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Silicone rubber nanocomposites containing a small amount of hybrid fillers with enhanced electrical sensitivity

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ABSTRACT

A conductive silicone rubber (SR) composite, filled with both carbon nanotubes (CNTs) and carbon black (CB) is prepared by a simple ball milling method. Because of the good dispersion and synergistic effects of CNT and CB, the SR composite (SR with 2.5 phr CB and 1.0 phr CNT hybrid fillers) shows improvement in mechanical properties such as tensile strength and strain to failure. As well, due to the assembly of conductive pathways generated by the CNT and CB, the nanocomposite becomes highly conductive at a comparatively low concentration, with high sensitivity for tensile and compressive stress. Long-term measurement of properties shows that the SR composite maintains the excellent electrical properties under different strain histories. These outstanding properties show that the SR composite has potential applications in tensile and pressure sensors.

1. Introduction

Conductive rubber nanocomposites, consisting of an insulating rubber matrix and conductive fillers, have stimulated great interest in recent years. Due to their resistance to corrosion and low density combined with increased tensile strength, improved stiffness, abrasion resistance and flame retardant behaviour, as well as high electrical conductivity and sensitivity, these composites can be used in many industrial fields, ranging from automobile components to electrical and sensing devices [1–3].

The electrical conductivity of rubber composites is based on conductive networks built by nanofillers such as carbon nanotube (CNT) and carbon black (CB). Generally, higher electrical conductivity is obtained by increasing the content of conductive fillers. However, employing conducting fillers is limited by the increase in bulk viscosity, which produces void-free composites and good dispersion of fillers in the matrix becomes more difficult [3–5]. Of particular interest is the so-called percolation threshold (PT), i.e., the minimal loading of conductive filler required to form a network or cluster that spans the whole system (the "percolation network"). From a technological point of view, the central issue is to produce a nanocomposite with controllable conductivity and as low as possible a loading of conductive filler [6,7]. Many factors, including the mean aspect ratio and the length and polydispersity of fillers, as well as interactions between them and the polymer matrix, potentially affect the PT that must be achieved in the liquid state before the structure freezes upon solidification of the polymeric host material [8].

Much effort and many techniques have been applied to create conductive rubber composites producing conductive and sensitive composites suitable for pressure sensor applications. Mahmoud et al. [9] claimed acrylonitrile butadiene rubber (NBR) filled with 70 phr (parts per hundred parts of rubber) of furnace black to be the composite most sensitive to variation of compressive strain in their research. In another study, natural rubber (NR) with a content of 20 wt.% CB had the highest pressure sensitivity than those of NR composites with other CB contents [10]. 14 vol.% CNT in SR was considered to be suitable for pressure sensors [11]. All these composite materials had very high filler content. They were fabricated by a casting or compression moulding technique and required higher pressures, solution mixing, or ultrasonic vibration for evaporation of the solvent. A pressure-sensitive wireless stress measurement system suggested by Wang et al. [12], made of SR containing 5 phr CB, was also prepared by solution mixing and ultrasonication. Mentioned for comparison reasons, polyolefins (HDPE and PP) have also been used as matrices for conductive and pressure-sensitive composites. They were compression moulded at 22 MPa and 180 °C and proposed for sensor-enabled geosynthetics [13].

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To illustrate the technical capabilities of conductive rubber composites, recent publications claim a few modern applications of these materials. Spray-deposited conductive layers of CNT on polydimethylsiloxane (PDMS) substrates can be used for transparent and stretchable electronic devices [14]. Another example is light-emitting devices which can be prepared by in situ photopolymerisation of a liquid monomer penetrating into a porous CNT-coating [15] or by screen printing of a CNT-paste on rubber sheets [16,17]. Moreover, the composite materials mentioned [13–15] show a change of electrical resistance during extension and therefore a tensile sensitivity.

Hybrid fillers of CB and CNT lead to enhanced electrical conductivity at low filler content due to a synergistic effect, as claimed and explained by Ma et al. [18]. They filled epoxy with both CB and CNT and noticed a remarkable increase in conductivity at concentrations of at most 2 wt.% CB and 0.4 wt.% CNT.

This study designs a simple silicone rubber nanocomposite fabrication technique with the nanocomposite having potential tensile and pressure sensor applications. The resulting SR composite has a low content of hybrid fillers of CNT and CB and can be prepared void-free in spite of high viscosity. Electrical conductivity and sensitivity have been characterised when the tension and compression forces were acted on the SR composite. The long-term electrical properties are also discussed here.

2. Experimental details

2.1. Materials and sample preparation

A room temperature vulcanising two-component silicone rubber: Part A and Part B (RTV-2 SR, Barnes Products Pty. Ltd., Australia) was used as matrix. Superconductive CB (Printex® XE2, nominal particle size 35 nm, Degussa Australia Pty. Ltd.) and multiwall CNT (MWCNT, degree of purity >95%, diameter 40–60 nm, length 5–15 μm, Shenzhen Nanotechnologies Co. Ltd., China) were used as fillers. The CB particles were made by the manufacturer into particle agglomerates with a diameter of up to 40 μm, for considerations of safety and convenience in transportation and handling. Therefore, for a uniform dispersion, master batches of the two components of the rubber containing 2.5 phr CB and 1.0 phr CNT were prepared using a planetary ball mill (Fritsch Pulverisette 5) for 24 h at 240 rpm. After that, the master batches were mixed, and the mixture was degassed for 10 min using a vacuum oven, manually pressed to a thin film (1 mm) and then cured for 2 h at 70 °C to accelerate the vulcanisation process. After curing, the SR composite film was cut into samples of 10 mm × 50 mm × 1 mm for tensile and fatigue tests and 25 mm × 40 mm × 1 mm for compression tests. Fig. 1 shows the preparation procedures for the SR composite samples.

2.2. Characterizations

Rheological temperature sweep measurements of the uncured pure rubber and rubber composite components were performed on an Anton Paar Physica MCR301 rheometer at the linear viscoelastic region of 2% and 0.2% strain, respectively. Temperature was linearly increased from room temperature to 80 °C and frequency was set to 10 Hz for each test. Electrical resistance was measured directly using a digital multimeter (Dick Smith Electronics Q-1559).

Tensile tests were performed on an Instron 5567 testing machine at room temperature in accordance with ASTM: D412. Samples of gauge length 20 mm were stretched at a crosshead speed rate of 50 mm/min until failure. The same parameters were used for tensile sensitivity experiments. Electrical resistance was measured after stretching and maintaining the samples at certain extensions (Fig. 2a). For pressure sensitivity tests the samples were compressed with the same testing machine at room temperature and at a deformation rate of 0.5 mm/min. Again, resistance was noted after compression and holding at certain loads (Fig. 2b).

Fatigue tests were carried out on an Instron 8800 testing machine with samples of gauge length 40 mm at room temperature with frequency of 1 Hz and strain of 25%. Resistance was measured before and after 1, 10, 100, 1000 and 10,000 cycles. The strain was applied as a haversine waveform, which can be expressed as

$$\varepsilon = \text{haversin}(t) = \sin^2\left(\frac{t}{2}\right) = \frac{1-\cos(t)}{2} \quad (1)$$

For each experiment in this study, at least three specimens were tested for statistical analysis.

3. Results and discussion

3.1. Viscosity of uncured materials

The complex viscosities of both the pure rubber components and the filled rubber components are shown in Fig. 3. Part A has a slightly higher viscosity than Part B. By dispersing 2.5 phr CB and 1.0 phr MWCNT in the rubber, viscosity increased from 5 Pa s to approx. 200 Pa s, which was about two orders of magnitude higher than that of the pure material. Due to this increase in viscosity, air could not escape automatically during the curing at atmospheric pressure [4,5]. Even heating up to 80 °C barely affected the viscosity of the filled rubber components and, as a consequence, did not benefit deaeration. Therefore, vacuuming is one possible fabrication step to produce void free composites.

3.2. Electrical and mechanical properties

To optimize the electrical resistance of the SR composite, many different contents of CB and CNT in SR were investigated. The results of electrical resistance measurements are shown in Fig. 4 and Table 1. Using a single conductive filler generates composite materials with fairly high electrical resistance. Due to the synergistic effects, the electrical resistance is lower when hybrid fillers are used than when a single filler is used with a similar overall concentration. Hence, we measured values of 250 kΩ for SR/4.0 CB and

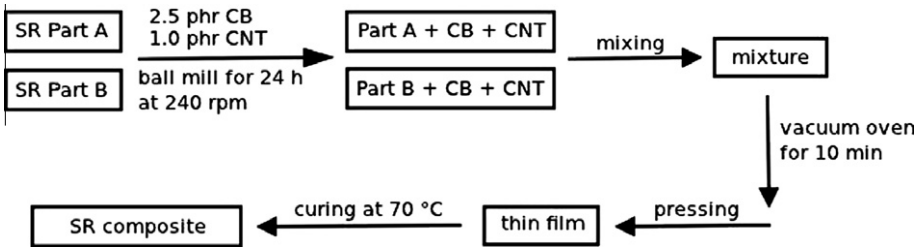

Fig. 1. Fabrication technique of the SR nanocomposite.