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Silver nanowire/thermoplastic polyurethane elastomer nanocomposites: Thermal, mechanical, and dielectric properties

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ABSTRACT

Films of polyvinylpyrrolidone (PVP)-stabilized silver nanowire (AgNW)/thermoplastic polyurethane (TPU) elastomer nanocomposites were fabricated and characterized. With increasing loading levels of AgNW, the transparency of the nanocomposite films was reduced, but their crystallization temperatures increased, suggesting that AgNW could serve as crystallization nucleating agents. The addition of AgNW also enhanced both the Young's moduli and storage moduli of the nanocomposite films, but caused a reduction in their strain-at-break (from 536% to 304% with 1.5 vol.% AgNW) and ultimate strength (from 12.7 to 9.8 MPa with 1.5 vol.% AgNW). The specific toughness was the highest for nanocomposites with AgNW loading levels of 0.03 vol.% and 0.05 vol.%. In addition, the dielectric constant of the nanocomposite films with 1.5 vol.% AgNW was 9 times higher than that of pure TPU at 1 kHz, while the dielectric loss of all nanocomposite films studied was less than 0.2. Thus, AgNW/TPU elastomer nanocomposites with varying mechanical, dielectric, and thermal properties can be engineered by adding a small amount of AgNW. These nanocomposites can potentially be used for a wide range of applications including dielectric materials.

1. Introduction

In recent years, there has been a growing demand for high-performance dielectric elastomers for various applications including electroactive materials [1–4]. Dielectric elastomer actuators offer high energy density, large strain, and fast response times, making them very attractive for a wide variety of applications on both the macro and microscale [1,5]. Thermoplastic polyurethane (TPU) elastomers are comprised of alternating soft and hard segments. They possess high elongation, moderate tensile strength and Young's modulus, and excellent abrasion and tear resistance, thus making them a promising material for electroactuation [6–9]. However, the application of PU as an electroactive material has been limited due to the very high actuating electric field (typically greater than 100 MV/m) required to generate a large strain and a high strain energy density due to its low dielectric constant, which is, in fact, a characteristic of all dielectric elastomers [1,2]. The high power requirement may also present a real hazard, thereby further limiting its potential application. In order to enhance the dielectric constant of TPU, various types of filler—including high- dielectric-constant ceramic fillers such as montmorillonites (MMT) [10–13], titania [14,15], and barium oxide [16]—have been blended with TPU. Conductive fillers such as carbon nanotubes [17,18], copper [19], graphene [20,21], and silver nanoparticles [22] have also been blended with TPU.

Among the various conductive fillers, silver has the highest electrical conductivity (6.3×10^7 S m^{-1}) and thermal conductivity (429 W m^{-1} K^{-1}) [23]. Silver nanowires (AgNWs) have been explored extensively in the past decade due to their intriguing electrical, thermal, and optical properties, as well as their high aspect ratio [24]. Compared with Ag nanoparticles, AgNWs have much larger aspect ratios leading to a lower percolation threshold when used as nanofillers [25]. AgNW/polymer composites have been investigated for a number of applications including stretchable electrodes [26], solar cells [27], capacitors [28], and transistors [29]. However, investigations of the dielectric properties of AgNW/polymer nano composites are relatively rare. In this study, a series of AgNW/TPU nanocomposite films with various AgNW loading levels were prepared and the thermal, mechanical, and dielectric properties of these films were fully characterized.

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2. Materials and methods

2.1. Materials

TPU (Texin Rx85A, medical grade) used in this study was kindly provided by Bayer Corp. (Pittsburgh, PA, USA). Poly(vinyl pyrrolidone) (PVP, $M_w \approx 55\,000$ Da), glycerol, and N-dimethylformamide (DMF), which was the solvent used to dissolve TPU and disperse AgNWs, were purchased from Sigma–Aldrich (St. Louis, WI, USA). $AgNO_3$ powder (Strem Chemicals), isopropanol (Fisher Scientific), and NaCl (Fisher Scientific) were used in the synthesis of AgNWs. All materials were used as received.

2.2. Synthesis of PVP-coated AgNW

AgNWs were synthesized through the polyol reduction of silver nitrate ($AgNO_3$) with the assistance of a polymeric surfactant (i.e., PVP) as reported elsewhere [30]. In this typical synthesis, 5.86 g PVP ($M_w \approx 55000$) were dissolved in 190 mL of glycerol at 210 °C under vigorous magnetic stirring. Once the PVP powders were completely dissolved, the solution was then cooled down to room temperature. A quantity of 1.58 g of $AgNO_3$ powder, 0.5 mL of an aqueous solution of NaCl (with 0.059 g NaCl), and 10 mL of glycerol were sequentially added to the PVP solution. The solution was then heated to raise its temperature from room temperature to 210 °C at a ramp of 2.6 °C/min under slow magnetic stirring (~50 rpm). The reaction was maintained at 210 °C for an additional 3.5 h, and was stopped by cooling down the reaction solution to room temperature. A quantity of 20 mL of product solution was then mixed with 30 mL isopropanol followed by centrifugation at 8500 rpm for 5 min. After removal of the supernatant, 50 mL isopropanol was added to re-disperse the precipitate and the dispersion was then centrifuged at 8500 rpm for 5 min. The resulting precipitate was re-dispersed in 6.67 mL DMF for future use. The morphology of synthesized AgNWs is shown in Fig. 1.

2.3. Fabrication of the AgNW/TPU nanocomposite films

TPU pellets were dried at 80 °C for 2 h prior to solution preparation to remove residual moisture in the pellets. Two grams of TPU pellets were dissolved in 15 mL of DMF under magnetic stirring at 70 °C for 8 h. A pre-determined amount of AgNWs was dispersed in 5 mL of DMF using a bath sonicator (FS 30D, Fisher Scientific) for 30 min. The AgNW solution was then added to the TPU solution to obtain the AgNW/TPU solution with a TPU concentration of 10 wt.%/vol. (g/ml). The resulting AgNW/TPU solution was further stirred for 2 h and then sonicated for 30 min to ensure good dispersion of the AgNWs. The final solution was casted into aluminum dishes, degassed under vacuum, and finally left in a fume hood for 7 days to allow the solvent to evaporate completely. The AgNW loading levels in the TPU film were 0%, 0.01%, 0.03%, 0.05%, 0.2%, 0.5%, 1%, and 1.5% (volume percentage relative to TPU). The films were named accordingly.

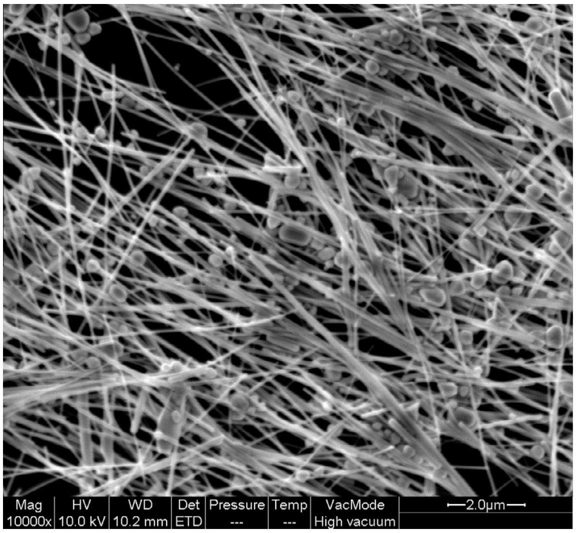

Fig. 1. Scanning electron microscopy (SEM) image of synthesized AgNWs.

2.4. Characterization of the AgNW/TPU nanocomposites

The thermal, mechanical, and dielectric properties of the AgNW/TPU composite films were characterized extensively using various methods.

X-ray diffraction (XRD, Bruker D8-Discovery) was used to characterize the AgNWs present in the nanocomposite film. The scanning 2θ angle ranged from 10° to 80°.

Thermal properties were measured using a differential scanning calorimeter (DSC, Q20 from TA Instruments). Nanocomposite films cut into small pieces (6–10 mg) were placed in standard aluminum pans and covered with lids. Samples were first heated to 220 °C and held isothermally for 5 min to remove any prior thermal history. They were then cooled to −80 °C and then reheated to 220 °C. The ramp rate in all of the heating/cooling/heating cycles was maintained at 5 °C/min. All tests were carried out under an N_2 atmosphere.

The dynamic mechanical properties of the nanocomposite films were measured using a dynamic mechanical analyzer (DMA, Q800 from TA Instruments) with a film tension clamp. Films were carefully cut into sections that were 30 mm in length and 7 mm in width. The tests were performed at a temperature ranging from −80 °C to 40 °C at a heating rate of 5 °C/min with a constant frequency of 1 Hz. Liquid nitrogen was used to regulate the temperature during heating and cooling.

The tensile properties of the films were measured according to ASTM: D882 using a universal testing machine (Instron 5967). The films were cut into rectangular shapes with a dimension of 40 mm in length and 8 mm in width. Measurements were performed at ambient temperature (~23 °C) with a crosshead speed of 10 mm/min. Five samples were tested for each film.

Scanning electron microscopy (SEM) was used to observe the AgNWs present in the AgNW/TPU nanocomposite films. The samples frozen in liquid nitrogen were broken along the thickness direction, and then coated with a thin layer of gold. The cross section images were taken using a digital LEO GEMINI 1530 SEM (Zeiss, Germany) at an accelerating voltage of 5 kV.

The dielectric properties of the nanocomposite films were measured using a precision LCR meter (Agilent E4980A) using the contacting electrode method. The dielectric constant and dielectric loss of the nanocomposite films were measured at different frequencies ranging from 10^2 to 2×10^6 Hz. The dielectric constant was calculated using Eq. (1) and the dielectric loss was directly recorded from the instrument,

$$\varepsilon_r = \frac{t_m \times C_p}{\pi\left(\frac{d}{2}\right)^2 \times \varepsilon_0} \tag{1}$$

where C_p was the equivalent parallel capacitance of the film measured by the instrument, t_m was the average thickness of the film, d was the guarded electrode's diameter, and ε_0 was the permittivity of free space, which equaled 8.854×10^{12} F/m [31].

3. Results and discussion

Fig. 2 shows the representative images of the series of nanocomposite films with increasing AgNW loading levels. The neat