

Reinforcement of Abrasion Resistance for Tire Tread filled with Multi-Wall Carbon Nanotubes (MWCNTs)

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ABSTRACT

A tire tread composites containing SBR/NR rubber blend and varying proportions of multi-wall carbon nanotubes (MWCNTs)/carbon black (CB) including a silane-coupling agent [Bis-(3-triethoxysilylpropyl) tetrasulfane] have been investigated in order to reinforce abrasion resistance. Tires have been stressed and abraded continuously as well as heat buildup when in contact with road surfaces during their life time. Thus, it is important to be compounded to resist wear and be kept as low as possible.

We found that the optimum conditions of the proportions between MWCNTs and CB. In order to increase dispersion of MWCNTs in the compositions of SBR/NR rubber, MWCNTs was functionalized by high energy (100~1000 kGy) and then coupled with silane-coupling agent. We got a preliminary data when MWCNTs 10 phr/ CB 40 phr were applied, hardness (18%), abrasion resistance (29%), 300% modulus (51%) were increased as compared to apply only carbon black (CB).

Keywords: multi-wall carbon nanotubes, silane coupling agents, tread, reinforce abrasion resistance,

INTRODUCTION

Recently, carbon nanotubes have been widely attracted electrically and mechanically. Due to their novel structures and remarkable mechanical, thermal, and electrical properties, carbon nanotubes (CNTs) have emerged as new materials with a variety of potential applications¹⁻⁴. These CNTs have attracted much interest in the field of CNT/polymer nanocomposites. Many groups have investigated the use of carbon nanotubes as fillers for polymer composites⁵⁻⁹. However, it is difficult to obtain homogeneous dispersion of carbon nanotubes in a polymer matrix on account of their tendency to bundle together due to van der Waals interactions. If these materials are to be utilized as reinforcements in advanced polymer composites, in addition to the homogeneous dispersion of the nanotubes, the silanization of functionalized nanotubes is preferred method used to enhance the interfacial adhesion between nanotubes and the matrix¹⁰⁻¹¹.

Multi-walled carbon nanotubes (MWCNTs) were functionalized via high energy (100 ~ 1000 kGy).

We introduce that varying proportions of carbon nanotubes (MWCNTs)/carbon black (CB) will make a tire tread to be reinforcement of abrasion resistance and heat buildup due to carbon nanotubes' own mechanical properties. The styrene-butadiene copolymer (SBR), natural rubber (NR), and other composites were carried out for this study.

EXPERIMENTAL

Materials

The elastomers were natural rubber (NR) and synthetic rubber [poly styrene butadiene (SBR)] with carbon black HAF N220. Multi-wall carbon nanotubes (MWCNTs) synthesized by catalytic chemical vapor deposition were obtained as a reinforcement reagent from NANO HUB Co.,Ltd. (South KOREA). The diameter range of the MWCNTs was a 5~15nm (Avg. 10nm), $\leq 10 \mu\text{m}$ length, 100~700 cm^2/g specific surface area analysis (BET), and 0.05~0.08 (g/cm^3) bulk density. The purity of MWCNTs was above 85%. MWCNTs contained $\text{SiO}_2 < 5.0\%$, $\text{MgO} < 8.7\%$, $\text{Al}_2\text{O}_3 < 0.7\%$ as an impurities and were functionalized via high energy (100 ~ 1000 kGy) without purification. The functionalized carbon nanotubes (f-MWCNTs) were analyzed by FT-IR spectrum. Bis-(3-triethoxysilylpropyl)tetrasulfane] were purchased as a silane coupling agent from AP resources Corp.

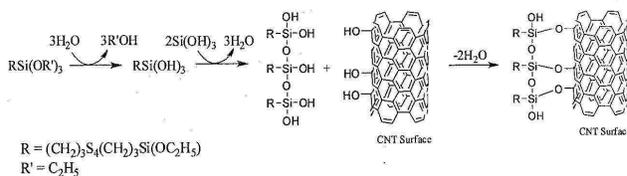


Fig.1 Mechanism of silane coupling agent with MWCNTs

Surface modification of MWCNTs

Figure1 shows the mechanism of the silanization of functionalized nanotubes. Triethoxy (-OC₂H₅)₃ is easily hydrolyzed to form a trisilanol and this group reacts readily with the hydroxyl groups on the nanotube surface produced through high energy.

Compounding and Tests

The total filler content was 50 phr and the filler compositions were carbon black 50phr itself, and multi-wall carbon nanotubes (MWCNTs)/carbon black (CB) = 10/40 phr, respectively. Additionally, the filler compositions were prepared with functionalized multi-wall carbon nanotubes (f-MWCNT/SB2494)/carbon black (CB) = 10/40 phr respectively. The formulations are given in Table 1.

Table 1. Formulations of the compounds (phr)

Ingredients	Mix 1	Mix 2	Mix 3
SBR 85 phr/ NR 15 phr	100	100	100
ZnO	5	5	5
Steric Acid	2	2	2
RD	2	2	2
Oil (Aromatic)	2	2	2
Carbon Black	50	40	40
MWCNTs	-	10	-
f-MWCNTs/SB2494	-	-	10
Sulphur	2	2	2
TBBS	1	1	1

RD: poly-2,2,4-trimethyl-1,2-dihydroquinoline resin
 f-MWCNTs: functionalized MWCNTs by high energy
 SB2494: bis(3-triethoxysilylpropyl)tetrasulfide
 TBBS: N-*tert*-butyl benzothiazyl 2-sulfenamide

The SBR/NR rubber and other composites were mixed for 25 min in a banbury mixer and the initial temperatures of the mixer was 80 °C. Three mixes were prepared as shown in table 1. Mix 1 served as control experiment. Mixing was carried out in a banbury mixer and vulcanized for 10 min at 170 °C¹²⁻¹⁴.

Cure characteristics were obtained using a rotorless rheometer (MDR type, GOTECH) at 170 °C. Cure characteristics of the compounds were listed in Table 2. Based on the results of a rheometer test, the rubber compounds were cured at 170 °C for 10 min. Physical properties of the vulcanization were measured with the UTM (AI-7000S, GOTECH). The abrasion resistances were measured with akcron abrasion tester (GT-7012A).

RESULTS AND DISCUSSION

The properties of the tire tread containing different filler blend composition (Table 1) are shown in Table 3. The mixtures of f-MWCNTs/SB2494 and carbon black filled compound had the highest minimum torque ($T_{min} = 6.25$ kg-cm). Since T_{min} is measure of effective viscosity of unvulcanized mixtures, the viscosity of the uncured compound was reduced as the MWCNTs and f-MWCNT/SB2494 was omitted.

Table 2. Cure characteristics of the compounds at 170 °C

	Mix 1	Mix 2	Mix 3
T_{min} (kg-cm)	3.04	6.16	6.25
T_{max} (kg-cm)	16.47	20.93	22.35
ΔT (kg-cm)	13.43	14.77	16.10
t_2 (min)	1.59	1.32	1.31
t_{90} (min)	5.56	6.06	6.48

Functionalized MWCNTs (f-MWCNTs) were determined by the Fourier transform infrared spectroscopy. Figure 2 compared functional group on f-MWCNTs and raw MWCNTs. After functionalization, the peaks at 3438 cm^{-1} ,

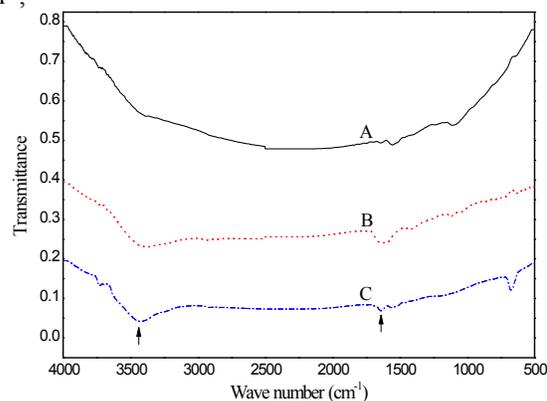


Fig.2 IR spectrum of raw MWCNTs and f-MWCNTs. (A) raw MWCNTs, (B) f-MWCNTs (100kGy) (C) f-MWCNTs (300kGy).

and 1645 cm^{-1} were appeared in FT-IR of f-MWNTs. This indicates that carboxylic, hydroxyl functional groups are chemically bonded to the surface of the MWNTs.

It is important to be compounded to resist wear and be kept as low as possible because tires are stressed and abraded continuously when they are running on the road surfaces during their life time.

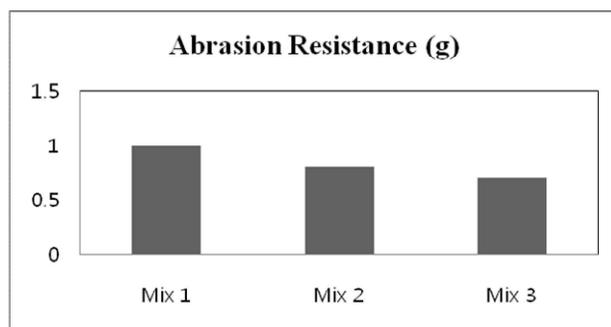


Fig.3 Abrasion Resistance of the mixture 1, 2, and 3

In order to improve abrasion resistance on the roads, we applied MWCNTs, and f-MWCNTs/SB2494. By adding f-MWCNTs/SB2494 with carbon black to the rubber composite, we observed the abrasion resistance increased

(Table 3) about 29%.

	Mix 1	Mix 2	Mix 3
Hardness (Shore A)	66	75	78
300% Modulus (kgf/cm ²)	115.5	155.0	175.4
Tensile Strength (kgf/cm ²)	234.1	265.6	270.1
Elongation (%)	650.5	462.1	456.1
Abrasion resistance (g)	1.006	0.805	0.708

Table 3. Physical properties of rubber formulations

As shown in Table 3 mechanical properties of hardness (13%, 18%), of 300% modulus (34%, 51%), of tensile strength (13%, 15%), and of abrasion resistance (19%, 29%) were increased respectively as compared to apply only carbon black.

CONCLUSION

We demonstrated the potential of multi-wall carbon nanotubes as reinforcing fillers in polymer composites. The most important to apply MWCNTs is the dispersion and it can be improved by using silane coupling agents.

Multi-wall carbon nanotubes and functionalized multi-wall carbon nanotubes were investigated as possible reinforcements of abrasion resistance in polymer composites in tire tread. Of the filler blend mixes that were incorporated in the polymer blend and studied, we found out that the f-MWCNT/SB2494 10 phr and carbon Black 40 phr loaded compound exhibited the best balance of properties in the critical parameters such as the abrasion resistance (0.708 g loss, 3,300 cycles), and 300% modulus 175.4 (kgf/cm²).

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