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Carbon nanotubes as Raman sensors of vulcanization in natural rubber

Qing Zhao [a], Rina Tannenbaum [b], Karl I. Jacob [a,*]

[a] School of Polymer, Textiles and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, United States
[b] School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, United States

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Abstract

A method has been developed to synthesize composites with cross-linked natural rubber (NR) and dispersed single-wall carbon nanotubes (SWNT). The mechanical response of the NR samples was observed to change as a function of the amount of sulfur used for cross-linking, based on the number density of cross-links resulting from the vulcanization process. The relationship between SWNTs D^* wavenumber shift and the amount of sulfur have been obtained by means of Raman spectroscopy. The cross-link densities of the NR and SWNT/NR samples have been calculated from uniaxial stress–strain measurements, and plotted as the function of the amount of added sulfur. Comparison of the results from mechanical measurements and Raman spectroscopic measurements showed that SWNT Raman sensors are sensitive to the cross-link density in natural rubber and can be used to evaluate the cross-linking process of rubbery materials.

Keywords: Carbon composites; Carbon nanotubes; Raman spectroscopy; Elastic properties; Interfacial properties; Mechanical properties

1. Introduction

It is well known that single-wall carbon nanotubes (SWNTs) may constitute excellent reinforcement material in polymer composites, due to their high aspect ratio, high Young's modulus, tensile strength and light weight [1–3]. Some work has been done on SWNT-filled rubber composites [4–6], though the preparation of high-strength composites with nanotubes still faces several technical obstacles that need to be resolved. Among these, one of the main problems is regarding to the nanotube dispersion. Sonication is an efficient dispersion method, although it can also cause damage when it is used for long times or with high power [7]. Thus, in our work, an optimum level of sonication, with trial and error but guided by literature, was used to obtain samples with a degree of uniformity required for reliable results from Raman spectroscopy. Another problem relates to the nature of interface. The structure and properties of the interfacial region are crucial for effective load sharing between the matrix and the reinforcement material, though direct studies to characterize interface load transfer are difficult because of the nanoscale dimensions of the filler and the corresponding interface. Another important obstacle is that SWNTs are still very expensive and the improvement of composite mechanical property may not be worth the cost. Since using SWNT for reinforcing applications still has to overcome some technical difficulties, it is worth to try to use nanotubes effectively for some other applications, such as Raman strain sensors, hydrogen storage material and high capacitance composites etc. [8–16].

Raman spectroscopy has been used to prove the existence of nanotubes, determine the diameter of nanotubes, the diameter distribution of nanotube bundles and the structural properties of nanotubes, as carbon nanotubes have distinctive Raman spectra [17–22]. In this work we are specifically interested in the disorder induced D^* (or G') Raman band of the nanotubes, which is the

* Corresponding author. Tel.: +1 404 894 2541; fax: +1 404 894 9766.
E-mail address: karl.jacob@ptfe.gatech.edu (K.I. Jacob).

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second-order overtone of D band and located at around 2500–2700 cm^{-1}. It has been demonstrated that SWNT can be used as stress sensors, since the D^* band responds appropriately to indicate the strain (or stress) and transitions in polymers, which could in turn be quantified by means of Raman spectroscopy [8–10]. This type of application only needs a small amount of nanotubes (less than 0.5 wt% of nanotubes) and the sensitivity of the measurement can be at the micro-scale and molecular level. Therefore, to use nanotubes as functional materials might be a more effective and less expensive research avenue. Adding a small amount of SWNT will make the dispersion obstacle easier to overcome, though the interfacial interaction still needs to be characterized when there are chemical bonds or partial bonds.

SWNTs could also be used within elastomers for measuring interfacial stresses. The properties of a particular elastomer are governed by the nature of the cross-linked network. It is known that rubbers are vulcanized at different conditions and with appropriate cross-linking agents, and hence an optimum balance of their mechanical properties could be obtained. While sulfur is still by far the most efficient vulcanization agent, the addition of small amounts of accelerators not only makes the process faster, but also determines the quantity and the type of cross-link formed during vulcanization. Studies to identify the influence of cross-link structures from rubber vulcanization by using sulfur have been conducted for several decades [23]. Cross-link density is an important factor that affects the physical properties of the vulcanized elastomer network. The cross-link density of a network depends mainly on the number of chains, molecular weight and the sulfur/accelerator ratio [24]. There are several methods to estimate the cross-link density. Swelling by an organic solvent is one of the most common methods for characterizing elastomeric networks [25]. Stress–strain measurements have been proved to be another indirect way of determining the cross-link density [25].

The main goals of this work were first to make SWNT/NR composites and compare the mechanical properties of the SWNT/NR composite and pure NR. Subsequently, we explored the possibility of using nanotube Raman sensors to characterize the curing conditions of NR by using different amounts of sulfur to vary the curing process and the cross-link density. Uniaxial stress–strain data have been used to analyze the cross-link densities of vulcanized rubbers, and then compared with the Raman analysis result.

2. Experimental

Natural rubber was supplied by Goodyear Tire and Rubber Company and SWNTs were commercially obtained from Rice University. Rubber compounds and SWNT/NR composite were prepared at room temperature with toluene as solvent.

The mixture of 15 g natural rubber and 500 ml toluene was sonicated first until NR dissolved completely. SWNTs (38 mg) were dispersed in 50 ml of toluene by sonication. The nanotube/toluene solution together with 450 mg zinc oxide (ZnO, Aldrich), 300 mg stearic acid ($C_{18}H_{36}O_2$, Fluka) and 225 mg cyclohexyl benzothaizole sulfonamide (CBS, $C_{13}H_{16}N_2S_2$, Sigma–Aldrich) were added to the NR/toluene solution and sonicated until the liquid was homogeneous. Then the mixture was divided into 15 equal parts and different amounts of sulfur (S, Fisher Scientific), from 0 mg to 60 mg, was added into each part. All the solutions were stirred until the sulfur was well dispersed, and they were left in the hood overnight for curing. After the toluene has evaporated completely, the SWNT/NR composite samples were placed on a hot press at 160 °C for 15 min under the pressure of about 500 kPa. The thin films of SWNT/NR composites with the thickness of about 0.3 mm were obtained. The NR samples were prepared using exactly the same procedure as described above without adding any nanotubes. An identical method was used to produce silicone rubber based SWNT composite where good dispersion of SWNTs was demonstrated by SEM results [5]. In our case, all the SWNT/NR composite samples have dark and even appearance and no obvious clusters have been observed under a Leitz Laborlux 12 POL polarized optical microscope with a maximum magnification of 400×. Since the degree of uniformity required is within micro-meter length scale, uniform dispersion of nanotubes was verified by optical microscopy for each samples.

All samples were cut into strips with a width of about 4 mm, 15 mm length and 0.3 mm thickness for tensile test. The mechanical properties of the NR and SWNT/NR samples were determined at room temperature using the static mode of a dynamic mechanical analyzer at a deformation rate of 6 mm/min. At least three samples for each type were prepared and tested. The stress–strain curves were obtained and moduli correspond to first 50% extension ratio were calculated for each sample.

Raman scattering spectra were recorded by Kaiser System in a backscattering geometry on the samples. A 785 nm laser was used as the light source and the illuminated spot on the sample surface was focused to about 2 μm diameter.

3. Results and discussion

Although there is only 0.25 wt% of SWNTs added in the NR matrix, the small diameter of SWNT results in having a large number of nanotubes in the system and all the SWNT/NR samples have much darker color than the NR samples. First we study if the presence of SWNT would change the mechanical properties of the natural rubber. At the final stage of sample processing, a hot press is used to reduce the sample thickness significantly for forming thin composite film for mechanical testing. The radial shear flow during this process removes the initial isotropy present in the system [26], but the resulting film has SWNTs distributed on the plane of the film. Since SWNTs are randomly oriented in the resulting film, the direction in