

Reinforcing Rubber with Carbon Nanotubes

Changwoon Nah,¹ Jee Young Lim,¹ Baik Hwan Cho,² Chang Kook Hong,³ Alan N. Gent^{1,4}

¹Department of Polymer-Nano Science and Technology, WCU Research Team (Energy Harvesting), Chonbuk National University, Jeonju 561-756, South Korea

²Department of Surgery, Jeonbuk Cancer Center, Chonbuk National University, Jeonju 561-756, South Korea

³School of Applied Chemical Engineering, Chonnam National University, Gwangju 500 757, South Korea

⁴Institute of Polymer Science, The University of Akron, Akron 44325-3909, Ohio

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ABSTRACT: We suggest a new reinforcing mechanism for carbon nanotube (CNT)/rubber compounds, based on a comparison of CNT reinforcement of natural rubber (NR) with that by carbon black (CB). The mechanical properties of the NR/CNT compounds were significantly higher, but the amount of bound rubber, an indication of the level of filler-rubber interaction, was lower than with CB. Moreover, the CNT-filled compounds showed a greater degree of strain-softening (Payne effect) and stress-softening (Mullins effect) and higher permanent set than the CB-filled compounds, indicating weaker bonding. In scanning electron microscope studies on cryogenically-fractured surfaces, the CNT bundles were seen to protrude

out of the surface when the sample was stretched and slid back in when the deformation was removed. We infer that interfacial interactions between CNT and NR are weak in comparison with the relatively strong adhesion between rubber and CB, as indicated by the high amount of bound rubber in that case. Thus, reinforcement by CNTs is attributed to their large aspect ratio and physical entanglement with rubber molecules, rather than to strong interfacial interaction. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1574–1581, 2010

Key words: CNT; rubber; reinforcing mechanism; bound rubber; aspect ratio

INTRODUCTION

There has been an increasing interest in carbon nanotubes (CNTs) because of their unique mechanical and electrical properties.^{1,2} They are excellent candidates to substitute or complement conventional fillers in multifunctional polymer nanocompounds, because of their high flexibility and strength, large aspect ratio and low density. Since the early work by Ajayan et al.³ on CNT-polymer compounds, extensive research has been carried out to produce strong composite materials with high electrical and thermal conductivity.^{4–6}

Rubber is usually filled with high amounts of carbon black (CB) or silica to increase its strength and stiffness.^{7,8} The extent of reinforcement depends on the strength of polymer-filler and filler–filler interactions.^{9,10} For CB-filled rubber compounds, reinforce-

ment is generally attributed to the formation of strong rubber-filler interactions, indicated by a large amount of bound rubber.¹¹ Recently, Fukahori has suggested that the bound rubber is composed of two layers; a hard layer near the CB surface and a softer outer layer.^{12,13} The hard layer serves to increase the effective diameter of the CB particles. The soft layer plays an important role at large extensions by inducing stress hardening, whereby the molecules orient along the extension direction and then create microvoids, as in the crazing of plastic materials. This stress-hardened feature is considered necessary to diffuse and weaken the high stress concentrations around the CB particles. However, the proposed reinforcing mechanism depends upon strong adhesion of the rubber molecules to the filler.

CNTs are reported to show relatively weak interaction with an elastomeric matrix,¹⁴ even though they have a considerable reinforcing effect.^{15–17} For more effective reinforcement, better interaction between CNT and rubber would seem to be required. The aspect ratio of CNTs and the quality of dispersion will also affect the properties of the compound. Their efficiency as reinforcing fillers compared to traditional CBs is attributed primarily to their nanoscale size and high aspect ratio. A direct comparison of the reinforcing effect of multiwalled CNTs (MWNTs) and CB in natural rubber (NR) is made here. The mechanical properties, stress–strain relations, bound

Correspondence to: C. Nah (cnah@chonbuk.ac.kr).

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TABLE I
Formulations of Rubber Compounds (the unit is phr)

	NR	CNT1	CNT3	CNT7	CNT20	CB1	CB3	CB7	CB50
NR	100	100	100	100	100	100	100	100	100
CNT	–	1	3	7	20	–	–	–	–
CB	–	–	–	–	–	1	3	7	50
ZnO	5	5	5	5	5	5	5	5	5
S/A	1	1	1	1	1	1	1	1	1
MBTS	1	1	1	1	1	1	1	1	1
Sulfur	2	2	2	2	2	2	2	2	2

rubber content, and volume expansion on extension, were examined. Scanning electron microscopy (SEM) was used to observe the morphological changes of CNT upon deformation and to interpret their reinforcing effect. A new reinforcing mechanism for CNT-filled NR compounds is suggested, based on the experimental findings.

EXPERIMENTAL

MWNT (purity >95%, diameter: 15–30 nm) was obtained from Nanotech, Korea and CB (N220, BET 112 m²/g, average particle size: 27 nm) was supplied by Korea Carbon Black NR (SMR CV60) was used as the rubber matrix. The other compounding ingredients were sulfur, zinc oxide (ZnO), stearic acid (S/A), and dibenzothiazole disulfide (MBTS, Monsanto). The rubber compound formulations are given in Table I.

The compounds were mixed using a HAAKE internal mixer (Technik GmbH, Germany). NR was first mixed with zinc oxide, stearic acid and reinforcing filler (CNT or CB) in an internal mixer at 120°C for 8 min at a rotor speed of 40 rpm. To produce crosslinked samples, sulfur and MBTS were then added using a laboratory two-roll mill at a temperature below 100°C for 2 min. NR/CNT and NR/CB vulcanizates were then prepared by compression molding at 150°C for an optimum period, determined by prior experiments with a cure rheometer (ODR 2000, Alpha Technologies).

Part of the compounds before addition of sulfur and MBTS were used to determine the amount of bound rubber in uncrosslinked material. Soluble materials were extracted by immersing samples in toluene for 7 days, followed by drying for 2 days at room temperature. The weights of the uncrosslinked samples before and after the extraction were measured, and the bound rubber contents were calculated using the following expression¹⁸:

$$R_b (\%) = 100 \times \frac{W_{fg} - W_t \left(\frac{m_f}{m_f + m_r} \right)}{W_t \left(\frac{m_r}{m_f + m_r} \right)} \quad (1)$$

where R_b (%) is the bound rubber content, W_{fg} is the weight of filler and gel, W_t is the weight of the test

sample, m_f is the fraction of filler in the compound, and m_r is the fraction of rubber in the compound.

A Universal tensile tester (LRX Plus, Lloyd Instruments, UK) was used for tensile measurements on the crosslinked materials. All tests were performed in accordance with ASTM D 412, at room temperature and using a crosshead speed of 500 mm/min. Samples were also stretched to 100% elongation and retracted three times at a crosshead speed of 300 mm/min to measure the hysteresis losses. The fractional hysteresis (FH), defined as the energy dissipated relative to the energy supplied on stretching, was determined from the areas A_{ext} (work done during extension) and A_{ret} (work returned during retraction), using the following expression:

$$FH = \frac{A_{ext} - A_{ret}}{A_{ext}} \quad (2)$$

The dynamic storage modulus of the compounds was measured at room temperature using a dynamic mechanical analyzer (GABO Qualimeter 150N, Germany). The sample size was 20(L) × 6(W) × 2(T) mm, and the pre-strain was 20%. The dynamic strain was varied from 0.1 to 10%. The frequency was 11 Hz.

A hydrostatic weighing technique was used for measuring volume changes on stretching the crosslinked materials, and hence changes in density.^{19,20} Ring-type rubber samples with a diameter of 10 mm were placed on glass cylinders which had different diameters, to give different degree of stretching. The measurement was carried out with the samples suspended and immersed in distilled water to which a small amount of detergent was added for better wetting and removal of air bubbles from the sample surface. The samples were conditioned by immersion in water for 180 min before starting the measurements. After taking measurements with the samples in the unstretched state, they were stretched to 90% and the density determined again. Measurements were repeated three times. The change in volume on stretching was then calculated from the difference in mean weights between the unstretched and stretched positions.

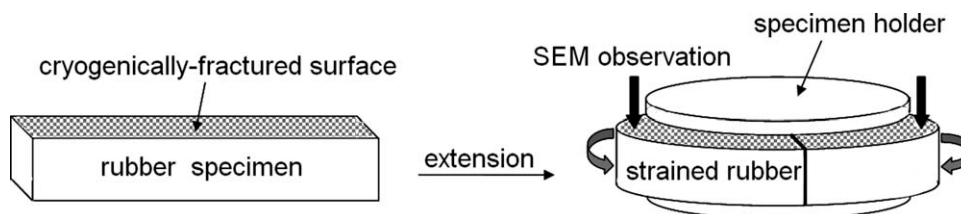


Figure 1 Sample preparation for SEM observation under deformation.

To examine the dispersion of CNT in the rubber, a sample was fractured cryogenically and the broken surface was studied using field emission SEM (FE-SEM, model S-4300 SE, Hitachi, Japan) operated at 15 kV. The samples were sputter coated to improve contrast. The fractured specimen was also extended by about 15%, and the extended specimen was adhered to a cylindrical sample holder, as shown in Figure 1, to examine possible changes in the morphology of CNTs under deformation.

RESULTS AND DISCUSSION

The stress–strain curves of NR, NR/CNT and NR/CB compounds are presented in Figure 2. The modulus at 100 and 300% elongation, tensile strength, and elongation at break of NR, NR/CNT and NR/CB are given in Table II. The 300% modulus is plotted in Figure 3 as a function of filler content. The modulus values increased with increasing filler content, but to a significantly greater degree for the CNT-filled compounds. This is attributed to the fact that CNTs are highly anisotropic compared to CB.^{21,22} Considerable improvement in the stiffness of nanocompounds has been reported previously using high-modulus fillers with high aspect ratio.²³ Theoretical models (for example, those proposed by

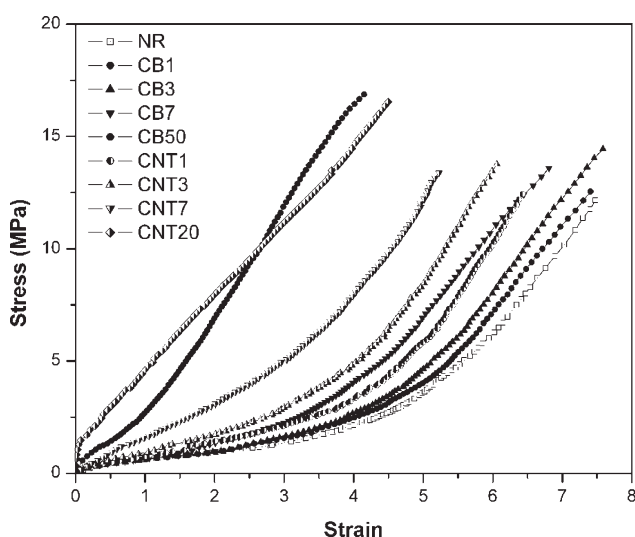


Figure 2 Stress–strain curves of NR, NR/CNT, and NR/CB compounds.

Guth⁹ and Halpin-Tsai²⁴) relate the elastic modulus of compounds directly to the aspect ratio and volume fraction of filler particles.

However, for high strength, good interfacial adhesion is also required. The tensile strength of a CNT-filled compound was found to be comparable with those of CB-filled compounds at the similar filler loadings. As the content of CNT increased, the tensile strength increased markedly, with a corresponding decrease in the elongation at break. These results suggest that the level of adhesion with CNT is sufficient to give good reinforcement.

The tensile behaviors of rubber compounds usually exhibits hysteresis in cyclic loading; the stress in retraction being lower than that in extension. Hysteresis loops are shown in Figure 4 for NR/CNT and NR/CB compounds with 1 phr of filler. Stress softening and incomplete recovery are seen. The stress softening phenomenon at large strains is termed the Mullins effect,²⁵ and is usually attributed to detachment of rubber molecules from the surface of filler particles.^{26,27} Houwink²⁸ suggested that it was due to slippage of the rubber molecules over the filler surface, and this might be a significant factor with CNT. We note that the CNT compounds exhibited a greater permanent set (incomplete recovery) than the CB compounds (Table III). However, permanent set has been attributed to a wide variety of causes.²⁵

Figure 5 shows the fractional hysteresis of the NR/CNT and NR/CB compounds. Energy dissipation was greatest in the first cycle and decreased in

TABLE II
Mechanical Properties of NR/CNT and NR/CB Compounds

	Modulus (MPa)		Tensile strength (MPa)	Elongation at break (%)
	100%	300%		
NR	0.62	0.46	12.16	747.75
CNT1	0.75	0.71	12.43	643.10
CNT3	0.92	0.97	13.76	606.04
CNT7	1.59	1.68	13.38	522.50
CNT20	4.59	3.74	16.55	449.99
CB1	0.62	0.52	12.55	740.82
CB3	0.62	0.55	14.44	758.54
CB7	0.66	0.76	13.58	680.83
CB50	2.69	3.98	16.88	414.99

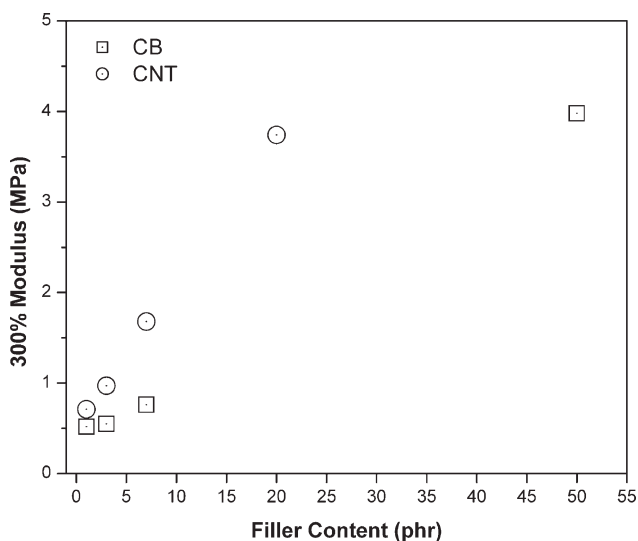


Figure 3 Moduli at 300% elongation of NR/CNT and NR/CB compounds at different filler loadings.

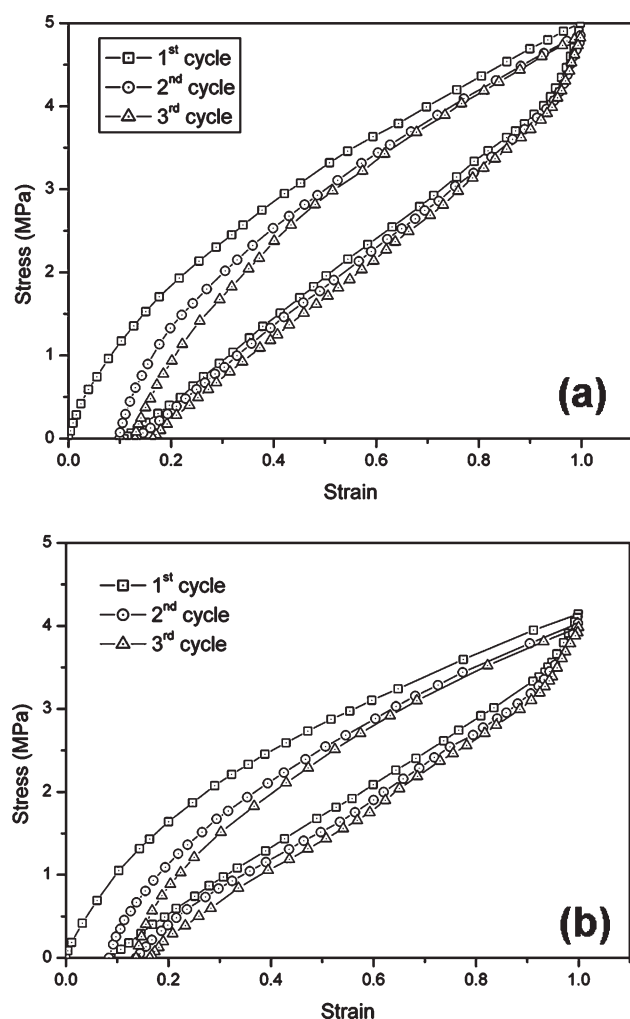


Figure 4 Hysteresis loops of NR/CNT and NR/CB compounds with 1 phr of filler content.

TABLE III
Permanent Set of NR/CNT and NR/CB Compounds (Elongation, %)

	Number of cycle		
	1st	2nd	3rd
CNT1	10.83	3.32	3.51
CNT3	20.00	2.73	3.12
CNT7	23.08	5.07	2.39
CNT20	23.68	6.27	7.16
CB1	8.78	5.29	2.67
CB3	8.34	5.27	4.07
CB7	9.20	5.29	5.87
CB50	12.99	6.85	6.35

the second and third cycles. The CNT-filled samples showed greater hysteresis than the CB-filled ones, suggesting that more debonding or detachment of rubber molecules occurred from CNT. However, it has been reported that a large contribution to the tensile stress in CNT-filled compounds arises from orientation effects, and that the pronounced lowering in the stress observed in the second stretching could thus be ascribed to a loss of orientation on releasing the stress.¹⁴

The dynamic storage modulus of the NR/CNT and NR/CB compounds with various filler loadings are shown in Figure 6 as a function of strain amplitude. While unfilled rubbers display little changes in dynamic properties with increasing strain amplitude, the storage modulus of filled rubber compounds decreases significantly. This nonlinear behavior at small strains is known as the Payne effect.²⁹ It has been attributed to a gradual breakdown of interparticle adhesion with increasing strain amplitude.¹⁰ It is more pronounced at higher filler loadings, and is seen here to be significantly higher in the CNT-filled compounds. This could reflect the presence of weakly-associating aggregates of CNT bundles,

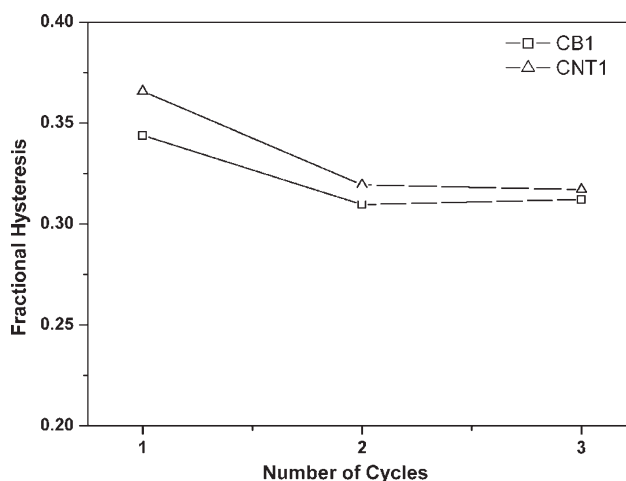


Figure 5 Fractional hysteresis of (a) NR/CNT and (b) NR/CB compounds with 1 phr filler upon cyclic loading.

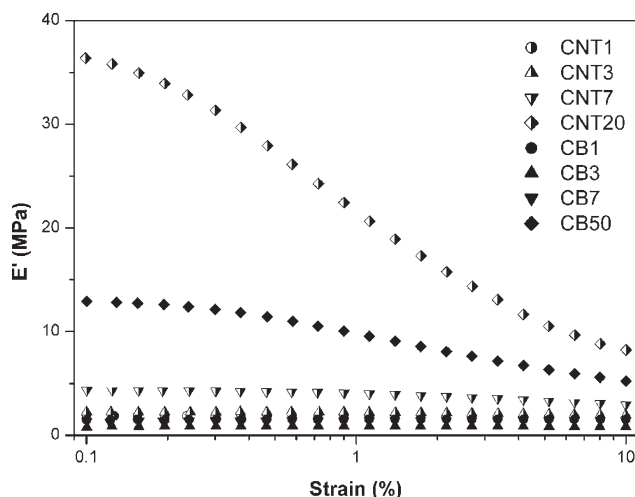


Figure 6 Storage modulus of NR/CNT and NR/CB compounds at different filler loadings as a function of dynamic strain amplitude.

formed because of the small size and large surface area of CNT.

Bound rubber has been attributed to polymer-filler interaction, and the amount of bound rubber is considered an important indicator of reinforcement. Figure 7 shows the bound rubber content of NR/CNT and NR/CB compounds as a function of filler loading. In both cases the amount increased with increasing filler content, but it was much lower with CNT, suggesting weaker rubber-filler interactions in that case. This conclusion is consistent with that reached by others.^{12,14} However, bound rubber depends on other characteristics of the filler (its structure and surface area, as well as its surface properties) and also on the chemical composition and functionality of the rubber.³⁰ It is inferred that the aggregate structure of CB is more efficient than the fibril struc-

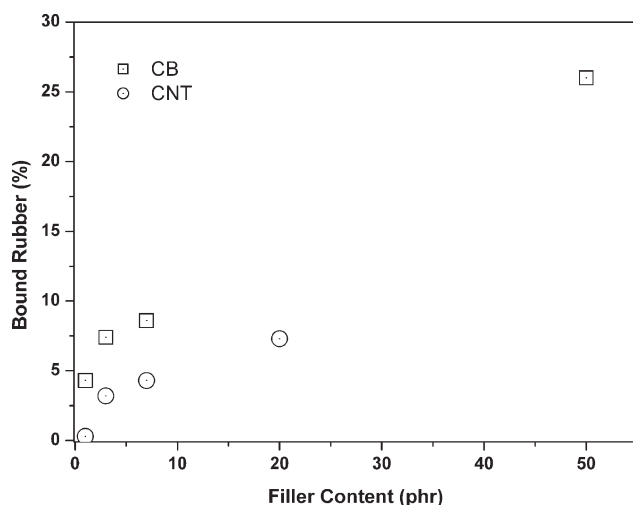


Figure 7 Bound rubber content of NR/CNT and NR/CB compounds at different filler loadings.

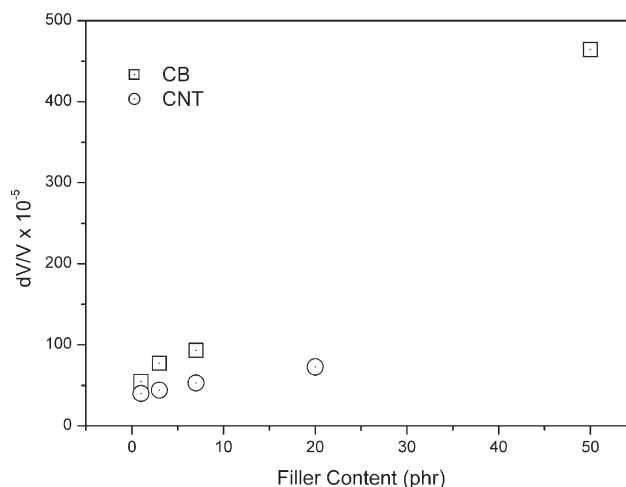


Figure 8 Volume expansion of the NR/CNT and NR/CB compounds at different filler loadings at 90% extension.

ture of CNT for making bound rubbers, if the surface activity is similar.

Figure 8 shows the volume expansions of the NR/CNT and NR/CB compounds, stretched by 90%, as a function of filler content. (On retraction, the volume returned almost completely to its original value.) With both fillers the volume expansion increased as the filler content increased, but to a greater extent with CB. When the volume expansion is plotted against the bound rubber content (Fig. 9) it is seen to increase approximately in proportion to the amount of bound rubber.

In well-reinforced CB-filled rubber compounds, volume expansion at large extensions has been attributed to the formation of microvoids; a craze-like phenomenon.^{12,13} It has even been suggested that this process is an essential factor in reinforcement by CB.^{12,20} Volume expansion may also occur in the bound rubber fraction by a meniscus instability mechanism.^{12,31}

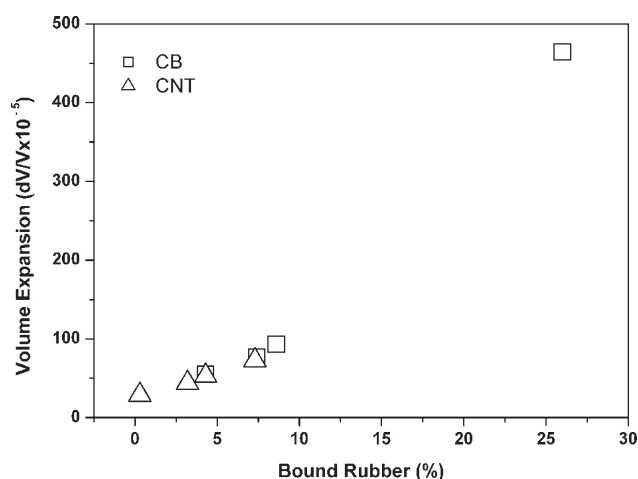


Figure 9 Relation between bound rubber and volume expansion in the NR/CNT and NR/CB compounds.

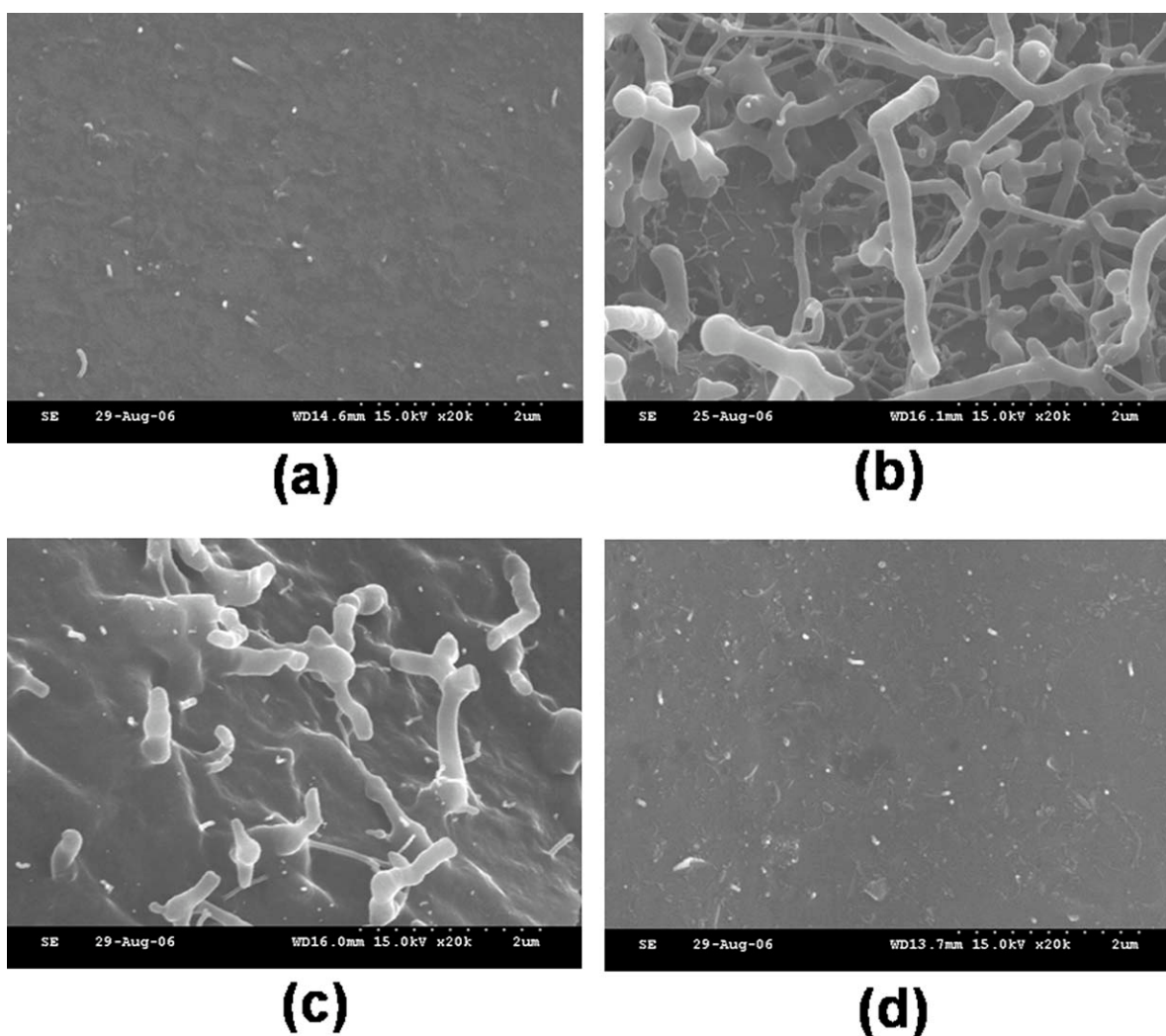


Figure 10 SEM images of CNT-filled rubber compound containing 7 phr CNT: (a) without stretching, (b) at 15% stretching, (c) 15 min after removal of stretching, and (d) 24 h after removal of stretching.

In general, the CNT compounds showed much better mechanical properties than the CB compounds. This suggests that the reinforcing mechanism of CNT is different from that of CB, and that the amount of bound rubber is not a main factor. Instead, the large aspect ratio is probably the most significant difference.

To study possible morphological changes in the CNT, a cryogenically-fractured specimen of the CNT-filled compound was stretched by about 15% and secured by bending it round a mandrel, Figure 1. The fracture surface of the sample was then observed using SEM. Figure 10 shows SEM micrographs after various times. In the unstretched state, the CNTs are seen to be well-dispersed [Fig. 10(a)]. When the specimen was stretched by about 15%, long coil-like CNTs with smooth surfaces are seen to protrude out of the fracture plane [Fig. 10(b)] indicating weak interaction between the CNTs and the rubber.³² The protrusion of CNTs is attributed to lat-

eral contraction of rubber on stretching, and a mismatch in Poisson's ratio between rubber and a network of rigid fibers. When the strain was released, the protruded CNTs slowly re-entered the rubber. Only a few smooth outcrops of CNTs were observed on the surface after 15 min [Fig. 10(c)], and after 24 h, the surface reverted back to the initial smooth condition [Fig. 10(d)]. However, no such protrusion behavior was observed for CB-filled case, as shown in Figure 11. These observations are direct experimental evidence for weak interfacial interactions and easy slippage between CNTs and the rubber matrix.

But CNTs obviously carry a substantial fraction of applied loads and thereby improve the mechanical properties of the NR/CNT compounds. Schadler et al.³³ observed similar poor interfacial load transfer in tension in a MWNT/epoxy system. They explained it on the basis of slippage of the inner layers of the nanotubes with respect to the outer layer, due to relatively weak adhesion between the

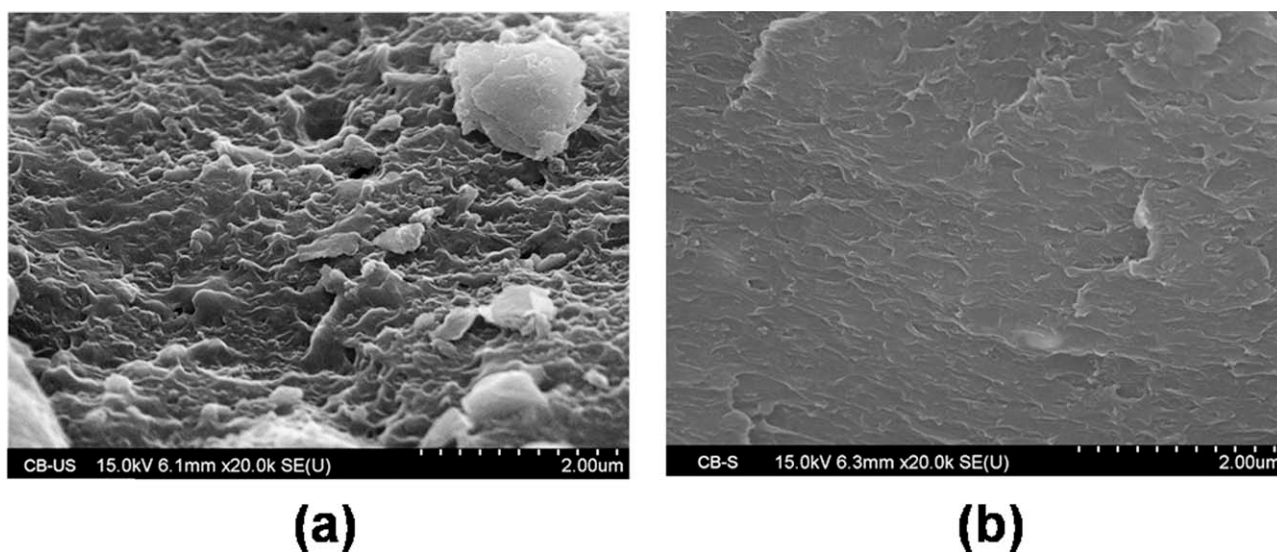


Figure 11 SEM images of CB-filled rubber compound containing 7 phr CB: (a) without stretching and (b) at 15% stretching.

layers. This mechanism is probably also operative in the NR/CNT system. However, the observations shown in Figure 10 suggest that the nanotubes have weak adhesion to rubber anyway. High tensile modulus and strength must therefore be attributed to the high aspect ratio of CNTs, overcoming the disadvantage of their poor adhesion to rubber.

To the best of our knowledge, such observations of the sliding of CNTs in the rubber matrix have not been previously reported. Wagner et al.³⁴ observed “telescopic” ruptures in MWNTs and attributed it to strong interfacial interaction between the nanotubes and the polymer matrix. However, no “telescopic” rupture was observed in the present NR/CNT system. Instead, our results suggest poor interfacial interaction. The most important factors in reinforcement by CNTs appear to be their large aspect ratio, and the resulting effective load transfer, rather than bonding to rubber. In contrast, interfacial bonding appears to be mainly responsible for reinforcement in conventional CB-filled rubber compounds.

CONCLUSIONS

The reinforcing mechanism in CNT-filled rubber compounds has been compared and contrasted that of CB. The CNT compounds showed much higher mechanical properties than the NR/CB compounds at the same filler content. On the other hand, the amount of bound rubber was lower, and also the expansion in volume upon stretching. The CNT-filled compounds also showed a greater degree of stress-softening at low and high strains (Payne effect and Mullins effect) than the CB-filled compounds. These results suggest that the interfacial interaction between CNT and rubber is relatively weak and the

interfacial bonds break down readily as the compound is stretched. This was directly confirmed by SEM observations showing protruded CNTs with smooth surfaces slipping out of the rubber surface on deformation and back in when the deformation was removed. Thus, the most important factor for reinforcement by CNTs appears to be their high aspect ratio, causing physical entanglement and effective load transfer, rather than strong interfacial adhesion. In contrast, the latter appears to be the main factor in reinforcement by CB.

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