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Highly stretchable dielectric nanocomposites based on single-walled carbon nanotube/ionic liquid gels

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ABSTRACT

We fabricated a highly stretchable dielectric composite using ionic liquid-based single-walled carbon nanotube gel (IL-SWCNT) as a dielectric filler and polydimethylsiloxane (PDMS) as an elastomer matrix. Transmission electron microscopy images showed that the SWCNTs were highly exfoliated and dispersed in the polymer matrix due to the addition of the ionic liquid (IL). The dielectric constant at 100 Hz of the IL-SWCNT/PDMS composite containing 1.6 wt% SWCNTs was twice that of the SWCNT/PDMS composite without IL, and the dielectric loss was one fifth that of the SWCNT/PDMS composite. In addition, the elastic modulus of the IL-SWCNT/PDMS composite was significantly lower (0.36 MPa at a strain of 20%) and the strain at break was higher (350%) compared to the corresponding values of the SWCNT/PDMS composites due to the plasticizer effects of the IL. These results provide the first feasibility study of the use of IL as both an exfoliation agent and a plasticizer in an effort to simultaneously improve the dielectric and mechanical properties of CNT-filled dielectric elastomers.

1. Introduction

The dielectric properties of polymer-based composites consisting of high-dielectric fillers have been intensively examined for a variety of potential applications, including dielectric elastomer actuators [1,2], high-*k* gate dielectrics [3,4], and embedded capacitor materials [5,6]. In conjunction with excellent dielectric behavior, the unique mechanical properties, including good stretchability and dimensional stability, of the dielectric elastomers are beneficial for realizing wearable flexible electronic devices and biomimetic transducers, such as artificial muscles or smart skin sensors [7–9]. Dielectric elastomer films with compliant electrode coatings applied to both surfaces have received considerable attention as electroactive actuator materials because they can mimic muscles through a combination of mechanical properties to achieve muscle-like actuation [1,10,11].

A large number of elastomers, including polydimethylsiloxane (PDMS), polyurethanes, and acrylonitrile butadiene copolymers, and their derivatives have been tested for their utility as dielectric composite matrices to take advantage of their outstanding mechanical properties [1,2,7,8]. Among them, PDMS is one of the most widely used elastomer due to its low viscoelasticity and modest actuation strain relative to the other elastomers. Additionally, PDMS is lightweight and biocompatible; however, PDMS has a low dielectric constant, preventing it from being used in dielectric elastomer applications. The mechanical stretching properties should ideally be enhanced prior to use in practical applications.

Of the nanoscale carbonaceous materials, carbon nanotubes (CNTs) have shown promise in composite materials, yielding high dielectric constants [12–20]. With a large aspect ratio and an intrinsic electrical property, well-dispersed CNTs in a polymer matrix can act as microcapacitors and impart a high dielectric constant to the composites [21,22]. Previous efforts to increase the dispersibility of CNTs have focused on chemical or physical modifications of the CNT surfaces [23–29]. Physical CNT surface modifications with organic molecules adsorbed through van der Waals or π–π interactions can improve the dispersibility of the CNTs in a liquid medium. Non-covalent functionalization avoids the destruction of π-conjugated CNT structures, which results from covalent functionalization approaches.

The dielectric properties of composites formed from CNT fillers and a PDMS elastomeric matrix were recently reported [30,31]. The use of CNT fillers in dielectric composites has been limited by several crucial challenges with respect to the dielectric and mechanical behaviors of the composites. Whereas the dielectric constants of a composite can increase with the number of CNTs present, dielectric loss in the percolative composites can be quite high due to an insulator–conductor transition near the percolation threshold [31]. Additionally, composites prepared with a high

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CNT content become stiff, yielding a relatively low stretchability, which has been ascribed to an increase in the elastic modulus and strength, as the CNTs act as reinforcing agents [32–34]. These studies demonstrate that despite intensive efforts toward fabricating CNT-filled dielectric elastomers, the dielectric properties and mechanical stretchability of these composites still must be improved.

Herein, we propose a solution to these challenges by using an ionic liquid (IL) as both an exfoliation agent for the CNT filler and as a plasticizer in the PDMS matrix. Single-walled carbon nanotubes (SWCNTs) and PDMS were selected as the conductive filler and dielectric elastomer, respectively. When mixed with imidazolium-based IL, SWCNT bundles can form a physical gel upon grinding [25,35]. Bundled SWCNTs can easily untangle in gels prepared with an IL to form finer bundles, therefore the IL-SWCNTs improved the dielectric properties of the SWCNT/PDMS composites. The use of IL as a plasticizer in flexible plastics has been examined previously. ILs improve the mobility of polymer chain segments in a composite when the IL molecules adsorb to bond sites inside composite networks [36,37]. Therefore, IL molecules in the IL-SWCNT gels may act as plasticizers in SWCNT/PDMS composites to attenuate the reinforcing effects of the SWCNT fillers. An IL-assisted SWCNT/PDMS composite (IL-SWCNT/PDMS) fabrication strategy should provide a dielectric material with enhanced dielectric and highly stretchable properties.

2. Experimental

2.1. Materials

SWCNTs (ASP-100F) were purchased from Hanwha Nanotech Corporation and were used without further purification. The SWCNT bundles were 20–30 nm in diameter and 5–20 μm in length. The PDMS (Sylgard 184) prepolymer and curing agent were supplied from Dow Corning Corporation. The IL, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIM][TFSI]), was purchased from Sigma–Aldrich and was used as an exfoliation agent without further purification.

2.2. Preparation of the SWCNT/PDMS composites

As-received SWCNTs were ground with the IL until gelation was observed. The IL-SWCNT gels were dispersed in toluene at 1 mg/mL for 1.5 h in an ultrasonic bath. The IL-SWCNT solution was mixed with the PDMS prepolymer followed by careful stirring for 6 h at room temperature. Excess toluene was removed under vacuum for 48 h at room temperature, and curing agent was added to the IL-SWCNT/PDMS mixture to a concentration of 10 wt% with respect to the total weight of the PDMS. The final solution was carefully mixed using a paste mixer for 3 min, cast onto a flat copper foil, and cured at 150 °C for 10 min. The quantity of SWCNT present in the PDMS matrix varied from 1 to 2 wt%.

2.3. Characterization

The microstructures of the SWCNT/PDMS composite thin films were examined by transmission electron microscopy (TEM, FEI, Tecnai G2) after spin coating of the SWCNT/PDMS solution onto TEM grids at 2000 rpm for 1 min. The dielectric properties of the composites were measured using an impedance analyzer (Agilent 4263B) after sputtering deposition of a gold electrode 10 nm in diameter on top of the film. At least five specimens of each sample were tested, and the average dielectric constants were obtained. The different specimens were prepared from the same batch in order to see any change in the dielectric properties before and after stretching. Gold electrodes with area of 2×2 mm^2 were deposited onto each composite film as a top and bottom electrodes. The mechanical properties of the composites were characterized by fabricating a free-standing film. The solution was coated onto a flat copper foil, and then the film was peeled off from the foil. The mechanical properties of the composites were measured using a universal testing machine (Instron-5567, Instron) with a 1 kN load cell at a crosshead speed of 10 mm min^{-1}.

3. Results and discussion

3.1. Effects of the ionic liquid on the exfoliation of SWCNTs

SWCNT-embedded composites with a high dielectric constant were fabricated by first debundling the SWCNTs without loss of their intrinsic electrical conductivity, then by dispersing the SWCNTs well into the given matrix. SWCNT bundles can be exfoliated to much finer bundles by grinding in an imidazolium-based IL without disruption of the π-conjugated CNT structure because the ILs interact with SWCNTs through van der Waals interaction [25,35]. As illustrated in Fig. 1, an IL-SWCNT gel was prepared by mixing as-received SWCNTs and [BMIM][TFSI] as an IL component. The IL-SWCNT gels were easily dispersed in toluene by sonication, then blended with PDMS to prepare a series of IL-SWCNT/PDMS elastomers after curing.

Fig. 2a and b show TEM images and EDS (energy dispersive X-ray spectroscopy) spectra of the SWCNTs and IL-SWCNT (IL:SWCNT = 5:1 in weight). As shown in Fig. 2a, SWCNTs usually exist as bundles that are heavily entangled to form agglomerates. Upon gelation with [BMIM][TFSI], the SWCNTs were exfoliated to form much finer bundles than those of the as-received SWCNTs. Subsequently, elemental analysis using EDS revealed that additional oxygen, fluorine, and sulfur atoms were present on the surfaces of the IL-SWCNTs, suggesting the presence of [BMIM][TFSI] molecules among the SWCNT bundles. The EDS data and TEM images of the as-received SWCNT and IL-SWCNT gel confirmed that [BMIM][TFSI] effectively exfoliated the SWCNTs to provide highly exfoliated fine SWCNT bundles, in accordance with previous reports [25,35]. The morphology of the IL-SWCNT gel dispersed in toluene was reflected in the level of SWCNT debundling and dispersion in the PDMS matrix. The morphologies of the PDMS composites prepared with 1.6 wt% SWCNT were analyzed using TEM. As shown in Fig. 2c and d, exfoliated SWCNTs with a diameter of approximately 30 nm were observed in the IL-SWCNT/PDMS composite (IL:SWCNT = 5:1 in weight), whereas the entangled SWCNT bundles with a diameter of more than 100 nm were observed in the SWCNT/PDMS composite prepared without IL. The exfoliation level and bundle thickness of the SWCNTs for a given loading content in the PDMS matrix were correlated with the dielectric and mechanical properties of the composites.

3.2. Dielectric properties of the composites

The weight ratio of IL to SWCNTs was optimized by preparing SWCNT/PDMS composites with different concentrations of IL (1.6, 8.0 and 16.0 wt% IL). The dielectric constants and dielectric losses were then measured at a frequency of 100 Hz. In these experiments, the quantity of SWCNTs in the PDMS was fixed at 1.6 wt%. As shown in Fig. 3, the SWCNT/PDMS composite without IL showed a high dielectric constant of 657, but it also showed a very high dielectric loss, in excess of 10, which was not detected using our instrument. By contrast, the incorporation of IL into the SWCNT dispersion dramatically reduced the dielectric losses of the composites to 2 and increased the dielectric constant by a factor of two relative to the dielectric constant for the composite pre-