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High elasticity and conductivity of elastomer composites with arrayed carbon nanotubes as nanosprings

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ABSTRACT

Previous studies using molecular simulation indicated that carbon nanotubes (CNTs) can act as nanosprings to adjust the viscoelasticity of elastomer composites. In this study, we prepared elastomer composites with both high elasticity and conductivity for the first time using carbon nanotubes array (CNTA) as nanosprings. A special CNTA bundle prepared by electrostatic self-assembly was directly blended with the polymethylvinylsiloxane (PMVS) matrix. The results indicated that these CNTAs were well dissociated into many single CNTs with almost no change in length in the PMVS matrix with low viscosity during mechanical shearing, and exhibited a nanospring effect. The CNTA composites exhibited not only higher conductivity and electromagnetic shielding effectiveness but also higher elasticity than the commonly used conductive carbon black composites at the same filler content. This study indicated that high performance conductive elastomer composites can be obtained by using special CNTAs as nanosprings.

1. Introduction

By virtue of the high flexibility, elasticity and sealability of elastomers as well as the high electrical conductivity of conductive fillers, conductive elastomer composites (CEC) have been widely used in applications such as electromagnetic interference (EMI) shielding, electrostatic charge dissipation, touch-control switches, sensors and surface heaters [1–5]. The formation of conductive network, which is mainly affected by the content and length to diameter ratio of conductive fillers and the dispersion of the fillers in the matrix, is a key to achieve high conductivity. Accordingly, increasing the content of conductive fillers is a simple and efficient method for achieving high conductivity. However, the increase in the content of fillers will inevitably lead to a loss in elasticity and deterioration in mechanical and processing properties [6–8].

Theoretically, the high elasticity of an elastomer derives from the relaxation ability of the elastomer macromolecules. During the relaxation of the macromolecules, the intra-macromolecular friction results in viscoelastic losses in the form of heat dissipation, leading to some irreversible deformation of the elastomer [9]. As a result, the elastic recovery ability of the elastomer decreases. With the addition of rigid conductive fillers, the elasticity of the composites further decreases because of the large increase in viscoelastic loss caused by the filler–filler and filler-macromolecules friction. Therefore, the preparation of elastomer composites with high elasticity and conductivity is always a challenge [10].

Carbon nanotubes (CNTs) with very small diameters and large length to diameter ratios can improve not only the conductivity of the elastomer at a low contents of fillers but also the mechanical properties of the composites [11–14]. However, only a few studies have been focused on the high elasticity of CNTs. For example, Falvo et al. reported that multi-walled carbon nanotubes (MWCNTs) can be bent repeatedly through large angles by using the tip of an atomic force microscope (AFM), suggesting that nanotubes have good flexibility and elasticity [15]. Cao et al. reported that a free standing film of vertically aligned carbon nanotubes exhibited super-compressible foam-like behavior. Under compression, the

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nanotubes collectively form zigzag buckles that can fully unfold to their original length upon load release [16]. In our previous study [17], we demonstrated by molecular simulation methods that CNTs with high flexibility and reversible elastic deformation can act as nanocoils or nanosprings to adjust the viscoelasticity and decrease the permanent set of elastomer composites when the CNTs are well dispersed in the rubber matrix and have a strong interfacial interaction with the rubber matrix. This motivated us to introduce CNTs into an elastomer matrix to prepare CEC with high elasticity and conductivity, which has not been reported yet.

In this study, we prepared CNTs/elastomer composites with high elasticity and conductivity for the first time by using carbon nanotubes arrays (CNTAs) as nanosprings. Polymethylvinylsiloxane (PMVS) with high flexibility, elasticity, thermal resistance, and processability (low viscosity) was used as the elastomer matrix [18,19]. A specially aligned CNTs bundle (called CNTA) prepared by electrostatic self-assembly was directly blended with PMVS. These CNTAs were well dissociated into many single CNTs with almost no change in length in the PMVS matrix with low viscosity during mechanical shearing, and exhibited a nanospring effect. The CNTA composites exhibited not only higher conductivity and electromagnetic shielding effectiveness, but also much higher elasticity than the commonly used conductive carbon black composites at the same content of fillers. This study indicated that high performance conductive elastomer composites can be obtained by using special CNTAs as nanosprings.

2. Experimental

2.1. Materials

Carbon nanotube arrays (CNTAs) was supplied by CNano Technology Co., Ltd., China. Polymethylvinylsiloxane (PMVS, $M_n = 570$ K) consisting of 0.12–0.2wt% vinyl was purchased from China National Blue Star (Group) Co., Ltd., China. Carbon black (CB, EC600-JD) was purchased from Akzo Nobel Corp. γ-(methacryloxy) proxyltrimethoxysilane (KH570, $CH_2{=}C(CH_3)COOCH_2CH_2CH_2$-$Si(OCH_3)_3$), was provided by Nanjing Crompton Shuguang Organosilicon Specialties Co., Ltd., China.

2.2. Preparation of composites

The volume fractions of nanofillers in the composites were 0.28 vol.%, 0.57 vol.%, 1.13 vol.%, 1.7 vol.%, 2.7 vol.%, 3.53 vol.% and 5.7 vol.% in this study. CNTA was first modified by KH570 [28] (the loading level of KH570 was 5 wt% of CNTA) using the method presented in Ref. [29]. For the CNTA/PMVS composites, PMVS and the modified CNTA were first mixed by using a two-roll mill (Zhanjiang Machinery Factory, China). The gap between the two rolls was adjusted to ~0.5 mm for high-shear blending, which was followed by the addition of a vulcanizer, weight ratio of 20:1). The optimum curing time was determined with an oscillating disc curemeter, and the composite was vulcanized on a lab platen press under 25-ton pressure. The vulcanization temperature was 170 °C. Then the composite was vulcanized in a draught drying cabinet under air atmosphere at 200 °C for 2 h. The same procedure was used to prepare CB/PMVS composites and CNTA/CB/PMVS composites. For the CNTA/CB/PMVS composites, CB was first mixed with PMVS before the above procedure.

2.3. Characterizations

The morphology of CNTA was observed under a scanning electron microscope (S-4800, Hitachi Company, Japan) with an acceleration voltage of 5 kV. The morphology of the CNTs in the composites was observed under the same scanning electron microscope (SEM), but the samples were first tensile fractured and coated with gold. The dispersion of CB and that of CNTA were observed by using an atomic force microscope (Multimode8, Bruker Daltonics Inc., Germany) and a transmission electron microscope (JEM-2100, JEOL, Japan), respectively.

The volume resistivity of the composites with a high resistivity ($\geq 10^4\ \Omega$) was measured by using a high resistance meter (PC68, Shanghai Precision & Scientific Instrument Co., Ltd., China). A DC Bridge (QJ84, Shanghai Zhengyang Instrument Factory, China) was used to measure the volume resistivity of composites with low resistivity according to Chinese standard GB/T 2439-2001. The volume resistivity (ρ) was calculated by

$$\rho = R \times S/L \tag{1}$$

where R is the electrical resistance of the sample, S is the cross-sectional area, and L is the length of the sample. The conductivity (σ) is the reciprocal of the volume resistivity. The conductive stability was characterized by the ratio of electrical conductivity measured before tension to that measured after tension. The samples were stretched to a strain of 20% by using a self-made tensile installation and kept there for 10 min. The volume resistance was measured after the sample was placed in the standard experimental conditions for 30 min. The size of samples used was 10 mm × 100 mm × 2 mm. At least five samples were tested for each composite and the average value was reported.

The measuring set-up used for testing the EMI shielding effectiveness (SE) consists of a Signal Generator (E8251A, Agilent, America) and a Spectrum Analyzer (E4407B, Agilent, America). EMI shielding measurement was carried out according to Chinese standard GJB 6190-2008 in the frequency range of 10 KHz–18 GHz. The SE in the frequency range of 10 KHz–1500 MHz was measured using the coaxial test method. The SE in the frequency range of 150 MHz–18 GHz was measured using the shielding chamber method.

The compressive properties of all the samples were measured by using a universal material testing machine (CMT4104, Shenzhen SANS Testing Machine, China). The samples were firstly compressed for 24 h at 100 °C under 25% of compression before the test of compression set. At least five samples were tested for each composite and the average value was reported. The samples used for testing the compression properties were in a disk shape with a diameter of 29 mm and a thickness of 12.5 mm. The error of the compression properties is within 10%.

The impact resilience was measured by using a rubber impact elasticity test machine (MZ-4065, Jiangsu Mingzhu Testing Machinery Co., Ltd, China). At least five samples were tested for each composite and the average value was reported. The samples used for testing the impact resilience were in a disk shape with a diameter of 29 mm and a thickness of 12.5 mm.

The hysteresis loss of composites was tested according to standard HG/T 3101-2011. The hysteresis loss (H, %) was calculated by

$$\mathrm{H} = (F_1 - F_2) \times 100/F_1 \tag{2}$$

where F_1 is the power consumption of the sample under tension, F_2 is the power recovery of the sample under shrink, the two are both expressed in the area of graphics. The size of samples used was 115 mm × 10 mm × 2 mm. At least five samples were tested for each composite and the average value was reported. The error of the hysteresis loss is within 5%.