

SBR에 산 처리된 MWCNT 및 커플링제 적용 시 발현되는 물리·화학적 특성 연구

송성호 · 정호균 · 강용구 · 조춘택[†]

넥센타이어 기술연구소

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Physical and Chemical Characteristics of Multi-walled Carbon Nanotube (MWCNT) with Acid-treatment and Coupling Agent on the Properties of Styrene Butadiene Rubber (SBR)

Sung Ho Song, Ho Kyun Jeong, Kang Yong Gu, and Choon-Tack Cho[†]

NEXEN Tire Corporation R&D Center,

30, Yusan-Dong, Yangsan-Si, Kyungnam 626-230, Korea

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초록: 본 연구는 MWCNT로 보강된 SBR 나노복합체료를 컴파운딩법(compounding)으로 제조하여 산 처리된 MWCNT와 커플링제 상호간의 물리적·화학적 특성을 조사하였다. 황산과 질산으로 산화된 MWCNT는 FT-IR 분석 결과 -COOH로 기능화됨을 확인하였고, Raman 분석 결과 표면의 defect 존재와 disorder됨을 확인하였다. 또한, 제조된 SBR 복합체료의 가황 특성, 전기적·열적 특성 및 기계적 특성을 비교 평가하였다. 그 결과 산 처리된 MWCNT와 커플링제와의 상호 결합력으로 인해 기계적 물성은 상대적으로 증가하였으나, 전기적·열적 특성은 MWCNT의 defects나 disorder의 형성과 chopping으로 인해 감소됨을 확인할 수 있었다.

Abstract: The effects of acid-treated MWCNT and coupling agent on properties of MWCNT/SBR are investigated in this work. The MWCNTs oxidized using sulfuric and nitric acids were analyzed by the Raman scattering and Fourier transformed infrared spectroscopy(FT-IR). The FT-IR results indicate the presence of -COOH groups in the treated samples, and Raman spectroscopy of the acid-treated MWCNTs further corroborates the formation of surface defect due to the introduction of carboxyl groups. And the nanocomposites reinforced with MWCNTs were characterized extensively using the scanning electron microscopy(SEM), electrical conductivity, thermal conductivity, and tensile properties measurements. The results showed that nanocomposites onto acid-treated MWCNTs enhanced mechanical properties compared to those containing MWCNTs without acid treatment. These findings confirmed the improved interfacial interactions between MWCNTs and SBR arising from the coupling agents. But the electrical and thermal conductivity of nanocomposites decreased due to the chopping and formation of surface defects of MWCNTs.

Keywords: multi-walled carbon nanotube(MWCNT), styrene butadiene rubber(SBR), coupling agent.

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 pro-

erties, 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} Nano-sized silica or titania particles within a host matrix have proved to be an excellent approach for exhibiting greatly improved mechanical properties. Layered silicates have generated significant interest because they can give rise to exfoliated systems in which the individual silicate nanolayers are homo-

[†]To whom correspondence should be addressed.
E-mail: brood805@snu.ac.kr

geneously and uniformly dispersed through the polymer matrix. The exfoliated nanocomposites exhibit significant enhanced mechanical and physical properties when compared to unfilled polymers or conventional composites.

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted much interested as the reinforcement for polymer matrix composites, which have unique structural and transparent properties, such as excellent strength, modulus, electrical and thermal conductivities along with a low density.¹³⁻¹⁵ However, the potential of employing CNTs as reinforcement has been severely limited because of the difficulties associated with dispersion of entangled CNTs during procession and the poor interfacial interactions for polymer composites, proper dispersion and good interfacial bonds between CNTs and polymer-matrix have to be guaranteed.¹⁶ And, in order to achieve high stress transfer, strong bonding between CNTs and polymer chains is necessary. Recent reports on the chemical compatibility and dissolution properties of CNTs have promoted a great deal of interest in developing modification or functionalization of their surface.

It has been reported that an acid treatment of CNT could improve the processability and performance of composites by introducing carboxylic acid groups on the surface of CNTs. The influence of surface functionalized CNTs on the properties of the polymer nanocomposites has been investigated by various researchers. Recent reports discuss the chemical functionalization of multiwall CNTs (MWCNTs) using silane coupling agents.¹⁷⁻¹⁹

In this paper, MWCNTs surface has been functionalized with nitric (HNO₃) and sulphuric acid (H₂SO₄) and it has been characterized using Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. And we study the mechanical properties of a styrene butadiene rubber (SBR) reinforced with pristine-MWCNTs, acid treated MWCNTs (acid-MWCNTs) and acid-MWCNTs and coupling agent. And the SBR-based nanocomposites reinforced with MWCNTs were characterized through performing mechanical, thermal

and electrical properties as a function of filler contents.

Experimental

Materials. CNTs (Carbon NanoTech, Korea) were MWCNTs whose diameter and length ranged between 10–20 nm and ~10 μm, respectively. The MWCNTs were prepared by the CVD process using the compound Zr(Fe_{0.5}Ni_{0.5})₂ as catalyst. These MWCNTs can be highly entangled with one another and formed an interconnecting structure from SEM image.

The matrix material was a styrene butadiene rubber (SBR) from Kumho petrochem Co. Ltd., Korea. The SBR1500 was consisted of 23% styrene and 77% butadiene. The coupling agent is bis-(3-triethoxysilylpropyl)tetrasulfane that have triethoxysilyl groups at both ends of a polysulfido (terasulfied, difulfide of mixture thereof) organic group. The coupling agent is made of EVONIC Industries. The carbon black (N-330) which was filled with SBR compounds was made of OCI Co. Ltd., Korea, and *N-tert-butyl-benzothiazole sulfonamide* (TBBS) with a role of curatives was purchased from Shandong Shanxian Co. Ltd., China. Zinc oxide (ZnO), stearic acid (S/A), sulfur, concentrated nitric and sulphuric acid were purchased from standard local suppliers.

Sample Preparation. Acid-MWCNTs were chemically prepared by nitric (HNO₃) and sulphuric acid (H₂SO₄) treatment in a ratio of 1:3, respectively. In a typical experimental, a 1 g portion of pristine-MWCNTs was added to 80 mL of the acid mixture in a flask at room temperature and stirred continuously for 24 h. The acid-MWCNTs were then washed thoroughly with water until the solution became neutral, and dried at 100 °C to remove the remaining moisture.

Composition Fabrication. The MWCNTs/SBR composites were prepared following standard procedures. First, the SBR was mixed with 50 phr (parts per hundred of rubber) carbon black in banbury mixer at a rotor speed of 60 rpm for master batch (MB). And then, the SBR compounds which contained 5 phr carbon black, pristine-MWCNTs, acid-MWCNTs and 0.8 phr coupling agent were prepared. Coupling agents are

Table 1. Formulation of the MWCNTs/SBR Composites

(Unit: phr)

	1	2	3	4	5	6	7	8	9	10	11	12	13
SBR	100	100	100	100	100	100	100	100	100	100	100	100	100
Carbon black	50	53	56	59	50	50	50	50	50	50	50	50	50
Pure-MWCNTs					3	6	9						
Acid-MWCNTs	–	–	–					3	6	9	3	6	9
Coupling agent	–	–	–	–	–	–	–	–	–	–	0.8	0.8	0.8
ZnO	3	3	3	3	3	3	3	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1	1
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
TBBS	1	1	1	1	1	1	1	1	1	1	1	1	1

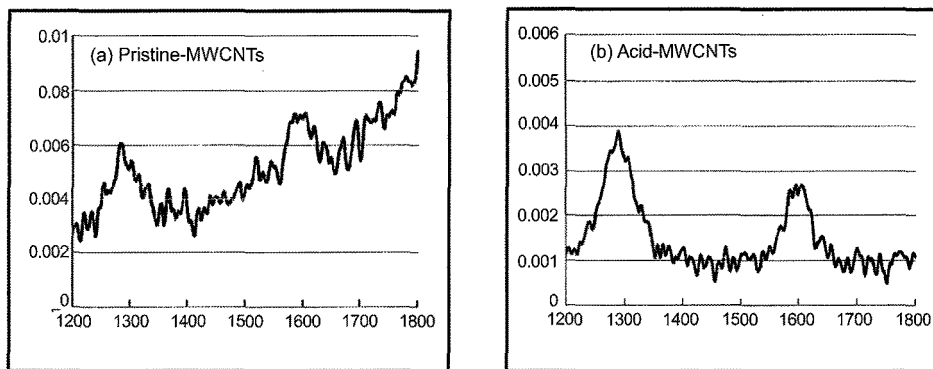


Figure 1. The Raman spectroscopy of MWCNTs: (a) Pristine-MWCNTs; (b) Acid-MWCNTs.

effective agents for modifying the surface chemistry of acid-MWCNTs and polymer. These react with the functional groups on the filler surface to give a strong bond, and also will link to the rubber during vulcanization. This gives a chemical “coupling” between the functional groups of MWCNTs on one end and the polymer on the other end of the molecule. The additives and vulcanization agent were added at the end since it helped to start the curing process of the mixture. The compounds were placed in the aluminum mold and cured at 160 °C for T_{90} by rheometer under pressure. The formulations of the MWCNTs/SBR composites are summarized in Table 1.

Characterization and Measurements. Scanning electron microscopy (SEM, JEOL JSM-6490LV) was used to observe the morphology of the pristine MWCNTs and acid-MWCNTs. Since MWCNTs are conductive, those could be examined at 20 kV accelerating voltage without gold coating. X-ray diffraction was used to verify the structure of them. X-ray measurements were conducted on an X-ray diffraction Bruker, Germany using $\text{CuK}\alpha$ radiation at 40 kV and 40 mA. The scanning range was 10~80° with a scanning speed of 1°/min.

Raman spectroscopy was mainly used to verify the nature of the MWCNTs and the overall homogeneity of the sample. The Raman spectra, obtained in the range 1000~2000 cm^{-1} , shows 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-induced mode.

Curing characteristics were measured over 30 min periods at 160 °C using a moving-die rheometer (DRM-100(LP-171)). Shore A hardness was measured by using a hand-held shore A durometer according to TECLOCK. 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 in

Table 2. Raman Spectroscopy Results of Pristine-MWCNTs and Acid-MWCNTs

	D-band	G-band	$I(D)/I(G)$
Pristine-MWCNTs	0.00604	0.00716	84.36%
Acid-MWCNTs	0.00388	0.00269	144.24%

each case.

The electrical resistance of these manufactured composites was examined using the two-probe method in the TERAOHM, MI2077 at room temperature and the thermal conductivity was characterized by a thermal conductivity analyzer (QTM-500).

Results and Discussion

Materials Characterization. Figure 1 and Table 2 show the Raman spectroscopy of pristine-MWCNTs and acid-MWCNTs. The main features in the Raman spectroscopy of MWCNTs are the so-called G and D bands, which lies at around 1580 and 1280 cm^{-1} respectively. G band of the pristine-MWCNTs almost appeared to increase that of the acid-MWCNTs, but the acid-MWCNTs demonstrated an increased D-band. In other words, $I(D)/I(G)$ ratio of acid-MWCNTs is higher than that of pristine-MWCNTs. Since, the D-band is proportional to the defects of MWCNTs, these results suggest significant devastation of acid-MWCNTs.^{20,21} The acid treatment of pristine-MWCNTs generates functional groups that facilitate both physical and chemical interactions between acid-MWCNTs and polymer.

The FT-IR spectra for the pristine-MWCNTs and acid-MWCNTs are shown in Figure 2. In the spectrum of the pristine-MWCNTs, the main feature observed at ~1550 cm^{-1} is characteristic of stretching of C-C bonds, related to the expected MWCNTs phonon modes. In the spectrum of the acid treated material, all those bands are enhanced, including a feature at 3884 cm^{-1} that were not well defined in the

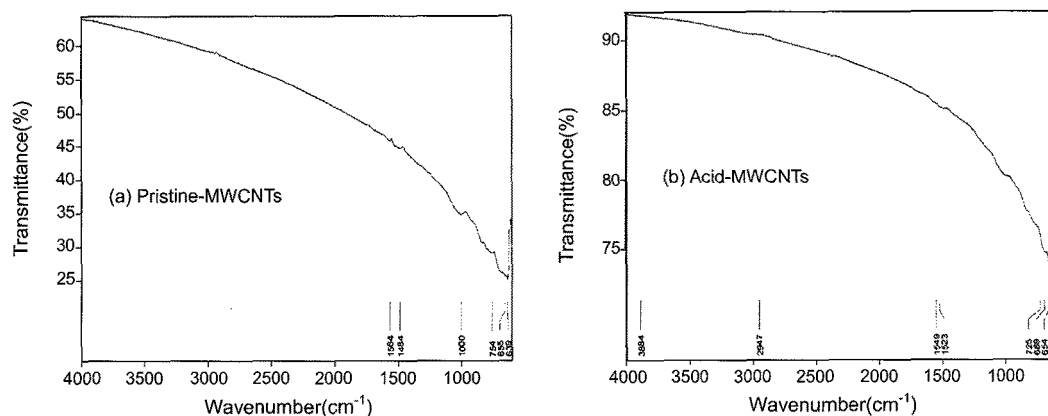


Figure 2. FT-IR measurements in the (a) pristine-MWCNTs; (b) acid treated MWCNTs.

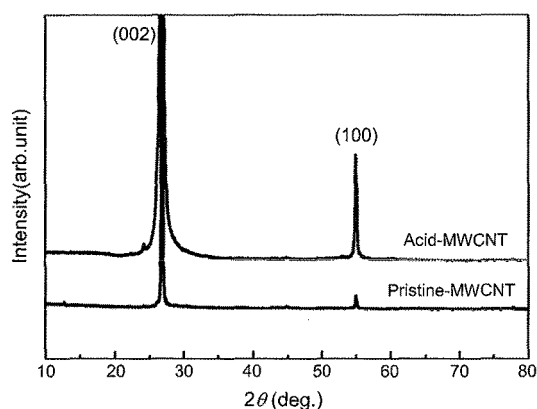


Figure 3. XRD patterns of pristine-MWCNTs and acid-MWCNTs.

spectrum of the pristine material. Likewise, a weak absorption band appearing at $\sim 2947\text{ cm}^{-1}$ is related to the $-\text{OH}$ of carboxylic group vibration.^{22,23} These results show that the acid treatment is responsible for an increase in the functionalization of the MWCNTs. These functional groups are usually attached to the ends of the MWCNTs or to defects along the MWCNTs wall, due to the enhanced reactivity of these areas.

Figure 3 shows the powder XRD diffraction patterns of pristine-MWCNTs and acid-MWCNTs. The most intense peaks of MWCNT correspond to the (002) and (100) reflection, respectively. The peak position of pristine MWCNTs at 26.6° (2θ) slightly shift to 26.9° (2θ) by modification with acid treatment. From the results, we can conclude that surface functionalization does not have much influence on the average d -spacing.

The pristine-MWCNTs and acid-MWCNTs were examined by SEM and are shown in Figure 4. MWCNTs samples show the curled structure of an individual tube. The MWCNTs can be highly entangled with one another and form an interconnecting structure. But, the lengths and thicknesses of acid-

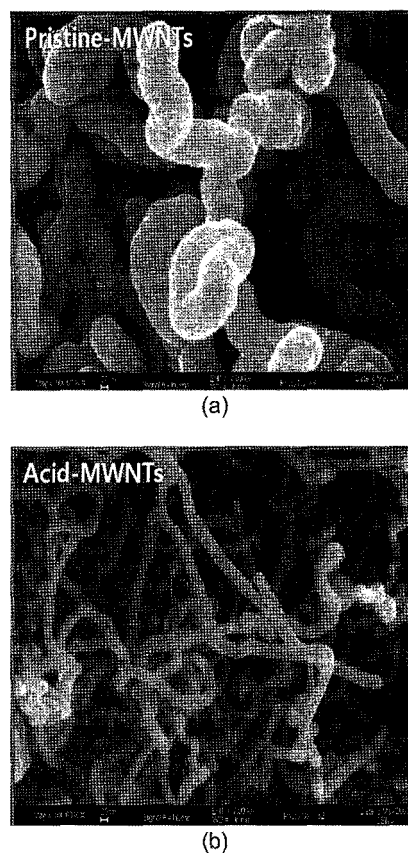


Figure 4. SEM image of MWCNTs (a) pristine-MWCNTs; (b) acid-MWCNTs.

MWCNTs are shorter and thinner than those pristine-MWCNTs respectively. The higher chemical reactivity of the MWCNTs by acid treatments results in the MWCNTs being destroyed and damaged throughout the process. Particularly, the surfaces of acid-MWCNTs are rougher than those of pristine-MWCNTs. Also, individual MWCNTs are visible with less aggregation when the MWCNTs are subjected to acid treatment.

Characterization of MWCNTs/Rubber Composites. The curing curves of MWCNTs/SBR composites are shown in Figure 5 and some parameters of curing properties are reported in Table 3. Three regions are observed in Figure 5. 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 composite using acid-MWCNTs is slower than pristine-MWCNTs composites. The reasons for the shorter cure time of the rubber composite using pristine-MWCNTs are probably due to the decrease of thermal conductivity of SBR in the presence of defects and shorter lengths of MWCNTs according to the acid treatment. Other reason is that the -OH groups of MWCNTs previously react amine groups of accelerator TBBS and ZnO, and then these chemical reactions could decline the fulfillment of vulcanization.

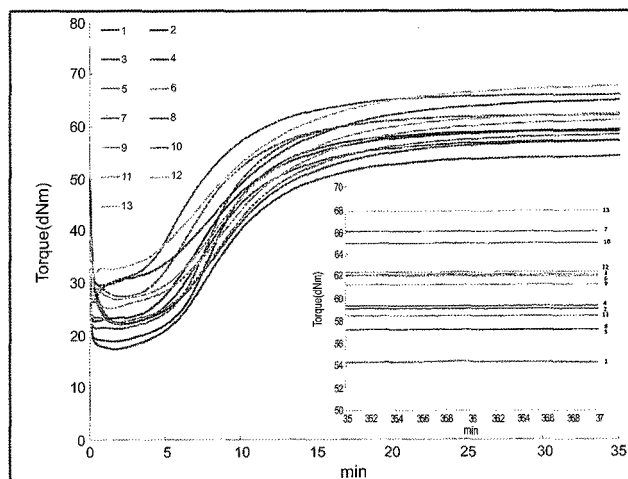


Figure 5. Curing curves of MWCNTs/SBR composites at 160 °C.

Table 3. Curing Characteristics MWCNTs/SBR Composites

	1	2	3	4	5	6	7	8	9	10	11	12	13
T_{40} (min)	8.0	7.9	7.8	7.4	7.7	6.9	5.8	8.6	8.8	8.5	8.6	8.6	7.7
T_{90} (min)	16.2	14.3	14.3	16.2	16.7	14.6	13.7	18.9	18.7	17.8	19.0	18.4	17.7
T_{max} (dNm)	54.4	59.2	62.2	59.5	57.3	62.1	66.0	57.4	61.3	65.1	58.6	62.5	68.0
T_{min} (dNm)	17.4	18.8	21.2	22.6	22	27.4	26.4	22.2	25.2	29.6	22.4	26.8	31.3
Δ Torque (dNm)	37	40.4	41	36.9	35.3	34.7	39.6	35.2	36.1	35.5	36.2	35.7	36.7

Table 4. Hardness and Tensile Properties MWCNTs/SBR Composites

	1	2	3	4	5	6	7	8	9	10	11	12	13
Hardness	71	75	77	77	76	76	79	76	77	81	75	78	81
M-300% (MPa)	21.2	22.9	21.5	27.0	24.0	26.5	27.7	24.1	26.7	27.6	26.0	27.2	28.5
Tensile strength (MPa)	28.3	28.9	24.6	27.7	27.2	27.5	29.9	28.3	25.6	26.7	28.3	28.4	30.0
Elongation (%)	376	362	330	307	333	338	309	317	304	308	325	329	323

The cure rate becomes faster as the MWCNTs content increases owing to the increase of thermal conductivity through the MWCNTs.

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 pristine-MWCNTs in comparison with loading the acid-MWCNTs and C/B. This indicates that addition of pristine-MWCNTs has a little effect on the crosslink density of rubber vulcanization.

The hardness and the mechanical properties of MWCNTs composites are summarized in Table 4. From this table, shore A hardness of the composites is slightly increased, according to the fillers content increment. And the composites using acid-MWCNTs and coupling agent are harder than any other composites.

Modulus tests performed on a SBR mixed with pristine-MWCNTs and C/B also display improvement in the mechanical properties as an increase of filler content, while the composites of MWCNTs sharply are more improved. When MWCNTs are added to elastomeric systems, MWCNTs composites usually are more increased in the modulus arising from the inclusion and increased in the cross-linking density created by polymer-filler interactions than C/B composites. According to these results, we conclude that the aspect ratio of the MWCNTs is important in the reinforcement. The well known model of Guth¹ for the modulus of rod-like particle reinforced elastomers is based solely on the aspect ratio and volume fraction of the filler, and does not take any other properties of the filler into account, except to assume that the fillers are stiff compared with the matrix:

$$E = E_0(1 + 0.67fc + 1.62f^2c^2) \quad (1)$$

Where E and E_0 are the modulus of the composite and the

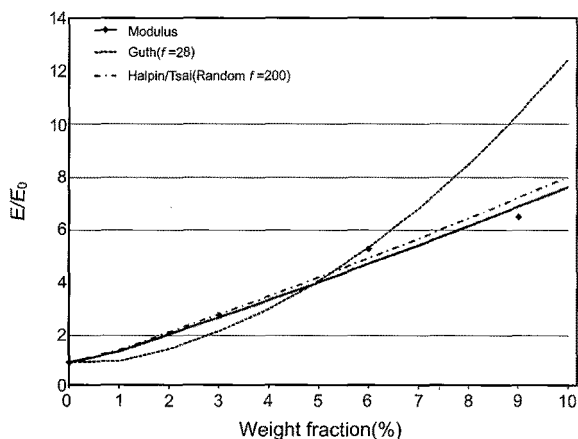


Figure 6. Experimental modulus plotted versus weight fractions of MWCNTs and comparison with theoretical predictions.

pure matrix respectively, and f and c are the aspect ratio and volume concentration fillers.

Another commonly used model for filled polymers is the Halpin-Tsai theory,²⁰ which in principle takes account of the modulus of the two phases as well as filler packing effects, but for low loadings of rod-like fillers which are much stiffer than the matrix it reduces to:¹²

$$\begin{aligned} E_{para} &= E_0(1+2fc)/(1-f) \\ E_{perp} &= E_0(1+0.5c)/(1-c) \\ E_{rand} &= 0.2 E_{para} + 0.8 E_{perp} \end{aligned} \quad (2)$$

for the modulus measured parallel (E_{para}) or perpendicular (E_{perp}) to perfectly oriented fibers or in any direction (E_{rand}) for fibers randomly oriented in three dimensions.

In Figure 6, the experimental values are compared with the Guth and Halpin-Tsai predictions using the respective aspect ratio. Guth's theory [Eq. (1)] shows good agreement using $f=28$ for the MWCNTs. In Halpin-Tsai model [Eq. (2)], assuming a random distribution of MWCNTs, aspect ratio of $f \sim 200$ is needed for the MWCNTs: much higher than observed and more similar the real aspect ratio $f \sim 250$ of pristine MWCNTs. Even perfectly oriented MWCNTs require aspect ratio $f \sim 38$ for the theory to fit the data. While the Guth model departs from the experimental results at the highest filler loading, the Halpin-Tsai model, for perfectly aligned MWCNTs shows good agreement within the volume fraction range investigated. It is interesting to mention that both models yield similar aspect ratios. The values required to fit the experimental data are lower than that calculated from the average dimensions of the MWCNTs. It is probably due to aggregation of the MWCNTs which reduces the aspect ratio of the reinforcement.

The modulus values of composites reinforced with MWCNTs

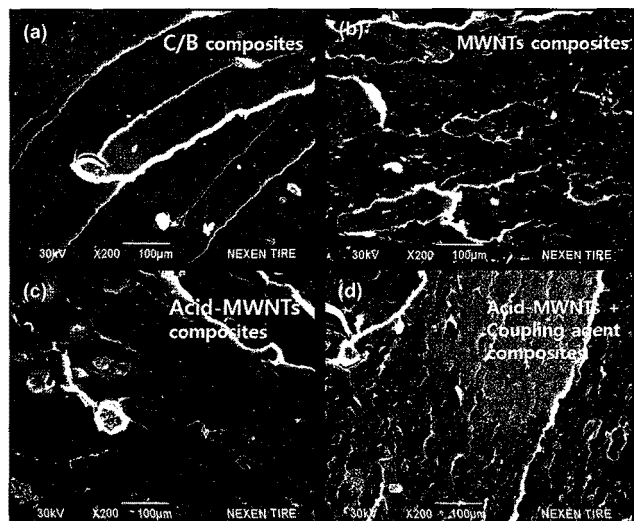


Figure 7. SEM images of MWCNTs rubber composites (a) C/B/SBR composites; (b) MWCNTs/SBR composites; (c) acid-MWCNTs/SBR composites; (d) acid-MWCNTs+coupling agent/SBR composites.

is similar to those of acid-MWCNTs, but the composites using acid-MWCNTs and coupling agent are slightly increase in modulus. The composite using acid-MWCNTs (9 phr) and coupling agent showed about 14% increase over C/B (9 phr) and about 3% increase over pristine-MWCNTs (9 phr) composite in modulus. Incorporation of acid-MWCNTs (9 phr) and coupling agent in SBR lead to the increase in both tensile strength and the elongation at break. The tensile strength of the composites increased roughly 8% and the elongation also increased approximately 5% compared with the carbon black (9 phr).

Figure 7 shows SEM images of the fractured surface for MWCNTs composites. The fracture surface of rubber composite using acid-MWCNTs and coupling agent is rougher than any other surfaces of composites, which is corresponded the upper mechanical properties results.

The reasons which are increased physical properties are chemical interactions between MWCNTs and polymer according to the coupling agent, and improving dispersions of MWCNTs due to the acid treatment.

Electrical and thermal properties of MWCNTs/SBR composites are shown Figure 8 and Table 5. Figure 8 shows the effect of filler loading on the volume resistivity of C/B and MWCNTs filled composites based on insulating SBR. In addition to improve the mechanical properties, C/B and MWCNTs impart conductivity to low resistivity elastomeric matrices. The electrical and thermal properties are improved by increasing the filler concentration due to facilitate the electrical and thermal transition through filler-filler and filler-matrix interactions. The higher aspect of the nanotube

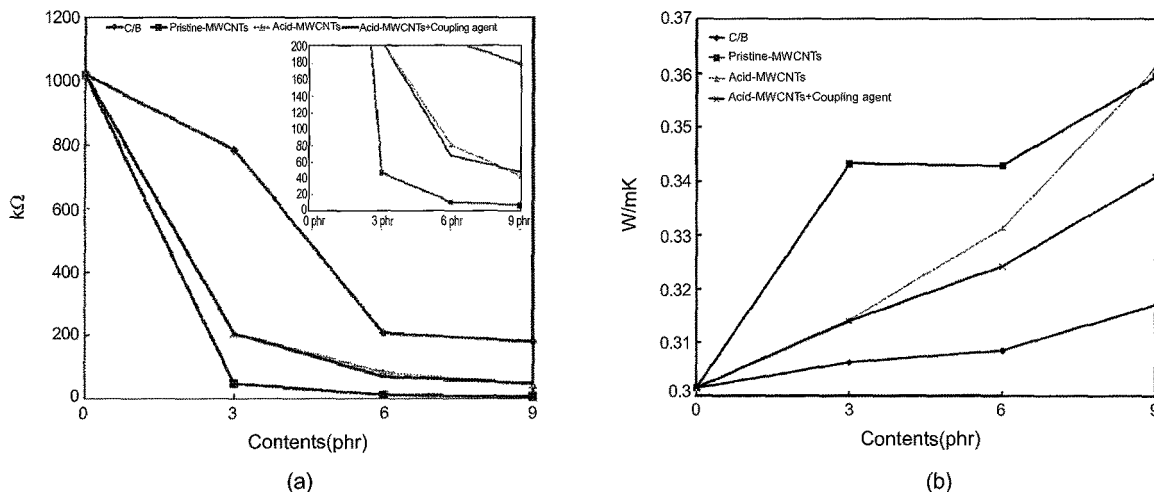


Figure 8. Electrical (a); thermal properties (b) of MWCNTs/SBR composites.

Table 5. Electrical and Thermal Properties MWCNTs/SBR Composites

	1	2	3	4	5	6	7	8	9	10	11	12	13
Resistance (kΩ)	1,020	785	207	179	47	11	7	206	81	43	206	68	48
Thermal conductivity (W/mK)	0.3015	0.3063	0.3085	0.3171	0.3433	0.3430	0.3595	0.3142	0.3313	0.3612	0.3141	0.3242	0.3509

bundles which increases the probability of particle-particle contacts explains the low percolation threshold. Electrical and thermal conductivity of MWCNTs composites is higher than C/B composites, and is increased approximately 416% and 14% respectively at the same content 9 phr. The reason is that the continuous network is formed at lower fillers loading of the nanotube bundles with MWCNTs than with C/B, and the higher aspect ratio of MWCNTs bundles increases the probability of particle-particle contacts. Moreover, the pristine-MWCNTs composites show also the highest thermal and electrical properties while properties of the acid-MWCNTs composites are similar to those of acid-MWCNTs and coupling agent composites. The reasons which are decreased electrical and thermal properties of the rubber composites using acid-MWCNTs are probably due to the presence of defects and shorter lengths of MWCNTs according to the acid treatment.

Conclusions

In the present work, the effects of acid-MWCNTs and coupling agent were investigated on the mechanical, thermal and electrical properties of SBR composites with different contents of MWCNTs. Major finding from this study is highlighted as following:

1) The acid-MWCNTs reveal the formation of surface defects due to the introduction of carboxyl groups by the Raman spectroscopy and FT-IR. Also, the XRD diffractions

results of acid-MWCNTs do not have much influence on the average d-spacing.

2) When pristine-MWCNTs are added to elastomeric systems, pristine-MWCNTs composites usually are more increased in the modulus arising from the inclusion and increased in the cross-linking density created by polymer-filler interactions than C/B composites.

3) Composites containing acid-MWCNTs and coupling agent exhibited better mechanical properties than those containing pristine-MWCNTs due to increase the chemical interactions between MWCNTs and polymer according to the coupling agents, and improve the dispersions of MWCNTs according to the acid treatment.

4) Electrical and thermal conductivity of MWCNTs composites is higher than C/B composites. The reason is that the continuous network is formed at lower fillers loading of the nanotube bundles with MWCNTs than with C/B, and the higher aspect ratio of MWCNTs bundles increases the probability of particle-particle contacts.

5) The electrical and thermal conductivity of nanocomposites containing acid-MWCNTs and coupling agent decreased due to the presence of defects and shorter lengths of MWCNTs according to the acid treatment.

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