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Mechanical and electrical behavior of rubber nanocomposites under static and cyclic strain

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ABSTRACT

Rubber nanocomposites based on carbon nanotubes (CNT), graphitic nanofiller (GR), and their hybrid (CNT+GR) were studied under static and cyclic strain for robotics applications. Room temperature vulcanized (RTV) silicone rubber was used as a matrix for the nanocomposites, which were prepared by solution mixing. The specimens based on CNT show a better modulus of 1.77 MPa than GR (0.71 MPa) and CNT+GR hybrid (0.85 MPa) specimens. The resistance was 0.27 kΩ (CNT) and 30.48 kΩ (CNT+GR hybrid) at 10% strain and increased to 0.35 kΩ and 46.49 kΩ at 100% strain. During cyclic strain (30%) tests, the CNT-based specimen shows larger hysteresis losses (slope m = -0.179) as dissipated heat than the GR (m = −0.032) and CNT+GR hybrid (m = -0.096) specimens. The specimens were tested as electrode materials in an actuator, and higher displacements of 1.992 mm (CNT), 1.489 mm (CNT+GR hybrid), and 0.075 mm (GR) were achieved at 10 kV (3 phr). Such improvements could be useful in intelligent objects as artificial muscles or electro-active locomotive parts.

1. Introduction

Carbon is well known for its allotropic forms [1], such as graphite [2], graphene [3], carbon nanotubes (CNT) [4], fullerene [5], and carbon black (CB) [6]. CNT and graphene have been studied extensively in the last decade for many applications [7–9]. Graphitic nanofillers (GR) are three-dimensional carbon nanomaterials with sp^2 hybrid carbon atoms and at least one dimension in the range of 1–100 nm [10]. The particle dimensions of graphene and CNTs are critically dependent on the synthesis method [11].

Recently, CNT and GR have been used as nanofillers to reinforce polymer composites for industrial applications [12]. Improved mechanical stiffness and electrical conductivity were obtained for polymer composites based on such nanofillers [13,14]. Such improvements were due to good filler networking, interfacial adhesion, and distribution of the filler particles in a highly exfoliated state [15–18]. However, nanofillers aggregate at higher concentration due to van der Waals forces between adjacent particles [16–19].

The characteristic features of elastomers are strongly influenced by dispersion of the filler [18–20]. In addition, the properties are affected by morphological features of the filler particles [20–23]. A strategy of using the filler particles in hybrid form was reported to be useful for obtaining higher properties at low filler content [24,25]. However, there has been little work on filler dispersion, especially for dispersing CNT particles or hybrid systems with the least amount of aggregates in a rubber matrix. Existing actuators using electro-active elastomers have many limitations, such as large dissipation losses, low stability of the elastomer components under cyclic and static strain, high filler content required to achieve the optimum balance in electro-active components, and poor lifetime stability. Basic challenges for reinforced elastomers include large dissipation losses, filler flocculation, and uniform filler dispersion [26,27]. These features are useful for designing locomotive parts. This work addresses some of these challenges by investigating the mechanical and electrical properties under static or cyclic strain, including the filler percolation threshold and different features of nanofillers as shown in Scheme 1.

Room temperature vulcanized (RTV) silicone rubber is composed of a base and curatives with variable hardness. The characteristic features of silicone rubber include easy processing, lower viscosity, and good acid resistance. RTV silicone rubber is traditionally used as an electro-active elastomeric matrix due to its wide range of applications, such as actuators. The present work

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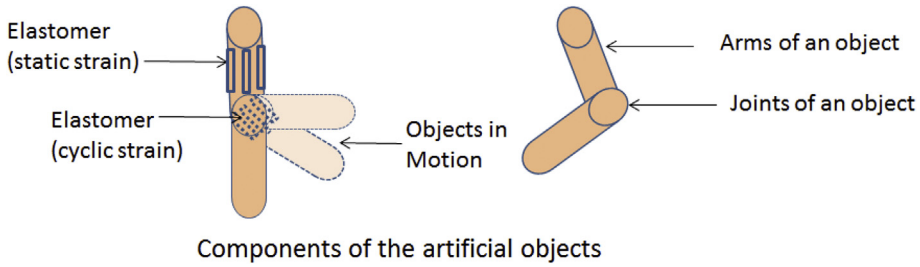

Scheme 1. Use of electro-active components in artificial objects.

examines GR, CNT, and their hybrid under static and cyclic strain in RTV silicone rubber. The components result in minimal dissipation losses, stable electrical properties at up to 100% strain, and efficient filler networking. The properties were measured through cyclic and static strain tests to mimic the stationary phase and movement phase in an actuator for a robot. In cyclic strain, the movement ranges from 0° up to 180°, while static strain is investigated under no strain or under strain in one dimension.

2. Experimental

2.1. Materials

The polymer matrix used in this work was a RTV silicone rubber (KE-12; viscosity = 100 poise at 25 °C, Shin-Etsu Chemical Corporation Ltd., Japan). Hardener (CAT-RM) was obtained from Shin-Etsu Chemical Corporation Ltd., Tokyo, Japan. The carbon nanofillers were multi-walled CNT (MWCNT, CM-100, Hanwha Nanotech Corporation Ltd., Seoul, Korea) and GR (Nano19, Asbury Mills Inc., California, USA). The GR was >99.5% carbon, while the CNT were >96%. The BET surface area of nanofillers was 125 m^2/g for GR and 215 m^2/g for CNT.

2.2. Characterization techniques

The morphological features of nanofillers were studied through SEM micrographs and XRD analysis. SEM micrographs were obtained in ambient conditions using an S-4100 (Hitachi, Japan). The XRD analysis was carried out using a diffractometer (D8 Advance, Bruker; Germany) at an accelerating voltage of 40 kV with monochromatic high-intensity CuK_α radiation (λ = 1.5406 Å) and a cathode current of 30 mA. The filler percolation threshold of the specimens was investigated using a tapping mode atomic force microscope (NanoScope IIIa, Digital Instruments, Santa Barbara, California, USA) at a scan rate of 0.6 Hz and scan size of 3 μm.

The nanocomposites were investigated using dynamic compressive tests with cylindrical samples (20 × 10 mm) under a load of 0.5 kN and a strain rate of 2 mm/min up to 35%. Tensile tests were done under a uni-axial load of 0.1 N at 50 mm/min until break. Loading and unloading cycles to 150% strain were applied for 10 consecutive cycles to dumbbell-shaped specimens with 2-mm thickness. The resistance profiles of specimens were obtained in ambient conditions with a digital multimeter (34401A, Agilent Technologies Inc., California, USA).

All mechanical tests were performed using a universal test machine (Lloyd Instruments, West Sussex, UK). Actuation displacement measurements were obtained with a laser sensor (Opto NCDT 1302, Micro-Epsilon Messtechnik GmbH & Co. KG, Ortenburg, Germany). The composite specimens were used as an electrode material to study the displacements. The electrodes were fabricated on either surface of an elastomer slab, and measurements were performed in ambient conditions on a dry specimen.

2.3. Preparation of nanocomposites

Specimens were prepared using RTV silicone rubber by normalizing a rubber matrix in a homogenizing machine for 30 min. Then, nanofillers were added (Table 1) and mixed thoroughly for 15–18 min.

After de-aeration in a vacuum for 12–15 min, 3 phr of hardener was added to the specimen and mixed for ~1 min. In the final step, the sample was poured in a cylindrical mold (20 × 10 mm) and kept in ambient conditions to dry.

3. Results and discussion

3.1. SEM micrographs

SEM micrographs of GR and CNT at lower and higher resolution are presented in Fig. 1. The micrographs of GR reveal a platelet-like shape at lower resolution (Fig. 1a). Few aggregated structures and some exfoliated, nearly transparent sheets (indicated by arrows) were observed at higher resolution (Fig. 1b). Very few isolated, transparent layers with corrugated features were found, while some were closer to the thick lamella of GR, which resembles graphene [11]. Stacks of graphitic layers in aggregated structures occurred with variable thickness, which depends on the number of layers in the flake [17,25]. The histogram for the number of layers in the GR flakes can be evaluated further through Raman spectroscopy [11].

SEM micrographs of CNT reveal tube-like features with different lengths and diameters. The lower-resolution images show that the tubes have random alignment and different sizes (Fig. 1c). The high-resolution images of CNTs show that the particles were entangled and arranged in a highly interwoven state (Fig. 1d). The length of the tubes was also estimated to be in range of a few nanometers to the sub-micron range. The diameters were in the range of 15–18 nm, but mostly below 20 nm. The CNT diameter can vary from 0.8 nm to 20 nm and sometimes exceeds 100 nm. Similarly, its length can range from less than 100 nm to several centimeters [13]. The dimensions and orientation of the CNTs can be controlled through the synthesis method [28].

3.2. XRD analysis

XRD analysis was used to investigate the crystal structure of the filler particles (Fig. 2). The XRD patterns of GR show a prominent

Table 1
Content of rubber nanocomposites in parts per hundred parts of rubber (phr).

RTV silicone = 100; Hardener = 3			
GR	2	3	5
CNT	2	3	5
CNT+GR	1 + 1	1 + 2	2 + 3