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Natural rubber nanocomposites with SiC nanoparticles and carbon nanotubes

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Abstract

Single-walled carbon nanotubes (SWNTs) and SiC nanoparticles were dispersed in natural rubber (NR) polymer solution and subsequently evaporated the solvent to prepare NR nanocomposites. Using this technique, nanoparticles can be better dispersed in the NR matrix. The influence of nano-fillers on the mechanical properties of the resulting nanocomposites was quantified.

Mechanical test results show an increase in the initial modulus with nanoscale reinforcements for up to 50% strain compared to pure NR. The modulus and strength of natural rubber with 1.5% SiC nanoparticles appear to be superior to those of SWNTs with the same filler content. In addition to mechanical testing, these nanocomposites were studied using the SEM and Raman spectroscopy techniques in order to understand the morphology of the resulting system and the load transfer mechanism, respectively. The Raman spectrum of the SWNT/NR system is characterized by a strong band at 1595 cm^{-1} (G mode—C–C stretching) and other two bands at 1300 cm^{-1} (D mode-disorder induced) and 2590 cm^{-1} (D* band). A shift of the 2590 cm^{-1} Raman band to the lower wavenumber was observed after subjecting SWNT/NR sample to cyclic stress testing. Ageing SWNT/NR specimen in distilled water for 30 days also provided a similar result. The Raman shift in aged samples indicates internal stress transfer from the natural rubber matrix to the SWNTs implying the existence of bonding at the interface.

Keywords: Single-walled carbon nanotubes; SiC nanoparticles; Natural rubber; Raman spectroscopy; Nanocomposites

1. Introduction

Composites filled with nano-fillers such as nanoparticles, known as nanocomposites, are gaining increased attention recently. It has been expected that nanocomposites could provide superior physical properties, because of the high surface-to-volume ratio of nanometer scale reinforcing fillers embedded in the matrix, compared to the conventional fiber or particle reinforced composites. While single-walled carbon nanotubes (SWNTs) have been widely used with different kinds of polymers, very little work has been done on incorporating the SWNTs in rubber. Elastomeric materials are usually reinforced with carbon black or silica, although the full effects of these fillers are diminished due to their

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agglomeration [1–3]. It becomes crucial to incorporate well-dispersed nano-fillers into rubber to obtain beneficial mechanical and physical properties.

The concept of nano-sized filler-reinforced elastomer was recently demonstrated by the incorporation of nanoparticles in a rubbery polymer matrix such as clay into natural rubber [4,5] and SWNTs into silicone rubber [6]. Although rubbers are known to be a thermal and electrical insulator, incorporation of conductive fillers into these materials could produce composite materials with some electrical conductivity. The properties of these composites vary as a function of volume fraction of the conductive fillers. Potential applications of rubber nanocomposites could vary from industrial applications such as rubber hoses, tire components, sensing devices to electrical shielding and electrical heating.

For clay, a large increase in modulus is observed even at low filler content as 10% by weight when partial exfoliation of layered silicates in natural rubber is achieved. Also, SWNT was found to provide some level of reinforcement to the silicone rubber. This is attributed to the high aspect ratio and low density of the SWNTs bundles which was confirmed by experimental evidence. It was expected that well-dispersed single nanotubes in the rubber matrix should provide a better reinforcement mechanism by providing more interface area for better interaction between the reinforcements and the matrix. The interfacial property of SWNT/silicone rubber, that is mostly responsible for the reinforcing effect, can be investigated using the Raman spectroscopy [6].

The interest in ceramic particle reinforced composites has begun a decade ago [7–12]. SiC nanoparticles have become popular recently as the reinforcement phase for polymer or ceramic matrices [7–10]. In addition to improving mechanical properties, ceramic reinforcements provide some control over adjusting electrical conductivity. It has been known since 1970s that when micron-sized SiC powder is embedded in a matrix where the particles have some level of contact with each other, the composite could conduct electricity. The electrical current was controlled by an induced potential barrier when conductive filler particles are in contact. In the last few years, SiC has attracted more interest due to its desirable properties for potential applications as semiconductor devices [11]. Niihara [12] has reported that nano-sized (20–300 nm) ceramic composites provided considerably higher fracture toughness and strength than conventional ceramic composite. Moreover, this material retains its strength at high temperatures while providing better creep properties. Thus it is logical to assume that incorporation of SiC nanoparticles into a polymer matrix could enhance the properties of the polymer as a nanocomposite material. It was reported that epoxy filled with 1.5% of nano-sized SiC particles showed an enhancement of mechanical properties of the order of 20–30% in relation to pure matrix, both in tension and flexure [8].

The present study was focused on the synthesis of two nanocomposite systems with nano-sized fillers: SWNT/NR and SiC/NR nanocomposites. Results of this comprehensive study are provided in the following sections, mainly characterizing the mechanical properties but also analyzing the morphology of the resulting composites. In addition, Mechanical testing (using Instron), scanning electron microscope (SEM) and Raman spectroscopy were employed in this study.

2. Experimental procedure

Two sets of nanocomposites were synthesized; namely SWNT/NR and SiC/NR nanocomposites. The synthesis of SWNT/NR composite system consists of dissolving SWNTs (0.5 mg/mL) and natural rubber gum in toluene (4 mg/mL) in two separate beakers. The SWNTs were provided by CNT Inc., (Houston, TX), pure natural rubber was supplied by the Goodyear Tire and Rubber Company (Akron) which was used as received. The SWNTs/toluene was subsequently dispersed in the natural rubber/toluene with ultrasonication at room temperature for 2 h. Vulcanizing agents were then added to the natural rubber solution, and the solution was mixed for 1 h. Finally, the SWNT/NR was prepared by evaporating the solvent off at 50 °C for approximately 6 h. The composition of NR used in the work is given in Table 1.

The vulcanization was carried out at 150 °C for 20 min using a hot press. The pressure of the hot press was adjusted (~300 kPa) to obtain rubber composite sheets with the desired thickness, usually in the order of 200–300 μm. The SWNT/NR nanocomposites were black. Natural rubber nanocomposite thin sheets with SWNT reinforcement were prepared with a filler content of 1%, 1.5% and 2% by weight. However, there was not enough SWNT/NR sample at 2% filler content for the tensile testing, thus no test results are provided for mechanical properties in Section 3.1 for composite with 2% SWNT filler.

The SiC/NR nanocomposites were prepared using SiC nanoparticles 29 nm in size purchased from MTI Corporation. Natural rubber nanocomposite thin sheets

Table 1
Rubber compound formulation

Ingredients	Parts per hundred rubber (phr)
Natural rubber	100
Zinc oxide	5
Sulfur	2
Stearic acid	2
Cyclohexyl benzothiazole sulfonamide (CBS)	0.8