

Improvement of the Mechanical and Electrical Properties of Waste Rubber with Carbon Nanotubes

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Received 17 April 2010; accepted 23 October 2010

DOI 10.1002/app.33650

Published online 22 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The effect of carbon nanotubes (CNTs) on the stability of the mechanical and electrical properties of recycled waste rubber was experimentally investigated. The stress–strain curves of the composites were studied. The results show that the toughness, the area under the stress–strain curve, of the recycled rubber increased monotonically as a result of the addition of CNTs. The modulus of the nanocomposites increased by 28 times when only 5 wt % CNTs was added to the recycled rubber matrix. The effects of the cyclic fatigue and hysteresis for the composites were also examined. The strain energy density, dissipation energy,

and linear damage accumulation versus the number of cycles are discussed for all of the samples. The analysis of the results showed that the strain energy density increased by 15 times at a CNT concentration of 5 wt %. The electrical properties were measured for all of the samples. The results indicate that the addition of CNTs to the recycled rubber improved its electrical conductivity by more than two orders. © 2011 Wiley Periodicals, Inc. *J Polym Sci* 121: 502–507, 2011

Key words: rubber; recycle; carbon nanotubes; mechanical; electrical

INTRODUCTION

Elastomers with a high electrical conductivity are critical for applications ranging from seals between pipes used for the transfer of flammable gases, electrostatic automotive painting, and electromagnetic shielding for mobile electronics. Traditionally, conductive fillers, such as carbon black, chopped carbon fiber, or metallic flakes are used.^{1–3}

Carbon nanotubes (CNTs), as self-assembling nanostructures, have attracted a great deal of attention as model systems for nanoscience and for various potential applications, including composite materials, battery electrode materials, field emitters, nanoelectronics, and nanoscale sensors. The interest in CNTs stems from their unique structure and properties, including their very small size (down to 0.42 nm in diameter); the possibility of CNTs to be metallic or semiconducting, depending on their geometrical structure; their exceptional properties of ballistic transport; their extremely high thermal conductivity and optical polarizability; and the possibilities of high structural perfection.

The main purpose of introducing CNTs into polymer composites is to exploit the CNTs' inherent pro-

perties of stiffness, tensile strength, damping properties, flame resistance, and thermal and electrical properties.^{4–9} Therefore, many efforts have been concerned with retaining the CNTs' large aspect ratio in the polymer matrix to achieve good interfacial stress transfer (surface modification) and to improve dispersion and alignment during composite processing.^{10,11}

The reclamation of scrap rubber products, for example, used automobile tires and tubes, hoses, and conveyor belts, is the most desirable approach for solving their disposal problem. The recovery and recycling of rubber from used and scrap rubber products can, therefore, save some precious petroleum resources and solve scrap/waste rubber disposal problems. For such an approach, the aim of this study was to examine the effect of CNTs on the stability of the mechanical and electrical properties of recycled rubber.

EXPERIMENTAL

Car tire waste rubbers were collected. These tires were washed by distilled water and acetone many times to remove any dust and other wastes from them, and then, they were left it in sunlight inside a homemade glass room to dry completely. The collected waste rubbers were subjected to degradation by oxygen and ozone; this resulted in the characteristic cracking shown by very old rubber products. The cracking was accelerated by heat and

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light and was dependent on the mode of deformation of the rubber. This means that the collected waste rubber had a very poor hardness and, of course, no conductivity.

A two-roll mill with a length of 0.3 m, a radius of 0.15 m, a speed of the slow roll of 18 rpm, and a gear ratio of 1.4 was used to prepare such composites. The samples of the waste rubber compound were prepared according to the recipe shown in Table I.

During the mixing process, different ingredients were added as follows: the waste rubber was milled for 10 min, after which stearic acid, used as a coactivator, was added and mixed for 5 min. Zinc oxide, which was used as an activator to enhance the action of organic accelerators, was added and mixed for 7 min. Single-wall CNTs (purchased from Helix Material Solution, Richardson, TX, with a 3-nm diameter and 250-nm length) were added and mixed for 5 min at different concentrations (1, 3, and 5 wt % phr). Dioctyl phthalate oil was added and mixed for 4 min. Dibenzthiazyl disulfide (MBTS) as an ultra-accelerator, was added and mixed for 3 min. Phenyl- β -naphthyl amine, as an antioxidant, was added and mixed for 3 min. Sulfur, which was used as a vulcanizing agent, was added and mixed for 5 min. The sample was passed endwise 10 times through the mill at a 1-mm opening and, after that, was sheeted off at a 2-mm thickness. This process took about 8 min. The total milling time was fixed at about 50–55 min. The compounded rubber was left for at least 2 days before vulcanization.

The main purpose of vulcanization was to convert the essentially raw waste rubber into an elastic and dimensionally stable material and also to render its physical properties temperature dependent to a greater extent and to make it insoluble in liquids that would dissolve unvulcanized rubber.¹² The samples were compression-molded into sheets with a steel die, which had dimensions of a 1×10^{-4} m² area and a 0.01-m height. The vulcanization was conducted under a heating press (KARL KOLB, USA) at a temperature (T) of 423 ± 2 K under a pressure of 4 MPa for 30 min. The vulcanized samples were shelf-aged for 48 h at a temperature of 70°C in an electric oven before testing. The vulcanization conditions were fixed for all of the samples.

Measurements

The stress–strain behavior was measured at room temperature with a material tester (Ametek, USA), which was connected by a digital force gage (Hunter Spring ACCU Force II, 0.01-N resolution, USA) to measure the stress forces. The force gage interfaced with the computer to record the obtained data. The stress–strain behavior was measured at a strain rate of 0.01 mm/s. For the electrical measurements, brass

TABLE I
Ingredients of the Investigated Recycled Rubber Composites

Ingredient	Sample			
	W ₀	W ₁₀	W ₃₀	W ₅₀
Waste rubber	100	100	100	100
Stearic acid	2	2	2	2
Zinc oxide	5	5	5	5
CNT	—	1	3	5
Dioctyl phthalate	10	10	10	10
MBTS	2	2	2	2
Phenyl- β -naphthyl amine	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5

electrodes were attached to the parallel faces of the samples during vulcanization, and a digital electrometer (616 Keithley, USA) was used. The morphology and microstructures of the samples were characterized by field-emission scanning electron microscopy (SEM; JEOL, JSM-6700F, USA).

RESULTS AND DISCUSSION

SEM

Figure 1(a) depicts the SEM photograph for the as-received CNTs. It was clear that the diameter of CNTs was about 3 nm and the length was up to 250 nm. Figure 1(b,c) shows the distribution of the CNTs in the recycled rubber matrix at two different concentrations, 1 and 5 wt %, respectively. At low CNT concentrations, the separation distance between the CNTs was very large and decreased as the CNT concentration increased. The aspect ratio of the distributed CNTs in the recycled rubber matrix was approximately 68. This value was less than the aspect ratio of the CNTs (~ 83) before mixture with polymer. This may have resulted from the destruction of the CNTs during the mixing process in the mill roll.

Stress–strain behavior

Figure 2 shows the stress–strain curves obtained with various amounts of CNTs dispersed in the recycled rubber matrix. The stress–strain curves were fitted by the Ogden model¹³ and are plotted in Figure 2:

$$\sigma = \frac{2\mu_1}{\alpha_1} \left([1 + \varepsilon]^{\alpha_1 - 1} + [1 + \varepsilon]^{-\left(\frac{\alpha_1}{2} + 1\right)} \right) \quad (1)$$

where $\mu_1 = \mu_o = E_o/2(1+\nu) = E_o/3$ for an incompressible material, where E_o is the Young's modulus at the small strain deformation and ν is Poisson's ratio, respectively. σ is the applied stress, ε is the strain, μ_1 is the uniaxial shear modulus, and μ_o is the shear modulus for nanocomposite. α_1 is a material

parameter that depends on the host polymer. The fitting parameters, which were derived from the Ogden model, for all of the samples are presented in Table II.

As shown in Table II, with increasing concentration of filler, a gradual improvement in the modulus was observed. The results were compared with the

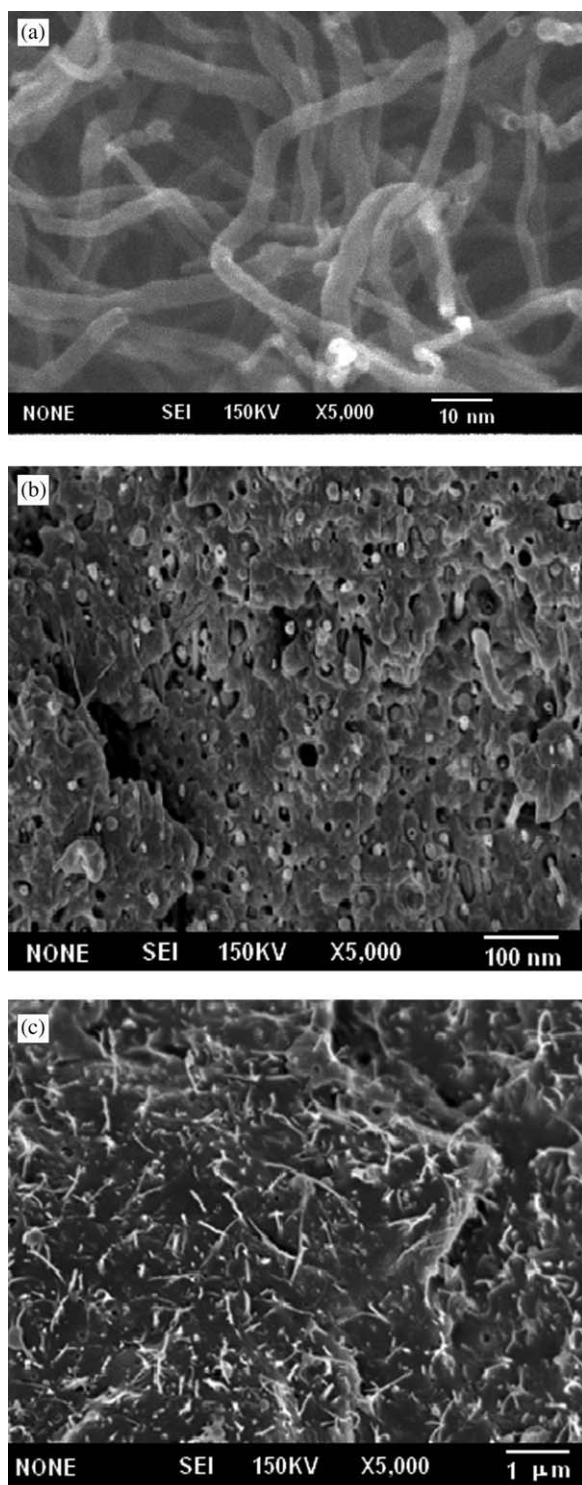


Figure 1 SEM photographs of (a) CNT, (b) recycled rubber/1 wt % CNT, and (c) recycled rubber/5 wt % CNT compounds.

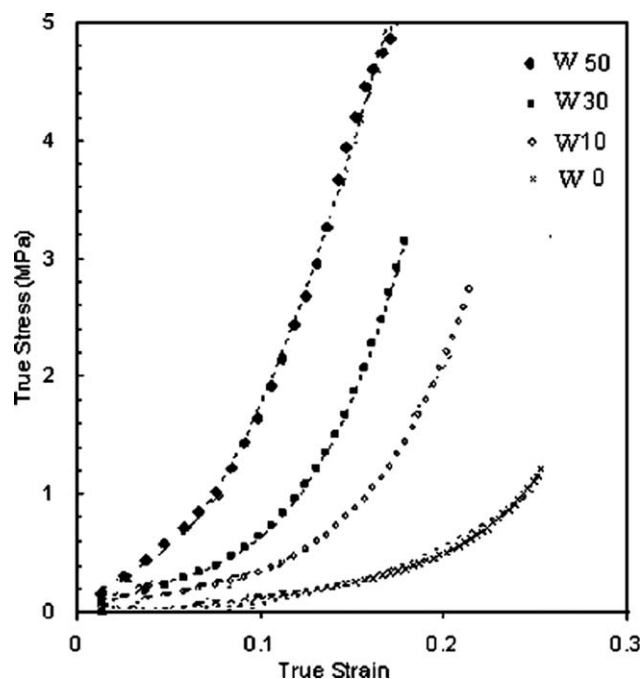


Figure 2 Stress–strain characteristic curves for the recycled-rubber-loaded CNTs. The dot lines are the fitting curves.

Guth reinforcement model.¹⁴ The model for spherical reinforcing particles has the following form:

$$E = E_0(1 + 2.5V + 14.1V^2) \quad (2)$$

where E is the modulus of elasticity at each volume fraction V .

An alternative formulation accounted for nonspherical particles. For rodlike particles of aspect ratio f , the reinforcement was given by the following equation:¹⁵

$$E = E_0(1 + 0.67fV + 1.62f^2V^2) \quad (3)$$

With f as an adjustable parameter, an excellent fit was obtained with $f = 65$ (Fig. 3). This result confirmed the SEM photographs for the filler rodlike shape.

Strain energy density

The energy absorbed per unit volume (W) in the deformation of rubber composites to a strain is simply the area under the stress–strain curve and can be written as¹⁶

TABLE II
Fitted Parameters of the Ogden Model for Stress–Strain Behavior

Parameter	Sample			
	W_0	W_{10}	W_{30}	W_{50}
μ_1 (MPa)	1.30 ± 0.02	2.93 ± 0.03	3.45 ± 0.12	4.96 ± 0.13
α_1	2.2 ± 0.02	2.2 ± 0.06	2.2 ± 0.03	2.2 ± 0.05

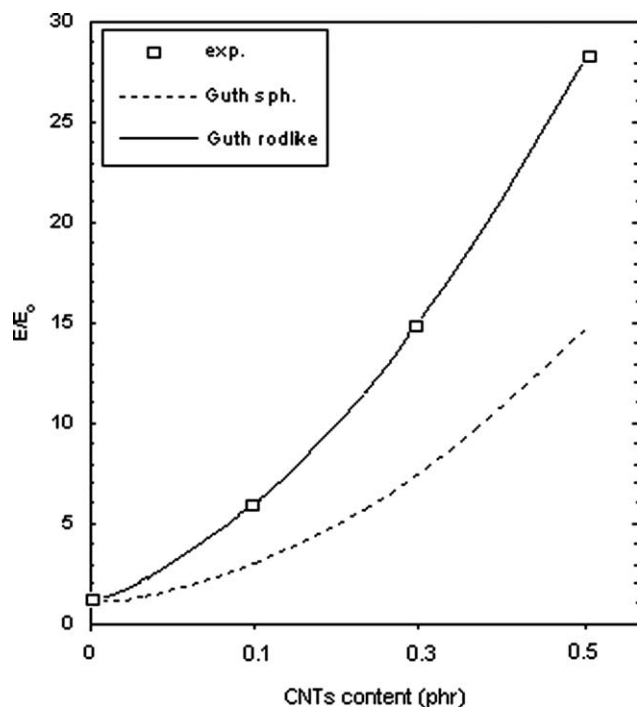


Figure 3 Relative modulus (E/E_0) as a function of the CNT concentration.

$$W = \int \sigma(\varepsilon)d\varepsilon \quad (4)$$

where $\sigma(\varepsilon)$ is the stress as a function of the strain. Obviously, the higher the stress–strain curve is, the higher the energy absorption capacity is. As shown

in Figure 4, among the composites, the recycled rubber free of CNTs had the lowest area under the stress–strain curve and, thus, had the weakest absorption, whereas the high concentration composites had the strongest absorption, as indicated in Table III. Compared with sample W0, the energy absorbed by sample W50 was 16.3 MJ/m^3 , whereas that absorbed by sample W0 was only around 1.47 MJ/m^3 according to eq. (4). On the other hand, the improvement in the absorption efficiency made the impact protection more effective and more reliable.

Cyclic softening and damage accumulation

Figure 5 shows the experimental cyclic stress–strain curves for 1, 5, 10, and 20 loading and unloading cycles. The permanent strain at the end of each cycle was observed. This indicated that irreversible damage had taken place and was apparently caused by rupture of the CNT network as a result of the accumulated dissipated energy. The accumulated dissipated energy gave an indication about the damage that took place in the samples. If the stress–strain relationship was linear, the damage (D) could be expressed by the following equation:¹⁷

$$D = \frac{\sigma_{1\max} - \sigma_{N\max}}{\sigma_{1\max}} = \frac{\frac{1}{2}(\sigma_{1\max} - \sigma_{N\max}) \varepsilon_{\max}}{\frac{1}{2} \sigma_{1\max} \varepsilon_{\max}} = \frac{\Delta E}{\text{Constant}} \quad (5)$$

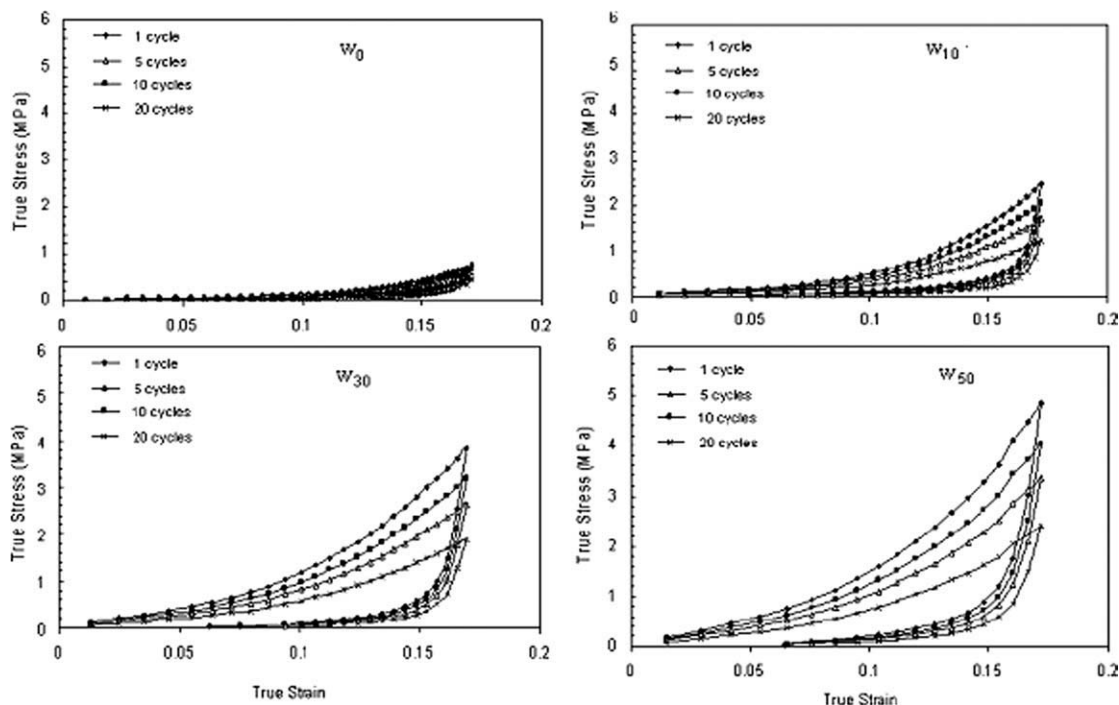


Figure 4 Cyclic stress–strain for the recycled rubber at different CNT concentrations.

TABLE III
Strain Energy Density for All of the Rubber Vulcanizates

	Sample			
	W ₀	W ₁₀	W ₃₀	W ₅₀
W (MJ/m ³)	1.47 ± 0.13	5.76 ± 0.11	7.52 ± 0.15	16.30 ± 0.13

where $\sigma_{1\max}$ is the maximum stress of the first cycle; $\sigma_{N\max}$ is the maximum stress of any other cycle, and ΔE is the linear damage energy (also abbreviated as LDE).

When the stress–strain relationship was nonlinear, the damage component could be determined by the difference between the dissipated energy for the first loading path and the N th loading path. In this case, LDE (N) is expressed by the following equation:¹⁸

$$\text{LDE}(N) = \int_0^\varepsilon [\sigma_{1d}(1, \varepsilon) - \sigma_{1d}(N, \varepsilon)] d\varepsilon \quad (6)$$

where $\sigma_{1d}(1, \varepsilon)$ and $\sigma_{1d}(N, \varepsilon)$ are the stress functions for loading the first and N th cycles, respectively. The rate of damage accumulation was calculated with eq. (6) and is represented in Table IV. As shown in Table IV, after a large amount of damage took place over the first 10 cycles, the rate of damage accumulation became marginal with subsequent cycling.

Electrical properties

Figure 5 represents the relation between $\ln \sigma$ and $1000/T$ for the recycled-rubber-loaded CNTs. The slope of conductivity against the temperature increased with increasing CNT concentrations. In fact, the conductivity–temperature plot had two slopes, one in the low-temperature range 303–343 K, which depended on the sample type, and the other slope in the high-temperature range 343–453 K. In the low-temperature range (303–343 K), there was a small change in the conductivity against temperature because of the competition between two different mechanisms, the thermal expansion of the host rubber and the tunneling or hopping mechanism. After

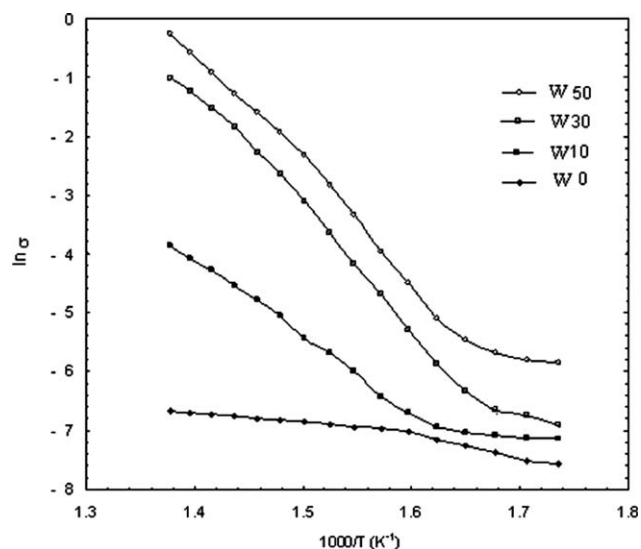


Figure 5 $\ln \sigma$ versus $1000/T$ for different concentrations of recycled-rubber-loaded CNTs.

a temperature of 343 K, a thermal activation took place that caused a progressive increase in the conductivity against temperature. The temperature dependence of the conductivity could be interpreted on the basis of an Arrhenius equation.¹⁹ The activation energy (E_a) values for the samples were calculated for the two different ranges of temperature and are presented in Table V.

With increasing CNT concentration, the value of E_a decreased. E_a at the high-temperature region was greater than that at the low-temperature region. Generally, we concluded that the mechanical and electrical properties of the waste rubber were improved by its recycling and also by the addition of the CNTs.

CONCLUSIONS

Rubber from wet tires was successfully recycled. This recycled rubber was filled with different amounts of CNTs. The SEM images indicated that the aspect ratio of the CNTs after the mixture with recycled rubber (~ 68) was less than that before the mixture (~ 83). This may have been due to the destruction of CNTs during the mixture with rubber

TABLE IV
Damage Accumulation (LDE) at Different Number of Cyclic Stress–Strain

Sample	LDE (MJ/m ³)					
	1 cycle	5 cycles	10 cycles	20 cycles	50 cycles	100 cycles
W ₀	0.06 ± 0.01	0.08 ± 0.01	0.11 ± 0.01	0.16 ± 0.02	0.16 ± 0.01	0.16 ± 0.03
W ₂₀	0.11 ± 0.03	0.23 ± 0.04	0.45 ± 0.02	0.52 ± 0.12	0.53 ± 0.11	0.51 ± 0.14
W ₃₀	0.21 ± 0.02	0.43 ± 0.06	0.65 ± 0.08	1.12 ± 0.14	1.13 ± 0.10	1.11 ± 0.26
W ₅₀	0.48 ± 0.13	0.83 ± 0.25	1.15 ± 0.21	2.02 ± 0.12	2.03 ± 0.10	2.01 ± 0.11

TABLE V
Calculated Values of E_a for the Recycled Rubber Samples

	Sample			
	W_0	W_{10}	W_{30}	W_{50}
Low-temperature E_a (meV)	3.67	2.83	1.64	0.81
High-temperature E_a (meV)	7.23	5.15	3.60	1.76

in the mill roll. The stress–strain test showed that there was a good adhesion force between the CNT filler and rubber. The mechanical measurements also showed that the stiffnesses of the recycled rubber increased by 6, 15, and 28 times as a result of the addition of different concentrations of the CNTs to the recycled rubber. Cyclic stress–strain measurements indicated that the hysteresis and the dissipation energy decreased as the number of cycles increased and increased as a function of the CNT concentration. The electrical measurements indicated that as the CNT concentration increased, the conductivity of the rubber composite increased by more than two orders.

References

- Guldi, D. M.; Rahman, G. M. A.; Jux, N.; Balbinot, D.; Tagmatarchis, N.; Prato, M. *J Am Chem Soc* 2005, 127, 9830.
- Lambin, P.; Fonseca, A.; Vigneron, J. P.; Nagy, J. B.; Lucas, A. A. *Chem Phys Lett* 1995, 245, 85.
- Mintmire, J. W.; White, C. T. *Synth Met* 1996, 77, 231.
- Breuer, O.; Sundararaj, U. *Polym Compos* 2004, 25, 630.
- Thostenson, E. T.; Li, C.; Chou, T. W. *Compos Sci Technol* 2005, 65, 491.
- Moisala, A.; Li, Q.; Kinloch, I. A.; Windle, A. H. *Compos Sci Technol* 2006, 66, 1285.
- Gou, J.; O'Braint, S.; Gu, H. C.; Song, G. B. *J Nanomater* 2006, 10, 3280.
- Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Kinloch, I. A.; Bauhofer, W.; Windle, A. H.; Schulte, K. *Polymer* 2006, 47, 2036.
- Shadler, L. S.; Giannaris, S. C.; Ajayana, P. M. *Appl Phys Lett* 1998, 73, 3842.
- Morales, G.; Barrena, M. I.; Gómez de Salazar, J. M.; Merino, C.; Rodríguez, D. *Compos Struct* 2010, 92, 1416.
- Ishikawa, T. *Adv Compos Mater* 2006, 15, 3.
- Mahmoud, W. E.; El-Eraki, M. H. I.; El-Lawindy, A. M. Y.; Hassan, H. H. *J Phys D: Appl Phys* 2006, 39, 2427.
- Mahmoud, W. E.; El-Eraki, M. H. I.; El-Lawindy, A. M. Y.; Hassan, H. H. *J Phys D: Appl Phys* 2006, 39, 541.
- El-Eraki, M. H. I.; El-Lawindy, A. M. Y.; Hassan, H. H.; Mahmoud, W. E. *J Polym Degrad Stab* 2006, 91, 1417.
- Mahmoud, W. E.; El-Lawindy, A. M. Y.; El-Erak, M. H. I.; Hassan, H. H. *J Sens Actuators A* 2007, 136, 229.
- El-Eraki, M. H. I.; El-Lawindy, A. M. Y.; Hassan, H. H.; Mahmoud, W. E. *J Appl Polym Sci* 2007, 103, 2837.
- Mahmoud, W. E.; Mansour, S. A.; Hafez, M.; Salam, M. A. *J Polym Degrad Stab* 2007, 92, 2011.
- Al-Ghamdi, A. A.; El-Tantawy, F.; Abdel Aal, N.; El-Mossalamy, E. H.; Mahmoud, W. E. *Polym Degrad Stab* 2009, 94, 980.
- El-Lawindy, A. M. Y.; El-Giziri, S. B. *J Phys D: Appl Phys* 2000, 33, 1894.