0 °C, for 4 h. Reaction mixture was precipitated into a 5-fold excess of isopropyl alcohol, filtered, and washed many times with distilled water to neutralize the reaction. After vacuum dried at 27 °C for 24 h, the polymer obtained was a dark green powder.

The polymer was dedoped by stirring 1 g of polymers powder in a 20 ml of 1 M ammonium hydroxide solution and a 5 ml of ethanol over night, washed with ethanol/H_2O (3/1 (v/v)), and then vacuum dried at room temperature, the polymer obtained was a purple powder [9].

2.3. Preparation of De_PDPA/D1114P blends solution casting

The blends were prepared by mechanical blending of De_PDPA with an SIS triblock copolymer (D1114P) [10]. D1114P was dissolved in toluene and stirred for about 2 h. Then De_PDPA powder was added to obtain 10% (w/v) toluene solution and further stirred for 24 h. The dispersion of particles was quite homogeneous. Volume fractions of De_PDPA in D1114P prepared were 5, 10, 20, and 30%v/v. The films were cast onto a mold and left in air for a slow removal of the solvent, and then vacuum-dried to reduce stresses and residues at 120 °C for 24 h [4].

2.4. Characterization and testing of De_PDPA and the blends

The identification of functional groups of the D_PDPA and De_PDPA was investigated by a Fourier Transform Infrared spectrophotometer, FT-IR (Thermo Nicolet, Nexus 670), operated in the absorption mode with 32 scans and a resolution of $\pm 4\ cm^{-1}$, covering a wavenumber range of 4000–400 cm^{-1}, using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PDPA particles were ground with a mortar, mixed with KBr at a ratio of PDPA:KBr = 1:20.

A thermal gravimetric analyzer (Perkin Elmer, TGA7) was used to study thermal stability, moisture content, and decomposition temperature of De_PDPA with the temperature scan from 30 to 800 °C at a rate of 10 °C/min under N_2 atmosphere. The sample was weighed in the range of 5–10 mg and loaded into a platinum pan.

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, model JSM-5200) to determine the morphology of D_PDPA and De_PDPA in powder forms, D1114P, and De_PDPA/D1114P blends at various particle concentrations. The scanning electron micrographs of the conductive polymers and polymer blends were obtained by using an acceleration voltage of 15 kV at the magnifications of 1500 and 2000 times. From the SEM micrographs, the size of De_PDPA particles was measured through a Scion Image (Beta 4.0.3) program.

Morphologies of SIS films (D1114P) were observed by a TEM (Transmission Electron Microscope JEOL, model JEM-2010). The transmission electron micrographs of the films were obtained by using an acceleration voltage of 200 kV with a magnification of 10,000 times. The sample films were prepared by embedding in an epoxy resin and cured at 80 °C for 12 h. Ultrathin sections were cut from the embedded specimens by using an ultramicrotome (Reica Ultracut FCS) and a diamond knife in liquid nitrogen at −90 °C. To enhance the contrast, the ultrathin sections of the sample films were stained with osmium tetroxide (OsO_4).

The density of D_PDPA and De_PDPA was determined by using an ultrapycnometer (Ultrapycnometer 1000, V 2.4) with a small cell size. The polymers were firstly vacuum-dried for 24 h and then weighted at ambient temperature, and then loaded into the cell. Density determination was carried out 10 times for each sample under the flow purge mode, the target gas pressure of 17 psi, and calibration volumes are: V_{added} 12.4159 cm^3; V_{cell} 20.8093 cm^3.

Particle sizes of D_PDPA and De_PDPA were determined by using a particle size analyzer (Malvern Instruments Ltd. Masterizer X Version 2.15). The lens used in this experiment was 45 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 of De_PDPA, D1114P and De_PDPA/D1114P blends was measured by using a custom-built two-point probe and a resistivity test fixture (Keithley 8009 resistivity test fixture) connected with a source power supplier (Keithley/Model 6517A). The specific electrical conductivity of De_PDPAs was obtained from the two-point probe using the following equation (Eq. (1)):

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (1)$$

where σ is the specific electrical conductivity (S/cm), ρ is the specific resistivity (Ω cm), R_s is the sheet resistance (Ω/sq), t is the thickness of sample pellet (cm), V is the applied voltage (Voltage drop) (V), I is the measured current (A), and K is the geometric correction factor of the two-point probe meter which can be determined by using standard materials whose specific resistivity values are known. The correction factor was investigated by using the following equation (Eq. (2)):

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} \quad (2)$$

where ρ is the resistivity of a standard silicon wafer (Ω cm), R is the resistance of film (Ω). In the case of D1114P and De_PDPA/D1114P blend films, the electrical conductivity was obtained using the resistivity testing fixture data and the following equation (Eq. (3)):

$$\sigma = \frac{1}{\rho} = \frac{t \times I}{22.9 \times V} \quad (3)$$

A melt rheometer (Rheometric Scientific, ARES) was used to measure electrorheological properties. It was fitted with a custom-built copper parallel plate fixture (diameter of 25 mm). A DC voltage was applied with a DC power supply (Instek, GFG 8216A), which can deliver electric field strength to 2 kV/mm. A digital multimeter was used to monitor the voltage input. The oscillatory shear strain was applied and the dynamic moduli (G′ and G″) were measured as functions of frequency, temperature, and electric field strength. Strain sweep tests were first carried out to determine the suitable strains to measure G′ and G″ in the linear viscoelastic regime. The appropriate strains of De_PDPA/D1114P