

Properties of Styrene-Butadiene Rubber Nanocomposites Reinforced with Carbon Black, Carbon Nanotube, Graphene, Graphite

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Abstract The characteristics of all polymer composites containing carbon materials are determined by four factors: component properties, composition, structure and interfacial interactions. The most important filler characteristics are particle size, size distribution, specific surface area and particle shape. As a consequence, in this paper we discuss the aspects of the mechanical, electrical and thermal properties of composites with different fillers of carbon black, carbon nanotube (CNT), graphene and graphite and focus on the relationship between factors and properties, as mentioned above. Accordingly, we fabricate rubber composites that contain various carbon materials in carbon black-based and silica based-SBR matrixes with dual phase fillers and use scanning electron microscopy, Raman spectroscopy, a rhometer, an Instron tensile machine, and a thermal conductivity analyzer to evaluate composites' mechanical, fatigue, thermal, and electronic properties. In mechanical properties, hardness and 300%-modulus of graphene-composite are sharply increased in all cases due to the larger specific surface. Also, it has been found that the thermal conductivity of the CNT-composite is higher than that of any of the other composites and that the composite with graphene has the best electrical properties.

Key words carbon black, carbon nanotube, graphene, graphite, styrene butadiene rubber (SBR).

1. Introduction

The high and reversible deformability of elastomers is of great industrial importance. However, the initial modulus and durability of such material is low, and an additional reinforcing material is required for practical use. Carbon black and silica particles have been used extensively for this purpose.¹⁻³⁾ And in order to create new material systems with superior properties, various nanoparticles have been also used as reinforcing fillers in elastomeric matrices. These nanometerscale reinforcing particles include spherical particles such as silica or titania,⁴⁻⁶⁾ platelets such as layered silicate⁷⁻⁹⁾ or clay fibers¹⁰⁾ and multiwall or single-wall carbon nanotubes.¹¹⁻¹²⁾ Especially, nano-sized carbon material particles within a host matrix have proved to be an excellent approach for exhibiting greatly improved mechanical properties.

Carbon exists in many modifications: three dimensional crystals (diamond, graphite), two-dimensional graphene, one-dimensional nanotubes and zero-dimensional fullerenes. Graphite is layered crystal with c-axis lattice and carbon atoms within a layer are covalently bonded. Graphite is

well known for its high strength and high thermal conductivity, it offers the possibility of making multifunctional composites in a cost effective way. Carbon nanotube (CNT) is molecule-scale tubes of graphitic carbon with outstanding properties and exhibits exceptional mechanical, thermal and electrical properties. And Graphene is defined as a flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice. Along with its unique structure, graphene possesses a range of unusual properties: most notably the thermal conductivity and mechanical stiffness may rival the original values of graphite; the strength may be comparable to that of carbon nanotubes; and individual graphene is found to have excellent electronic properties.

Nanocomposites of polymers with previous carbon nanomaterials have been shown to exhibit a significant increment in the properties of polymers and even generate certain new properties that cannot be derived from their counterparts, as the mixing of phases in them occurs over a much smaller length scale in comparison to micronmeter length scale of conventional composites.¹³⁾ Therefore, in recent years, nanoparticles based composites have drawn considerable attentions. The most promising materials are polymer/CNT nanocomposites,¹⁴⁻¹⁷⁾ polymer/graphene nanocomposites,¹⁸⁻²²⁾ polymer/graphite nanoplatelet nanocomposites.²³⁻²⁵⁾

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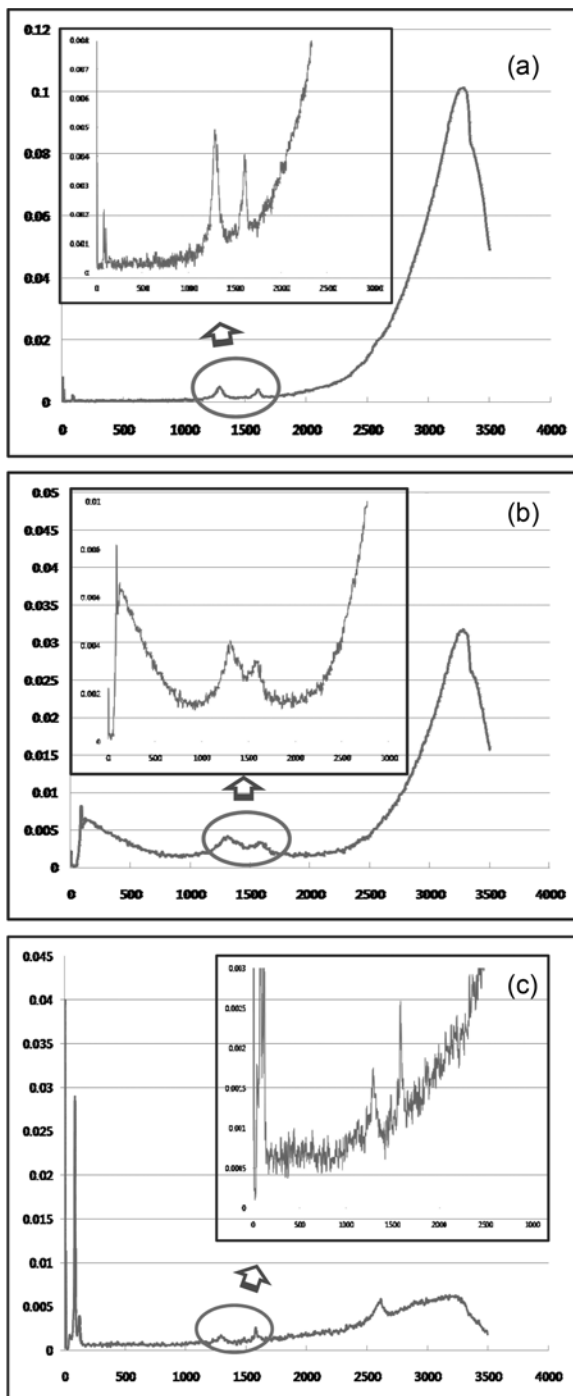


Fig. 1. Raman spectroscopy of (a) CNT (b) graphene and (c) graphite.

Curing characteristics were measured over 30-min period at 160°C using a moving-die rheometer (DRM-100(LP-171)). Tensile tests were carried out in an Instron tensile machine (Instron Co. UK) at a crosshead speed of 300 mm/min. The dumbbell shape samples were 100 mm in length, 1 mm in thickness and 5 mm in width. At least four tests were carried out for each case.

Table 2. Raman spectroscopy results of CNT, graphene and graphite.

	D band	G band	I(D)/I(G)
CNT	0.00492	0.00404	122%
Graphene	0.00422	0.00337	125%
Graphite	0.00337	0.0035	96%

Shore A hardness was measured by using a hand-held shore A durometer according to TECLOCK. The fatigue properties of composites were characterized by using Demmattia (UESHIMA).

3. Results and Discussion

3.1 Materials characterization

Fig. 1 and Table 2 show the Raman spectroscopy of carbon nanofillers. The main features in the Raman spectroscopy of carbon nanofillers are the so-called G and D bands, which lies at around 1588 and 1357 cm^{-1} respectively. All carbon nanofillers are observed G and D bands, and I(D)/I(G) ratio of graphene is higher than any other materials. This result suggests minimal damage of graphite and significant devastation of graphene.

Microstructures of carbon materials were examined by SEM, and are shown in Fig. 2. Fig. 2a shows highly entangled and randomly organized CNT, and Fig. 2b shows the worm-like shape of graphene. And also Fig. 2c shows irregular honeycomb network of graphite sheets and reveals the dense structures composed of many graphite sub-layers.

3.2 Characterization of Carbon Materials/Rubber composites

The curing curves of carbon nanofillers/rubber composites and some parameters of curing properties are shown in Fig. 3, Fig. 4 and Table 3.

Three regions are observed in Fig. 3 and Fig. 4. The first region is the scorch delay or induction period where the torque of compounds decreased. The second region is where the curing reaction occurred. The network structure was formed in this period, leading to the sharp increment of the torque. In third region, curing curves reached to a plateau when the network matured by equilibrium. The cure time of rubber composites using Graphene is faster than other rubber composites in both Carbon Black-Based Composites (CBC) and Silica-Based Composites (SBC). The reason for the shorter cure time of the rubber composite using Graphene is probably due to the more spacious

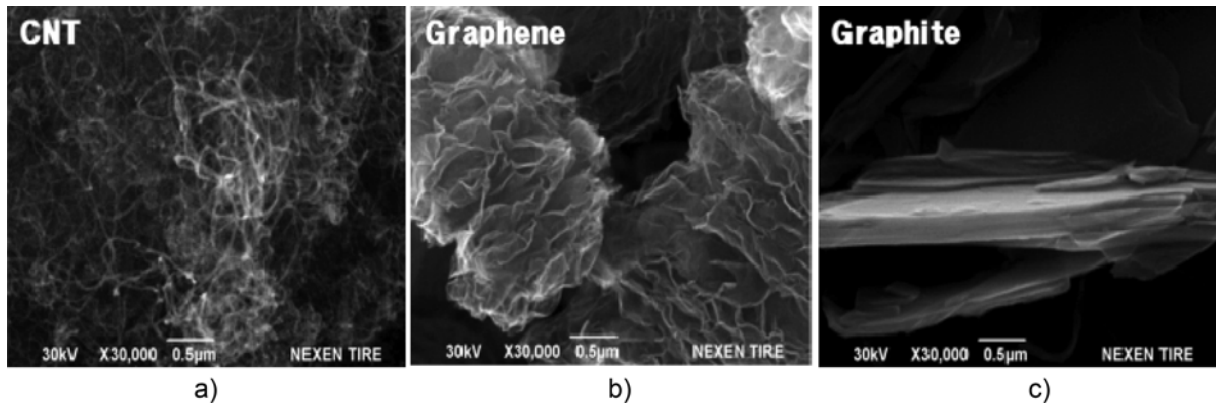


Fig. 2. SEM image of (a) CNT (b) graphene and (c) graphite.

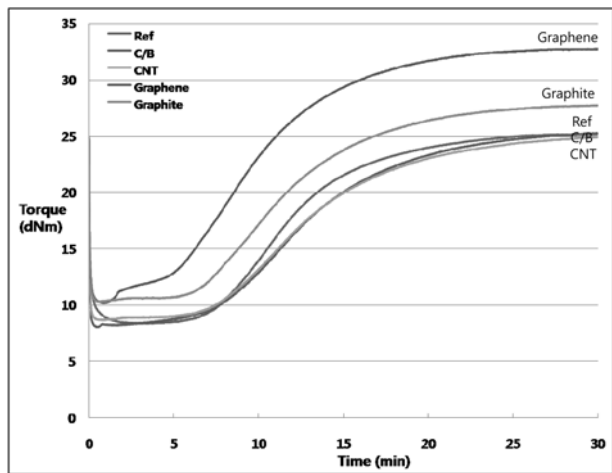


Fig. 3. Curing properties of carbon nanofillers/CBC.

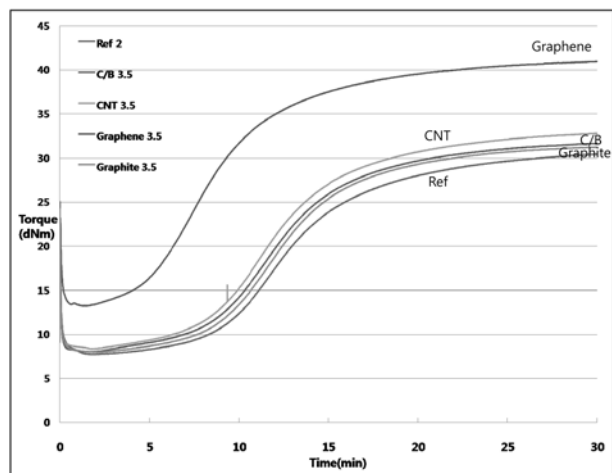


Fig. 4. Curing properties of carbon nanofillers/SBC.

specific surface by two dimensions.

That is to say, Graphene increases the bonding force with the rubber, and thermal conductivity through the result is also enhanced. However, the composites of the other carbon materials with different dimensions are similar with the cure properties because of the small specific surface.

M_L is the lowest torque and M_H is the highest torque at curing curves. $M_H - M_L$ represents the crosslink density of vulcanization. $M_H - M_L$ slightly increases after loading Graphene. This indicates that the addition of Graphene has

a little effect on the crosslink density of rubber vulcanization.

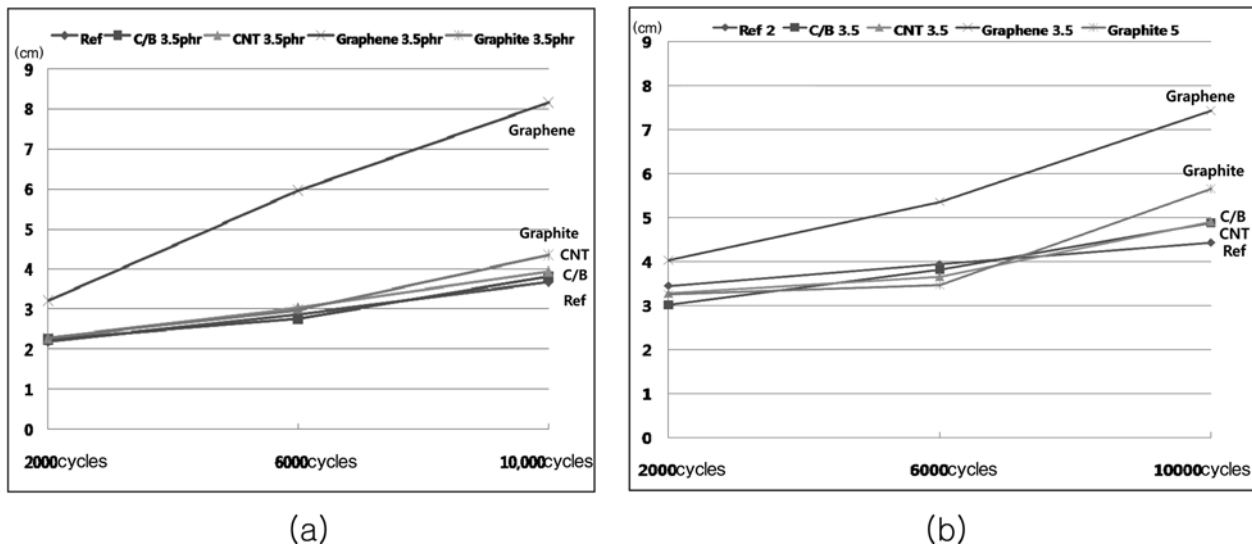
The mechanical properties of carbon nanofillers/rubber composites are summarized in Table 4. From this table, shore A hardness of the composites of Graphene is highly increased, indicating that small additions of the filler largely influence the rubber matrix. In CBC, the composite reinforced with Graphene showed about 115% increment over Ref 1 in modulus, while led to the decrement in both tensile strength and the elongation at break. And in

Table 3. Curing Properties of carbon nanofillers/SBR composites

	1 (Ref 1)	2	3	4	5	6 (Ref 2)	7	8	9	10
T40 (min)	10.6	11.3	11.3	8.2	10.1	11.8	11.2	11.0	7.6	11.5
T90(min)	18.7	20.6	20.7	16.8	18.9	20.4	19.2	19.2	16.2	19.1
Min Torque (ML, dNm)	8.4	8.1	8.7	10.2	10.3	7.7	8.0	8.3	13.2	8.0
Max Torque (MH, dNm)	25.2	25.3	24.9	32.8	27.7	30.4	31.6	32.8	41.0	31.2
Δ Torque	16.8	17.2	16.2	22.6	17.4	22.7	23.6	24.5	27.8	23.2

Table 4. Physical properties of carbon nanofillers/SBR composites.

	1 (Ref 1)	2	3	4	5	6 (Ref 2)	7	8	9	10
Hardness	51	54	54	65	57	61	62	63	73	65
M-300% (MPa)	4.51	4.9	4.51	8.33	5.1	5.98	6.47	6.96	10.49	6.67
Tensile Strength (MPa)	18.52	17.54	17.35	17.44	16.76	20.48	20.48	18.82	17.64	20.48
Elongation (%)	746	714	761	623	724	720	720	640	510	690
Electrical Properties (Ω)	1070K Ω	425K Ω	249K Ω	31K Ω	146K Ω	768G Ω	662G Ω	507G Ω	160G Ω	460G Ω
Thermal Properties (W/mK)	0.2756	0.2815	0.2931	0.2861	0.2897	0.2661	0.2707	0.2988	0.2814	0.2822

**Fig. 5.** Fatigue properties of carbon nanofillers/ SBR composites. a) Carbon-based composites and b) Silica-based composites.

SBC, composite with Graphene also revealed about 75% increase in modulus over Ref 2, while the tensile strength and elongation at break are decreased 18% and 40% respectively. The composites using Graphene showed much higher reinforcement effects than conventional fillers, and the reason which is increased hardness and modulus of Graphene composites is due to the widest specific surface by the two-dimension. And, when rubber is compounded with carbon nanofillers, the mechanical properties are similar except for Graphene rubber composites. This reason is that the Graphene Composites increases the cross-linking density created by polymer-filler interactions as compared with other composites.

The fatigue properties of carbon nanofillers/rubber composites are shown in Fig. 5 and Table 5.

$$dc/dn = AG^n \quad (1)$$

Where, c is the crack length, n is the cycles, G is the tear energy.

Fatigue crack growths (dc/dn) of composites using carbon nanofillers are similar except graphene composites in both CBC and SBC. In other words, fatigue crack growth of composites using graphene is increased because the composites are more brittle than other rubber composites. This means that the tearing energy is decreased and fatigue life is increased from Eq. (1).

Thermal and electrical properties of carbon nanofillers/rubber composites are shown Table 5. Generally, the specific heat and thermal conductivity of carbon systems are determined primarily by phonon. At low temperatures, the phonon contribution to these quantities dominates and is due primarily to acoustic phonons. And, the phonon specific heat of Graphene has a quadratic temperature contribution due to longitudinal acoustic and in-plane transverse

Table 5. Fatigue properties of carbon nanofillers /SBR composites. (unit: cm)

	1	2	3	4	5	6	7	8	9	10
2000 cycles	2.19	2.24	2.27	3.21	2.28	3.45	3.02	3.28	4.03	3.26
6000 cycles	2.86	2.76	3.03	5.97	2.98	3.94	3.82	3.66	5.36	3.47
10,000 cycles	3.67	3.81	3.95	8.17	4.35	4.43	4.88	4.91	7.43	5.66
dn/dc	0.74	0.79	0.84	2.48	1.04	1.76	1.81	1.81	2.65	1.94

acoustic phonons, and linear contribution due to the out-of-plane transverse acoustic phonons. Also, the Graphite is dominated by the three acoustic phonons. In the case of the CNT, CNT yields linear wavevector dependence of all four acoustic branches: longitudinal, twist, and doubly-degenerate transverse ones.²⁶⁾ And also a large aspect ratio of the materials is advantageous for the thermal conductivity within the composite, as recognized by Yu et al.²⁷⁾

The electrical conducting mechanism of polymer composites is associated with two questions: 1) how to form the conducting paths and 2) how to conduct after the formation of the paths. Concerning the second question, several theories exist, such as contact conducting, the tunneling effect, dielectric breakdown, and field emission. It is generally believed that conductivity depends on their combined effect and could be summarized by the general statement that the microscopic migration of electrons might have several mechanisms. With regard to the first question, there are, for example, the percolation theory²⁸⁾, the effective medium theory,²⁹⁾ the microstructure theory,³⁰⁾ and thermodynamic theory.³¹⁾ These theories are related to the dispersed morphology and internal microstructure of conducting fillers in polymer matrices.

In case of CBC, in addition to improve the mechanical properties, Carbon Nanofillers impart conductivity to low resistivity elastomeric matrices. The electrical and thermal properties are improved by adding the carbon nanofillers due to facilitate the electrical and thermal transition through filler-filler and filler-matrix interactions. Especially, the CNT composite has the most predominant thermal property, and is increased nearly 7% compared with Ref 1, because the CNT transfers the heat by four acoustic phonons, and the higher aspect ratio of MWNTs bundles increases the probability of particle-particle contacts. The composite using the graphite has the next best thermal properties by the three acoustic phonons, and then composite using the graphene has the thermal properties as follows by the two acoustic phonons according to the dimensions.

However, electrical property of Graphene composites is higher than any other composites. The reasons are that the Graphene particles with the large specific surfaces can abut or contact and then form a conducting network at lower Graphene contents. Also, while CNT and graphite have the metallic and semi-conductive properties, Graphene has metallic property of zero band gaps and is easy to make the formation of the conducting paths.

In case of SBC, Thermal properties are improved by adding the carbon nanofillers by the same reasons and the orders of the thermal conductivity are alike the orders of the CBC. But, electrical properties of carbon nanofillers/rubber composites are shown higher resistivity $\sim G\Omega$, due to decrease the probability of particle-particle contacts by adding the small amounts. That is, there is a critical volume fraction known as the percolation threshold at which the conducting inclusions form an interconnecting filler network leading to a sharp drop in the electrical resistance. Below the critical volume fraction of carbon nanofillers, an interconnecting filler network is not formed, which results in a high increase of the electrical resistance of the nanocomposites.

4. Conclusion

Carbon nanofillers/SBR composites were prepared and evaluated their mechanical, fatigue, thermal and electrical properties according to the fillers. Rubber composites using graphene are improved the cure time and increased the crosslink density of rubber vulcanization.

And mechanical properties, the properties of the composites using other carbon nanofillers were similar except the graphene composites in both CBC and SBC.

That is, hardness of graphene rubber composites was sharply increased and modulus showed about 115%, 75% increment respectively over Ref 1 and Ref 2, while the tensile strength and elongation at break were decreased in CBC and SBC.

In the fatigue properties, fatigue crack growths of composites using carbon nanofillers are similar except for the graphene-composites.

The composite using CNT has the most predominant thermal property by four acoustic phonons, and electrical property of composite using graphene is higher than any other composites due to metallic properties by zero band gaps in CBC. However, in case of SBC, the electrical properties of carbon nanofillers showed the $\sim G\Omega$ resistivity because of decreasing the probability of particle-particle contacts by adding the small amounts. Thermal properties are improved by adding the carbon nanofillers and the orders of the thermal conductivity are alike with CBC.

The carbon nanofillers/SBR composites hold the promise of delivering exceptional mechanical properties and multi-functional characteristics.

The unique properties of the composites with carbon nanofillers are probably one of the most important processes in rubber industry and essentially in modern tire technology. Also, composites using carbon nanofillers in CBC will be excellent candidates for application in organic and hybrid electronics.

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