



Investigation of the Mechanical, Electrical and Thermal Properties of Rubber Composites Filled with Various Carbon Nanomaterials, Carbon Nanotube, Graphene and Graphite[†]

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Rubber composites containing carbon black as a general fillers and multiwalled carbon nanotube, graphene and graphite as specific fillers were fabricated. Carbon materials were modified chemically and physically through an acid, heat and latex treatment to enhance the dispersion in rubber matrices. The acid, heat and latex treatment of carbon nanomaterials improved the mechanical properties, such as hardness, modulus, fatigue properties, electrical and thermal conductivity compared to pristine carbon materials. The modified graphene showed the most enhanced hardness, modulus and electrical conductivity but a significant decrease in the fatigue property and elongation. The modified carbon nanotube showed better thermal conductivity than the others, whereas the electrical and thermal conductivity of the nanocomposites decreased due to the formation of surface defects of multiwalled carbon nanotube by chipping.

Key Words: Carbon nanotube, Graphene, Graphite.

INTRODUCTION

Since carbon nanotube was discovered in 1991, carbon nanotubes and related carbon nanomaterials have attracted considerable attention because of their outstanding mechanical, electrical and thermal properties.

Carbon materials exist in many allotropes *e.g.*, three dimensional crystals (diamond, graphite), two-dimensional graphene, one-dimensional nanotubes and zero-dimensional fullerenes¹. Graphite is a layered crystal with c-axis lattice and carbon atoms within a layer bonded covalently. Graphite is well known for its high strength and high thermal conductivity and it offers the potential of fabricating multifunctional composites in a cost effective manner. carbon nanotubes are molecule-scale tubes of graphitic carbon with outstanding properties and exceptional mechanical, thermal and electrical properties. Graphene is defined as a flat monolayer of carbon atoms packed tightly into a two-dimensional honeycomb lattice. Along with its unique structure, graphene possesses a wide range of unusual properties. Most notably the thermal conductivity and mechanical stiffness are as high as the original values of graphite and the strength might be comparable to that of carbon nanotubes. Individual graphene has excellent electronic properties.

Nanocomposites of polymers containing previously mentioned carbon nanomaterials exhibited significant improvement

in the properties of polymers and even generate novel properties that cannot be derived from their counterparts because the mixing of phases in them occurs over a much smaller length scale compared to the micrometer length scale of conventional composites². Therefore, in recent years, nanoparticle based composites have attracted considerable attentions. Among them the most promising materials are the nanocomposites of carbon nanotube³, graphene⁴ and exfoliated graphite⁵.

Although the properties of carbon nanomaterials are excellent, they have not brought any remarkable improvements in the properties of composites because of their poor dispersion due to the large surface area and weak interaction with polymer chains, which causes large aggregations and clumps and as a result, significant decreases in hysteresis and elongation and fatigue properties⁶.

To obtain the expected properties, the improved dispersion of carbon nanomaterials within polymer matrices *via* increased interactions between the nanomaterials and polymer chains should be achieved. Many technical alternatives are available to enhance the dispersion of carbon nanomaterials.

First, there are physical treatments, such as ultrasonication, ball milling and heat treatment. Ultrasonication applies ultrasound energy to the mixture of solvent and nanomaterials over a period of several hours. Ball milling is a treatment to crush nanomaterials with a rotating ball. Heat treatment applies a

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high temperature thermal shock in nitrogen gas to nanomaterials. The advantages of these physical methods are the efficient elimination of impurities adsorbed on nanomaterials and the relatively easy achievement of a narrow distribution of length and diameter of nanomaterials and efficient exfoliation of graphite. On the other hand, such treatments enable nanomaterials to be dispersed only at the level of the aggregate units and result in a decrease in length and diameter as well as defects on the surface of the nanomaterials.

Chemical treatments, such as acid treatment, *in-situ* polymerization and latex treatment, are also used widely. An acid treatment involves the treatment of nanomaterials with nitric acid or sulphuric acid to functionalize them like $-C=O$, $-COOH$ and $-OH$ *via in-situ* polymerization, in which nanomaterials are added to the monomer solution followed by polymerization. A latex treatment was performed to mix the nanomaterials with polymer latex as dispersion media. The advantages of an acid treatment are the good dispersion of aggregates and functional groups to make nanomaterials interact with polymer chains, but this treatment results in more defects on the surface of the nanostructure than sonication. Ball milling has a huge negative effect on the electrical conductivity. *In-situ* polymerization and latex treatment can achieve better dispersion compared to other methods and has no defects on the surface of nanomaterials. The above chemical and physical treatment lead to a better dispersion and interaction with polymer chains but it is extremely difficult to produce treated carbon nanomaterials on a mass production scale. Therefore, the broader use of carbon nanotube and graphene is still limited due to the high cost.

This study was carried out to enhance the dispersion of carbon nanomaterials in rubber to improve various properties of rubber composites.

Rubber composites with nanofillers, such as multiwalled carbon nanotube, graphene and graphite, were fabricated and their mechanical, fatigue, electrical and thermal properties were examined. Carbon materials were modified chemically and physically to enhance their dispersion in rubber matrices.

EXPERIMENTAL

The matrix materials were a styrene butadiene rubber (SBR) with 23.5 % bound styrene. A styrene butadiene latex (30 % aqueous suspension and 70 % SBR) was used as a dispersion media of nanofillers. The carbon-based nanofillers used in this study were carbon black N330 (OCI Co. Ltd.), entangled multiwalled carbon nanotube (E-MWNT, Carbon Nanotech Co. Ltd.), graphene (N-Baro Tech Co. Ltd.) and graphite (Timcal Co. Ltd.). *N-tert-butyl*-benzothiazole sulfonamide (TBBS), zinc oxide (ZnO), stearic acid (S/A), sulfur and processing oil were supplied by standard local manufacturers.

Modification and treatment of carbon nanomaterials

Latex treatment of multiwalled carbon nanotube, graphene and graphite: The carbon nanomaterials were added to the styrene butadiene rubber latex and stirred vigorously for 24 h at 80 °C and the mixture was then coagulated with acetic acid, washed with water and dried at 100 °C.

Acid Treatment of multiwalled carbon nanotube and graphite: Nitric acid and sulphuric acid at the volume ratio

(v/v) of 1:4 were mixed with graphite or multiwalled carbon nanotube at room temperature and stirred for 18 h and then washed with water until the solution became neutral. The samples were dried at 100 °C to remove the remaining moisture. This enables the surface of the multiwalled carbon nanotube and graphite to adopt functional groups, such as $-C=O$, $-COOH$ and $-OH$.

Heat treatment of acid treated graphite: The acid treated graphite flakes were heated to 850 °C for 3 min in nitrogen gas to obtain an expanded or exfoliated structure.

Characterization and measurement of properties

Scanning electron microscopy (SEM, JEOL JSM-6490LV) was used to observe the morphology of the pristine carbon nanomaterials and fracture surface of composites.

Raman spectroscopy was used mainly to verify the nature of the carbon nanomaterials and the overall homogeneity of the sample. The Raman spectra, obtained in the range 2000-1000 cm^{-1} , showed a band at 1588 cm^{-1} (G-band) due to the vibration mode and a band at 1357 cm^{-1} (D-band) arising from the disordered mode.

The curing characteristics were measured over 0.5 h period at 160 °C using a Oscillating disk rheometer (ODR) and the tensile properties were measured using a Universal Testing Machine (UTM, Instron Co., UK) at a crosshead speed of 300 mm/min.

The hardness was measured using shore A durometer (TECLOCK) and the fatigue properties of the composites were determined using a Demattia flex cracking tester (DMFC, UESHIMA).

The thermal conductivity was characterized by placing the probe on the sample surface using a thermal conductivity analyzer (QTM-500).

The electrical resistance of the rubber composites was examined at room temperature on a high voltage insulation resistance tester (TERAOHM, MI2077). At the interface between the probe tip and nanocomposites, two probes measured the electrical resistance.

RESULTS AND DISCUSSION

Latex treatment

Characterization of pristine materials: Fig. 1 shows SEM images of the carbon materials. Fig. 1a shows highly entangled and randomly organized E-MWNTs and Fig. 1b presents the worm-like shape of graphene, Fig. 1c presents the irregular honeycomb network of graphite sheets revealing the dense structures composed of many graphite sub-layers.

Fig. 2 and Table-1 show the Raman spectra of carbon nanofillers. The so-called G and D bands, which appear at approximately 1588 and 1357 cm^{-1} , respectively are the main features in the Raman spectra of the carbon nanofillers. All carbon nanofillers exhibited G and D bands and the I(D)/I(G) ratio of graphene was higher than any other materials, suggesting minimal damage to graphite, which is in contrast to the significant devastation of graphene.

Characterization of the rubber nanocomposites mixed with carbon nanomaterials: Table-2 lists the formulations of the styrene butadiene rubber composites with and without a latex treatment of carbon materials. All the carbon

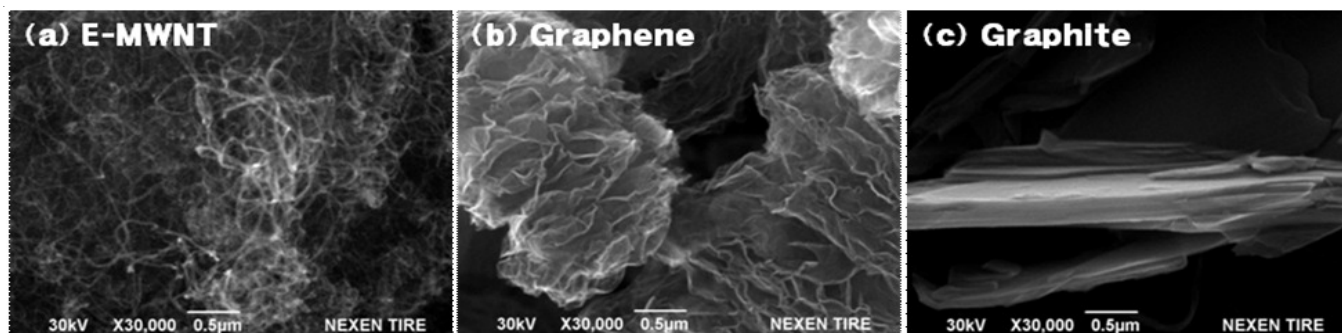


Fig. 1. SEM images of (a) E-MWNT, (b) Graphene and (c) Graphite

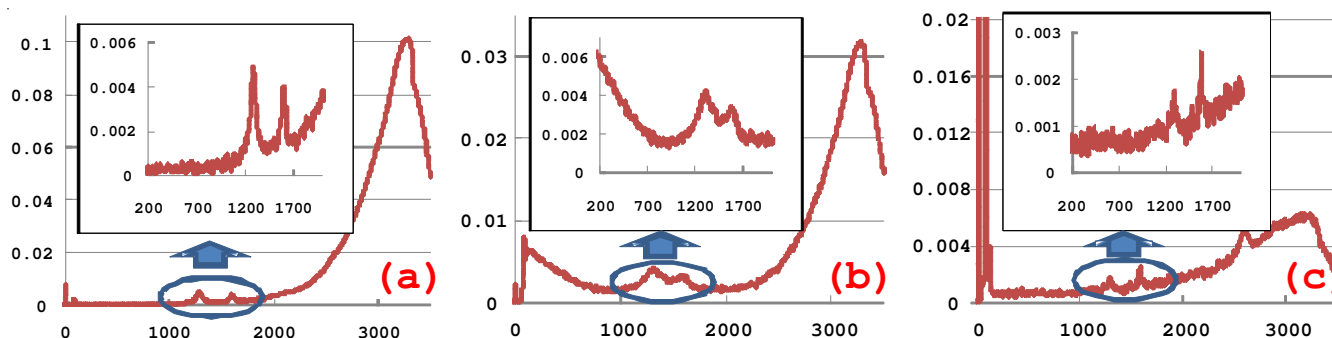


Fig. 2. FT-Raman spectra of (a) E-MWNT, (b) Graphene and (c) Graphite

nanomaterial contents in the rubber composites were maintained at 3 phr.

TABLE-1
D BAND AND G BAND OF THE RAMAN SPECTRA OF CARBON MATERIALS

Material	D band	G band	I(D)/I(G) (%)
E-MWNT	0.00492	0.00404	122
Graphene	0.00422	0.00337	125
Graphite	0.00337	0.0035	96

TABLE-2
FORMULATIONS OF THE SBR COMPOSITES CONTAINING CARBON MATERIALS WITH AND WITHOUT LATEX TREATMENT

Material	Compound name (unit : phr)									
	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
E-SBR	100	100	100	100	100	70	70	70	70	70
C/B	50	53	50	50	50	50	50	50	50	50
E-MWNT	-	-	3	-	-	-	-	-	-	-
Graphene	-	-	-	3	-	-	-	-	-	-
Graphite	-	-	-	-	3	-	-	-	-	-
C/B-Latex	-	-	-	-	-	33	-	-	-	-
MWNT-Latex	-	-	-	-	-	-	33	-	-	-
Graphene-Latex	-	-	-	-	-	-	-	33	-	-
Graphite-Latex	-	-	-	-	-	-	-	-	33	-
SBR Latex	-	-	-	-	-	-	-	-	-	30

Carbon nanomaterials contents in rubber compound : 3phr

Table-3 presents the curing properties of the carbon nanofillers/styrene butadiene rubber composites. The curing time of the rubber composites mixed with graphene was faster than the other rubber composites, regardless of the latex treatment. This was attributed to the more spacious specific surface by the two dimensions of graphene. The curing time of the rubber composites after the latex treatment became faster than without treatment because the presence of ammonium groups

of styrene butadiene rubber latex facilitates the curing reactions. MH-ML, where ML is the lowest torque and MH is the highest torque at the curing curves, represents the crosslink density of the vulcanizates. MH-ML increases slightly after loading graphene indicating that the addition of graphene has a little effect on the crosslink density of rubber vulcanization. Table-3 lists the physical properties of the rubber composites. The composites with graphene showed a much higher reinforcing effect than the other fillers. The increased hardness and modulus were attributed to the highest specific surface area, whereas it showed a strong decrease in the elongation at break. The physical properties of the latex treated nanocomposites were better than those without treatment, which indicates that the dispersion of nanomaterials is increased by the latex dispersion media.

Fig. 3 shows the fracture surfaces of the rubber composites. The fracture surfaces of the rubber composites with graphene were rougher than the other surfaces of the composites corresponding to the physical properties.

Table-3 shows the swelling ratio and apparent crosslink density of the carbon nanocomposites with styrene butadiene rubber Latex. In the field of high polymers, there are many examples of materials that absorb large quantities of suitable solvents without dissolving. Vulcanized rubber, vinyl-divinyl copolymers and lightly gelled thermosetting resins, when placed in solvents, swell through imbibition to a degree depending on the solvent and polymer structure. The original shape was preserved and the swollen gel exhibited elastic behaviour rather than plastic properties. This phenomenon of limited swelling is characteristic of polymers possessing network structures. A state of equilibrium swelling may be attained if the network structure is permanent in the sense that its essential skeletal structure is not disrupted by the action of

TABLE-3
PHYSICAL, THERMAL AND ELECTRICAL PROPERTIES OF THE NANOCOMPOSITES
WITH LATEX TREATED CARBON NANOMATERIALS

	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
T40	8.4	11.3	11.3	8.2	10.1	4.9	4.6	3.8	5.2	4.8
T90	16.6	20.6	20.7	16.8	18.9	10.8	11.9	11.2	11.1	11.0
Max Torque (Mpa)	0.25	0.25	0.24	0.33	0.27	0.42	0.43	0.54	0.42	0.36
Min Torque (Mpa)	0.08	0.08	0.07	0.1	0.10	0.19	0.22	0.31	0.19	0.17
ΔTorque (Mpa)	0.17	0.17	0.17	0.23	0.17	0.23	0.21	0.23	0.23	0.19
Hardness	51	54	54	65	57	75	77	83	75	71
200 % Modulus (Mpa)	4.5	4.9	4.5	8.3	5.1	14.9	13.8	23.1	14.0	10.9
Tensile strength (Mpa)	18.5	17.5	17.3	17.4	16.8	27.7	26.3	24.5	28.4	27.8
Elongation (%)	550	510	560	420	520	320	330	240	350	370
Q (Swelling ratio)	4.78	-	-	-	-	4.61	4.51	4.19	4.42	4.66
1/Q (crosslink density)	0.209	-	-	-	-	0.216	0.221	0.239	0.226	0.215
Crack growth 2,000 cycles (cm)	2.19	2.24	2.27	3.21	2.28	3.45	3.28	4.03	3.26	3.02
Crack growth 6,000 cycles (cm)	2.86	2.76	3.03	5.97	2.98	3.94	3.66	5.36	3.47	3.82
Crack growth 10,000 cycles (cm)	3.67	3.81	3.95	8.17	4.35	4.43	4.91	8.43	5.66	4.88
Thermal conductivity (W/mK)	0.276	0.282	0.293	0.286	0.289	0.318	0.353	0.332	0.337	0.307
Electrical resistivity (KΩ)	1070	425	249	31	146	265	43	9	119	914

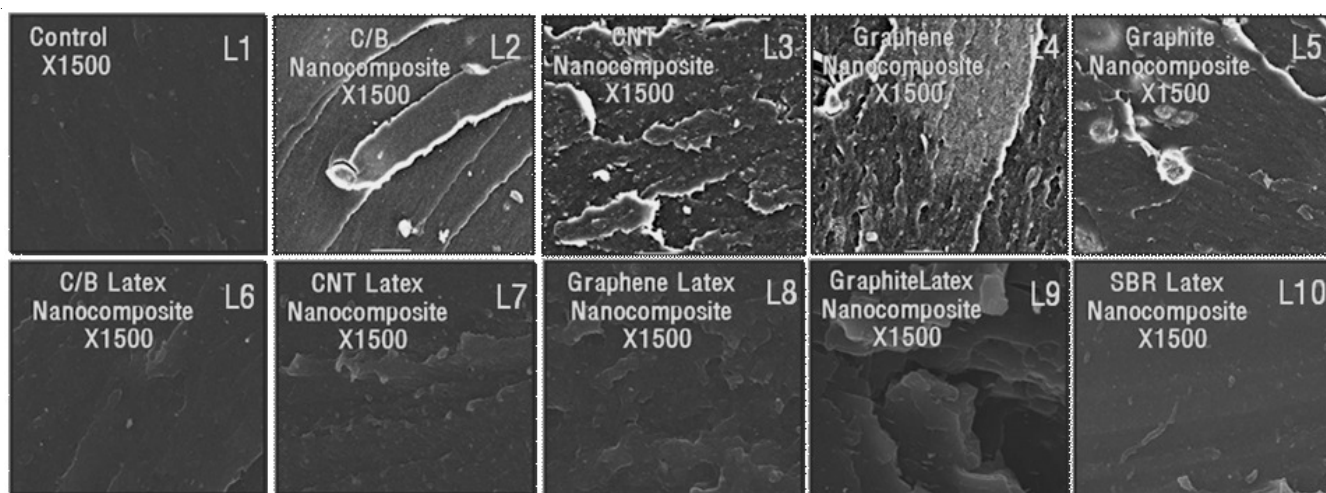


Fig. 3. SEM images of the fracture surface of nanocomposites with and without latex treated carbon nanomaterials

the solvent. As an increasing amount of solvent is absorbed by the polymer, the network is expanded progressively. The chains connecting the multifunctional network junction points are forced to assume more elongated, less probable, configurations. The swelling ratio Q of Eqn. (1) was recognized by the Flory-Rehner equation⁸. The calculated Q is representative of the degree of crosslinking of the rubber composites. This means that the reciprocal swelling ratio Q is generally proportional to the crosslinking rubber composites.

$$Q = (W_r/\rho_r + W_s/\rho_s)/(W_r/\rho_r) \quad (1)$$

where Q is the ratio of swelling, W_r the weight of rubber composite, W_s is the weight of the absorbed solvent, ρ_r is the density of the rubber composite and ρ_s is the density of solvent.

The swelling ratio of the latex treated graphene nanocomposites is lower than any other latex treated nanocomposites, which shows good agreement with the fact that the hardness and modulus of the graphene latex nanocomposite are higher than the other nanocomposites.

Table-3 shows the fatigue properties of the nanocomposites. Fatigue crack growth of the composites containing carbon nanofillers was similar except for the graphene composites. Fatigue crack growth of graphene is remarkably higher because

the composites are more brittle than the others due to the higher hardness and modulus.

Table-3 also lists the thermal and electrical properties of the nanocomposites. Generally, the specific heat and thermal conductivity of carbon systems are determined primarily by phonons. At low temperatures, the phonon contribution to these quantities dominates and is due primarily to acoustic phonons. In addition, the phonon specific heat of graphene has a quadratic temperature contribution due to the longitudinal acoustic and in-plane transverse acoustic phonons and a linear contribution due to the out-of-plane transverse acoustic phonons. In addition, graphite is dominated by the three acoustic phonons. In the case of E-MWNT, carbon nanotubes yield a linear wave vector dependence of all four acoustic branches: longitudinal, twist and doubly-degenerate transverse⁹. A large aspect ratio of the materials is advantageous for the thermal conductivity within the composite as reported by Yu *et al.*¹⁰.

The electrical conducting mechanism of the polymer composites is associated with two questions: 1) how to form conducting paths and 2) how to conduct after the formation of these paths. Regarding the second question, several theories exist, such as contact conducting, tunneling effect, dielectric

breakdown and field emission. The conductivity depends on their combined effect and can be summarized by the general statement that the microscopic migration of electrons might have several mechanisms. For example, percolation theory¹¹, effective medium theory¹², microstructure theory¹³ and thermodynamic theory¹⁴ are used to address the first question. These theories are related to the dispersed morphology and internal microstructure of the conducting fillers in the polymer matrices.

In addition to improving the mechanical properties, carbon nanofillers impart conductivity to elastomeric matrices. The electrical and thermal properties are improved by the addition of carbon nanofillers, which facilitate the electrical and thermal transition through filler-filler and filler-matrix interactions. In particular, the E-MWNT nanocomposites have the most predominant thermal conductivity regardless of adding the latex because E-MWNT transfers heat *via* four acoustic phonons and the higher aspect ratio of E-MWNT increases the probability of contact with each other. The composites with graphite have the next best thermal properties by three acoustic phonons and the composites using the graphene have the least improved thermal properties by the two acoustic phonons.

On the other hand, the electrical properties of the graphene composites were superior to the other composites, which suggest that graphene particles with large specific surfaces can abut or contact and form a conducting network, even at lower graphene contents. In addition, while E-MWNT and graphite have metallic and semi-conducting properties, graphene has metallic properties with a zero band gaps and can easily forms a conducting path.

Latex media enables rubber composites to obtain highly improved thermal and electrical properties without negative effects, indicating the increased dispersion of carbon nanofillers by latex.

Acid and heat treatment

Characterization of treated nanomaterials: Table-4 shows the Raman spectra of graphite and E-MWNT with and without treatment. The I(D)/I(G) ratio of the modified nanomaterials was higher than that of the untreated nanomaterials, which indicates that the amount of disorder or defects in the nanostructure are increased by the treatment. Such disorder and defects might involve functional groups on the graphite and E-MWNT surfaces, exfoliated graphite layers and destruction of the graphite and E-MWNT structure.

Characterization of carbon nanomaterial/rubber nanocomposite: Table-5 lists the formulations of the styrene butadiene rubber composites containing carbon materials with and without acid/heat treatment. All the carbon nanomaterial contents in the rubber composites were fixed to 5 phr.

Table-6 shows the physical, thermal and electrical properties of the rubber composites mentioned above. The hardness and modulus of the nanocomposites with E-MWNT were higher than the composites with graphite due to the larger surface area and higher aspect ratio of the E-MWNT than the untreated multiwalled carbon nanotubes. Moreover, the acid-treated multiwalled carbon nanotubes showed lower tensile strength and elongation at break due to the poor interaction between E-MWNT and rubber chains indicating that the acid treatment of multiwalled carbon nanotube is barely suitable for improving the mechanical properties. An acid or acid/heat treatment of graphite increases the modulus and tensile strength compared to untreated graphite, showing that the treatment of graphite causes a higher surface area and lower thickness of graphite layers.

Fatigue crack growth of modified graphite is lower than other composites. This shows that the tearing energy is decreased

TABLE-4
D AND G BAND OF RAMAN SPECTRA OF THE CARBON MATERIALS WITH AND WITHOUT TREATMENT

Material	Treatment	D band	G band	I(D)/I(G) (%)
Graphite	-	0.00337	0.0035	96
	Acid	0.00206	0.00099	208
	Acid & Heat	0.0024	0.00091	264
E-MWNT	-	0.00492	0.00404	122
	Acid	0.00388	0.00269	144

TABLE-5
FORMULATIONS OF THE SBR COMPOSITES CONTAINING CARBON MATERIALS WITH AND WITHOUT ACID AND HEAT TREATMENT

Material	Compound Name (unit : phr)						
	A1	A2	A3	A4	A5	A6	A7
E-SBR	100	100	100	100	100	70	70
C/B	50	55	50	50	50	50	50
Graphite	-	-	5	-	-	-	-
Acid-graphite	-	-	-	5	-	-	-
Acid & heat-graphite	-	-	-	-	5	-	-
E-MWNT	-	-	-	-	-	5	-
Acid-MWNT	-	-	-	-	-	-	5

Carbon nanomaterials contents in rubber compound: 5 phr

TABLE-6
PHYSICAL, THERMAL AND ELECTRICAL PROPERTIES OF THE NANOCOMPOSITES CONTAINING CARBON NANOMATERIALS WITH AND WITHOUT ACID/HEAT TREATMENT

	Compound Name						
	A1	A2	A3	A4	A5	A6	A7
Hardness	73	75	75	75	75	76	77
300 % Modulus (Mpa)	20.0	24.4	19.8	26.5	24.6	26.5	26.7
Tensile strength (Mpa)	26.6	27.6	28.5	31.4	29.5	27.5	25.6
Elongation (%)	380	330	440	350	350	340	310
Crack growth 2,000 cycles (cm)	8.99	23.4	8.19	6.65	5.35	8.99	23.4
Crack growth 6,000 cycles (cm)	20.14	24.65	14.28	12.68	7.8	20.14	24.65
Crack growth 10,000 cycles (cm)	22.16	Failure	16.08	14.22	11.19	22.16	Failure
Thermal conductivity (W/mK)	0.307	0.314	0.338	0.344	0.364	0.343	0.331
Electrical resistivity (KΩ)	636	386	439	459	383	11	81

and fatigue life is increased due to improved dispersion and interaction between functionalized and expanded graphite and rubber chains.

The acid and heat treatment of graphite improved the thermal and electrical properties of the nanocomposites, showing the highest thermal conductivity. This was attributed to the improved dispersion and interaction between expanded graphite and rubber chains. In the case of the electrical resistivity, the unmodified E-MWNT showed the best electric conductivity, whereas the acid-treated E-MWNT showed lower thermal and electrical properties. This suggests that the acid treatment of E-MWNT causes a decrease in length and defects on the surface and/or nanostructure, which has an adverse effect on the thermal and electrical properties.

Conclusion

Carbon nanofillers/styrene butadiene rubber latex composites were prepared and their mechanical, fatigue, thermal and electrical properties were evaluated according to the fillers. The latex nanocomposites showed substantially improved mechanical properties due to the increased polymer-filler interactions and filler dispersions and enhanced electrical and thermal properties due to the increased formation of connected filler structures. In particular, composites containing graphene exhibited a higher modulus, hardness and better electrical properties than the other nanocomposites. In the swelling result, the latex-treated nanocomposites using graphene showed less swelling than the other latex treated nanocomposites, which is consistent with the higher hardness and modulus of graphene latex nanocomposite. In addition, the fracture surface of the nanocomposites with graphene was rougher than those with carbon black or graphite. The composite containing E-MWNT had the best thermal properties due to the four acoustic phonons, while the electrical properties of composites containing graphene were better than the other composites

due to metallic properties by zero band gaps. Thermal and electrical properties of latex-treated nanocomposites were better than the nanocomposites without treatment, which was attributed to the increased dispersion of carbon nanofiller by the latex dispersion media.

The effects of the acid and heat treatments on the nanocomposite properties were also investigated. Acid and heat treatment generates functional groups and expanded the structure of graphite, which facilitated both physical and chemical interactions between graphite surface and polymer chain. Consequentially, the treatments improved physical, thermal, electrical and fatigue properties without adverse effects except for elongation. In contrast, acid treatment of multiwalled carbon nanotube generates defects on the multiwalled carbon nanotube structure and a shorter length. Therefore it has few positive effects on the mechanical properties and a significantly negative effect on the electrical properties.

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