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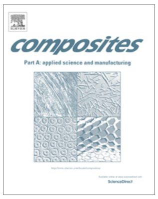

Carbon nanotubes based high temperature vulcanized silicone rubber nanocomposite with excellent elasticity and electrical properties

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ABSTRACT

In the present study, we have fabricated a series of high temperature vulcanized silicone rubber (HTVSR)/carbon nanotubes (CNTs) nanocomposites with different CNT contents. The CNTs were pretreated by the chitosan salt before being incorporated into the HTVSR. The nanocomposites were then characterized in terms of morphological, thermal, mechanical and electrical properties. It was found that the chitosan salt pretreated CNTs dispersed uniformly within the HTVSR matrix, improving the thermal and mechanical properties of the HTVSR. The nanocomposites could remain conductive without losing inherent properties after 100 times of repeated stretching/release cycles by 100%, 200%, and even 300%. Moreover, the nanocomposites had good response to the compressed pressures. The results obtained from this study indicate that the fabricated nanocomposites are potential to be used in many electrical fields such as the conductive elastomer or the pressure sensor.

1. Introduction

Silicone rubber, as a well-known elastomer, has been widely applied in various industrial fields due to its excellent properties including nontoxicity, biocompatibility, flexibility, low cost, and ease of fabrication [1,2]. The high temperature vulcanized silicone rubber (HTVSR) is a representative class of the silicone rubber which has been used for more than fifty years [3]. Generally, the HTVSR raw rubbers are gum-like methyl vinyl polysiloxanes with low molecular weight and mechanical strength. The crosslinking among the vinyl along the HTVSR molecular chains at high temperature, normally initiated by some vulcanizing agents, forms a firm network with very high molecular weight [4], which is the reason why vulcanized HTVSR is stretchable and durable. Recently, the conductive elastomers have received tremendous interest because of their various application areas in electronics, sensors and textiles, etc. [5–8], and the HTVSR may be a potential candidate due to its remarkable elasticity. Moreover, since the HTVSR is biological friendly and nontoxic, it could be even used in fabricating the wearable electronic and the artificial skin [9].

However, the HTVSR is an insulating polymer which is not electrically conductive. To make the HTVSR conductive enough for practical use, it is necessary to integrate conductive fillers into the HTVSR matrix. Traditionally used fillers are metals and metal oxides [10,11]. Recent studies have found the carbon nanotube (CNTs) as an ideal conductive filler [12–14], since the CNTs exhibit not only exceptional electrical properties, but also excellent thermal and mechanical properties [15,16]. Thus compared with the traditional fillers, the CNTs are able to enhance both the electrical and the mechanical properties of the elastomers [17–19].

One challenge of applying the CNTs in large scales is the large van der Waals interaction among the CNTs bundles, which hinders the uniform and individual dispersion of the CNTs within the polymers [20,21]. The aggregation of the CNTs may also limit their reinforcing effect to the matrix polymers [22]. One feasible and simple approach to improve the CNTs dispersion is to physically attach some compatibilizing molecules on the surface of the CNTs [23–25]. These foreign compatibilizers are embedded into the CNTs bundles, reducing the interfacial forces among the CNTs and increasing the dispersion of the CNTs. In our previous study [26], it has been found that the chitosan salt had good capability in increasing the dispersion of the CNTs in the HTVSR. Hence, the chitosan salt was used as the compatibilizer to increase the dispersion the CNTs in this study.

In the present study, a series of highly stretchable conductive elastomers were fabricated based on the CNTs filled HTVSR nanocomposites. Considering that mixing the HTVSRs with different vinyl contents together was able to increase the mechanical strength of the final composites [27], an HTVSR hybrid was used as the matrix, in which one HTVSR with higher vinyl content and

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the other with lower vinyl content were blended together. The thermal stability, mechanical strength and electrical resistance of the prepared elastomers as a function of the CNTs content were investigated. Furthermore, the resistance changes of the prepared elastomers during stretching and pressing cycles were also investigated and discussed. The results showed that even being stretched to 100%, 200%, or even 300% of their original length for 100 times, the prepared elastomers did not lose their mechanical and electrical properties. Moreover, the resistance of the elastomers also had a good response to the pressure changes. It is indicated that the prepared HTVSR elastomers are potential to be applied in diverse electrical fields.

2. Experimental

2.1. Materials

Methyl vinyl HTVSR with vinyl molar contents of 0.20% (HTVSR-0.2) and 0.05 (HTVSR-0.05), and 2,5-bis(tert-butyl peroxy)-2,5-dimethyl hexane(DBPMH) were supplied by Shenyang Silicon materials company (China). Both the HTVSR-0.2 and the HTVSR-0.05 were methyl-terminated transparent polymers and had a molecular weight of around 600,000 g/mol. CNTs (multi-walled), with diameters between 10 and 20 nm, length of 15 um, and purity over 95%, were purchased from Shenzhen Nanotech Port Co. Ltd. (China). Chitosan (CS), with a degree of deacetylation of 95% and viscosity-average molecular weight of 600,000 g/mol, was supplied by Shandong Chitin Powder Factory (China). Hydrochloric acid (37%) and chloroform were purchased from Accuchem (Canada). Deionized-distilled water (DDW) was used exclusively in this study.

2.2. Preparation of CNTs filled HTVSR elastomers

The process of preparing the chitosan salt pretreated CNTs was described in detail in our previous study [24]. Typically, the CS (1 g) and 37% HCl (3 mL) were first added into 100 mL DDW. After the mixture was sonicated and stirred for about 30 min, a clear solution was obtained. The solution was then stirred at 50 °C for 24 h, dried in the vacuum oven at 60 °C for another 24 h, and the yellow colored chitosan salt was obtained. The prepared chitosan salt was then mixed with the CNTs (mass ratio: 1/4) afterwards. The mixture was grounded in a mortar, stirred at 90 °C for 1 h, and the chitosan salt pretreated CNTs were finally obtained. The chitosan salt here acted as a kind of compatibilizer to enhance the dispersion of the CNTs in the HTVSR and built an interaction between the CNTs and the HTVSR.

The CNTs filled HTVSR elastomers with different CNTs contents were prepared as follows. An HTVSR hybrid was firstly obtained by mechanically mixing HTVSR-0.2 and HTVSR-0.05 (mass ratio: 45/55) together. The hybrid was then dissolved in 50 mL chloroform to form a uniform solution. After a certain amount of the chitosan salt pretreated CNTs were added, the resulted solution was sonicated for 30 min. Chloroform was then evaporated at 40 °C and the residue was dried subsequently at 60 °C for 24 h in a vacuum oven. DBPMH, the curing agent was then mechanically blended with the vacuumed mixture and the resulting compound was vulcanized at 170 °C for 15 min. Finally, the HTVSR/CNTs nanocomposites with CNTs weight contents of 4.0 wt%, 6.0 wt%, 8.0 wt% and 11.0 wt% were obtained. For comparison, the pure HTVSR hybrid was also prepared following the similar procedures. All the HTVSR samples were vulcanized before characterizing and testing.

2.3. Characterization

The surface morphology the HTVSR/CNTs nanocomposites were observed by scanning electron microscopy (SEM, JEOL SEM 6490). All the samples were cryogenically fractured and coated with a thin layer of gold before being observed. The thermal stability of the HTVSR and the HTVSR/CNTs nanocomposites was characterized in terms of thermogravimetric analysis (TGA) which was measured by a TGA instrument (Mettler Toledo TGA/DSC 1 Simultaneous Thermal analyser) with the temperature increasing from 25 °C to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere (with a flow rate of 50 mL/min). The X-ray diffraction (XRD) patterns were recorded with a Rigaku Smartlab XRD instrument using Cu Kα radiation source (1.54 Å).

The Instron 5566 universal testing machine was used to test the stress–strain behavior of the HTVSR samples, in which the load cell was 500 N. The test was carried out at room temperature, with a constant extension speed of 20 mm/min and gauge length of 20 mm. All the samples were cut into a 40 × 5 mm rectangular shape with the thickness of 1 mm before testing.

The resistances of the HTVSR/CNTs nanocomposites being bended or twisted at different angles were recorded with a Keithley 2010 digital multimeter. All the samples were cut into a 40 × 5 mm rectangular shape with the thickness of 1 mm before testing. The two-probe method was used and two conductive silver wires connecting to Keithley 2010 were linked to each end of the samples. The resistance change during the stress–strain test was conducted by the Instron 5566 universal testing machine and recorded by the Keithley 2010. The resistance data of the samples was acquired simultaneously as a function of the applied strain. Two conductive silver wires connecting to Keithley 2010 were linked to each end of the samples before testing.

The resistance response of the HTVSR nanocomposites under repeated stretching and pressing was recorded utilizing a Keithley 2010 digital multimeter and an Instron 5566 universal testing machine as well. The two-probe method was used to investigate the resistance of all the samples throughout the test and all the samples were 1 mm in thickness. In the stretching test, the HTVSR/CNTs nanocomposites were cut to a 40 × 5 mm rectangular-shape sample. The gauge length of the Instron 5566 was set at 20 mm and the stretching/relaxing rate was set at 20 mm/min for 100 times. The HTVSR/CNTs samples were stretched to diverse degrees of their original level and released to original level thereafter repeatedly. Before stretching, two conductive silver wires connecting to Keithley 2010 were linked to each end of the testing part of the samples. During stretching/relaxing, Keithley 2010 recorded the resistance change of the samples simultaneously. In the pressing test, the HTVSR/CNTs nanocomposites were cut to a 20 × 20 mm square-shape sample, and two conductive silver wires connecting to Keithley 2010 were linked to the center of the top and bottom surfaces of the samples, respectively. With the gauge length set at 1 mm, and the compressing/relaxing speed 1.0 mm/s, a 20 × 20 mm square-shape compression stage with load cell of 200 N was used to provide axial pressure. The samples were compressed to 0.5 mm and released to 1 mm in thickness for 50 repeated times. Both the stretching clamps and the compression stage were wrapped with parafilms to prevent testing errors. All the resistance testing experiments were duplicated with an observed deviation of less than 5%. The schematic illustration of the stretching and compressing was shown in Fig. 1.

3. Results and discussion

The dispersion state of the CNTs in the HTVSR nanocomposites was investigated first. Fig. 2 shows the typical SEM images of the