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Material properties

Investigation of carbon black/silicone elastomer/dimethylsilicone oil composites for flexible strain sensors

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ABSTRACT

Conductive carbon black (CB) nano-particle filled silicone elastomer (SE) composites with dimethyl silicone oil (SO) as a diluting agent and plasticizer were fabricated for potential strain sensing applications. Heat treatment was used to stabilize the composites, and thermal gravimetric analysis confirmed the good stability of the composites after heat treatment. Effect of CB loading on electrical properties of the composites was studied and a percolation transition range of 0.5–2.5 wt% was observed. I–V characteristics and impedance analysis were used to reveal the conductive mechanisms of the composites. The presence of SO reduced the Young's modulus of the composites without lowering the elongation at break. Characterization of coupled electromechanical properties of the composites demonstrates that, in the post-percolation range, the 9.0CB composite possesses suitable strain sensitivity, good repeatability and linearity as well as slight strain rate dependence, so that it can be used in flexible strain sensors for measuring repeated large deformations.

1. Introduction

Electrically conductive elastomeric composites have been intensively investigated for smart structure applications in electromagnetic shielding [1], electrostatic charge dissipation [2], electronic switch [3], self regulating heaters [4] and sensors [5–7]. Their perceived advantages include excellent flexibility, low weight, high environmental stability and safety as well as low manufacturing cost. One of the very promising applications is flexible strain sensors that can measure large repeated strain or displacement, which are important elements for wearable electronics and human–machine interaction devices. These flexible strain sensors require the following essential material properties: sensitive to strain; large strain measurement range; good repeatability in electromechanical response; predictable temperature effect; predictable strain rate effect; high resistance to fatigue; long-term environmental and chemical stability, and low Young's modulus that is comparable to human skin. They represent a new type of sensing device as the current metal based strain gauges and fiber optic strain sensors cannot deliver the required performance.

Elastomers filled with electrically conductive fillers show piezoresistivity and are promising candidates for such sensors [8]. The matrix materials studied include synthetic and natural rubbers [9,10], thermoplastic elastomers [11,12]and silicone elastomer (SE) [13–15]. However, high temperature and pressure are employed for vulcanization of the materials [14,16], which significantly limits their application in textiles that are easily damaged under such conditions [17]. Room temperature vulcanized SE that has low levels of viscosity, vulcanizing temperature and pressure, along with good biocompatibility, excellent mechanical properties and thermal/chemical resistance, is a promising matrix material for flexible conductive composites.

Among the three major groups of conductive fillers, i.e., metallic fillers, carbonaceous fillers, and intrinsically

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conductive polymers, the second group is more attractive because of their low density and high environmental stability, or good chemical stability. Conductive composites with graphite powders and carbon fibers have been studied for strain sensing applications [18,19]. However, a higher filler loading was required, and sliding wear behavior of graphite and brittleness of carbon fiber composites resulted in poor repeatability in electromechanical responses under cyclic mechanical tests. Although carbon nanotube [20] and graphene [21] composites can be applied in strain sensing applications with a low loading, the high price, uncertain safety effect on humans, as well as the availability of large scale industrial production hinder their usage as compared to low priced conductive carbon black (CB).

There are great challenges in mixing high loadings of CB with SE in the post-percolation threshold region since the viscosity of the mixture increases drastically with increasing CB loading. One possible way to solve the problem is to add organic solvents such as hexane to reduce their viscosity and disperse CB particles. However, the Young's modulus of the resultant composites increases significantly [15], leading to undesirable high rigidity. Conductive composites with CB loadings in the percolation range have high sensitivity. However, the significant resistance change of several orders of magnitude in small strain ranges make their measurement difficult.

In the present work, highly porous CB nano-particle filled SE composites were fabricated with dimethyl silicone oil (SO) as a diluting agent and plasticizer. Electrical, mechanical and thermal properties of the composites were studied experimentally. Desirable sensitivity, linearity and working ranges were identified with consideration of their potential applications as flexible strain sensors.

2. Experimental

2.1. Materials

Low structure but highly porous (more than 80%) CB nano-particles (Carbon® ECP600JD, Akzo Nobel, diameter of about 30 nm) were heated at 80 °C for 24 h to remove the moisture. The surface area of the CB particles is ca. 440–510 ml/100 g expressed by dibutylphthalate (DBP) absorbing value. SE (ELASTOSIL®LR6200 A and B, Wacker Chemie AG, Germany) was used as received. Nontoxic dimethyl SO with kinetic viscosity of 5.0 mm^2/s at 25 °C (Che Scientific Co., Hong Kong) was used as solvent to reduce the viscosity of the mixture paste and as plasticizer to reduce the modulus of the composites. Silver coated nylon yarn was used as conductive connecting wire between the conductive composite and measuring equipment.

2.2. Fabrication

CB, SE (with equal weight of the two parts), and SO were weighed and mixed in a plastic beaker, and then further blended on a three-roll mill (PTR 65, Puhler, Germany) for 15 min at ambient temperature. The mixture was cast into a polytetrafluoroethylene (PTFE) mold and degassed in a vacuum oven for 10 min. Then, silver coated nylon yarns were embedded parallel in the film as conductive wire with a distance apart of 12 mm and vulcanized at 100 °C for 2 h to obtain the specimens (20 mm × 10 mm × 1 mm). For I–V characterization, pellet shaped composite samples with a diameter of 13 mm and thickness of 2 mm were fabricated with two parallel stainless steel electrodes pasted on both sides of the composites before curing to reduce the contact resistance. The compositions and codes of all samples are listed in Table 1. The samples were heated in a vacuum oven at 100 °C for 100 h to release stress and volatilize excessive SO before further characterization.

2.3. Characterization

Scanning electron microscopy (SEM) observation of the CB/SE/SO composites was performed with a field emission scanning electron microscope (JEOL JSM-6335F, JEOL Ltd., Japan). The specimens were prepared by freeze-fracturing in liquid nitrogen followed by applying a gold coating. The CB/SE/SO mixture paste was heated at 100 °C for 200 h and its weight was recorded every 2 h for the first 50 h and every 10 h after the 50th hour. Thermo-gravimetric analysis (TGA) of the materials and the heat treated composite samples were carried out from 35 to 1300 °C (900 °C for CB) under nitrogen atmosphere by using a NETZSCH TGA/DSC instrument with a heating rate 20 °C/min.

I–V curves of the pellet shaped composite samples were measured with a814 photomultiplier detection system (Photon Technology International) with voltage gradually increasing from −50 to 50 V under ambient temperature. The impedance analysis was performed by a Solartron SI 1287 electrochemical interface combined with a 1252A frequency response analyzer with potential and current controlled at 10 V and 0.1 A, respectively. The frequency varied from 10^5 Hz to 10^{-1} Hz with an interval of 1 Hz.

The electrical resistance of the samples without strain was measured by a digital multi-meter (Keithley 2010, Keithley Instruments Inc. USA) using the 2-wire method for resistance lower than 10^8 Ω, while an insulation resistance tester (YD 2683, Yangzi Electronics, China) was used for higher resistance. The volume resistivity, ρ, is calculated by

$$\rho = R \cdot w \cdot d / l \quad (1)$$

where R is the resistance (Ω), l, w and d are the length, width and thickness of the samples, respectively.

The measurement setup for coupled electromechanical properties of the composites is shown in Fig. 1. The force and displacement were obtained with a Universal Material Tester (Instron 5566), and resistance from the digital multimeter (Keithley 2010), simultaneously. The initial gauge

Table 1
Composition of samples.

Sample code	Composition (weight ratio)	Sample code	Composition (weight ratio)
SE	CB/SE/SO 0.0/100.0/0.0	2.5CB	CB/SE/SO 2.5/97.5/45.0
SE/SO	CB/SE/SO 0.0/100.0/20.0	3.0CB	CB/SE/SO 3.0/97.0/50.0
1.0CB	CB/SE/SO 1.0/99.0/45.0	4.5CB	CB/SE/SO 4.5/95.5/75.0
2.0CB	CB/SE/SO 2.0/98.0/45.0	6.0CB	CB/SE/SO 6.0/94.0/100.0
2.3CB	CB/SE/SO 2.3/97.7/45.0	9.0CB	CB/SE/SO 9.0/91.0/150.0