

Synthesis and Characteristics of Functionalized Carbon Nanofibers/HNBR Rubber Composite

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Abstract: Rubber composite materials were prepared by adding various contents of carbon nanofiber reinforcing materials functionalized with amine groups to HNBR rubber matrix. Effects of the addition of functionalized carbon nanofibers on improvement of physical properties were investigated by measuring basic properties, heat resistance, oil resistance, and compression sets of these composite materials. Results showed that mechanical properties such as tensile strength and elongation were substantially improved when 7 phr of functionalized carbon nanofibers were added to rubber composite materials. In addition, tensile stress which was 100% modulus was improved as much as other properties. Heat resistance, oil resistance, and high-temperature compression sets were improved for carbon nanofibers functionalized with amine groups in comparison with virgin HNBR rubber materials. In conclusion, the optimum content of carbon nanofibers for HNBR is 7 phr within the measurement range.

Keywords: Carbon nanofiber, HNBR, Rubber composite, Amine, Surface modification.

1. INTRODUCTION

In classical surface chemistry, plastic surface has been thought to be very hard with very low molecular mobility. This definition can be applied to some solids. Most surfaces of solids can form a thermodynamically stable surface structure by coping with the surrounding environment. They are closely related to temperature ranges of glass transition and other molecular motions. In other words, molecular aggregation or dispersion state is determined by the environment and the surface of a polymer having unique characteristics and structure due to functional groups (polarity and non-polarity) with long chains in various shapes. Molecular aggregation affects various physical properties including friction, abrasion, adhesion, and heat resistance [1-5].

It is known that physical properties of composite materials are not influenced by the physicochemical properties of the surface such as particle size of the reinforcing agent, specific surface area, particle structure or type of unsaturated atoms or terminals, or interface environment [6]. In other words, physical properties and processability of composite materials are determined by the degree of physical bonding between filler and reinforcing agent or between reinforcing agents with different characteristics. Studies on physical-mechanical properties of reinforcing agents depending on surface treatment and

modification are being actively conducted [6-8]. Ehrburger and Donnet reported that there were basically two ways to improve the interfacial adhesion of carbon fiber composite materials. The first one is to increase the surface area of the interfacial surface by making the fiber surface rougher. The second one is to increase the surface activity. Therefore, many researchers are developing surface treatment methods to improve the interfacial adhesion between carbon fibers and matrix [9]. Thus, researchers have used reinforcing methods (such as chemical surface treatment, electrochemical surface treatment, coupling agent treatment) or surface-treated polymers to improve mechanical and functional physical properties of composite materials [10, 11].

Hydrogenated acrylonitrile butadiene rubber (HNBR) used as a matrix is prepared by selective and controlled hydrogenation of NBR. Its highly saturated methylene main chain has excellent heat resistance and ozone resistance. Its nitrile group has resistance against oil and fuel. As a result of hydrogenation reaction, heat resistance and ozone resistance are improved with increasing degree of hydrogenation. Two types of polymers are commercially available depending on the degree of hydrogenation. The first one is a nearly saturated one with 1% of double bond. It is crosslinked with peroxides only. The other one has a high proportion of double bonds (5~10%). It is crosslinked with peroxides or sulfur.

The best physical property of HNBR can be obtained by using completely hydrogenated rubber. It has oil resistance shown by NBR with heat resistance and ozone resistance shown by EPDM. With increasing

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content of nitrile in HNBR, the swelling of mineral oil decreases. However, the loss of low-temperature flexibility is surprisingly small compared to that of normal NBR. This means that H-NBR products obtained with high-nitrile NBR can be used to optimize balance between oil resistance and low-temperature flexibility.

In this study, basic properties, heat resistance, oil resistance, and compression set of rubber composite materials prepared by adding carbon nanofiber reinforcing materials surface treated with amine groups to HNBR rubber at various ratios were measured to determine effects of surface modified carbon nanofibers on physical properties of HNBR composite materials.

2. EXPERIMENTAL

2.1. Materials

The matrix used in this study was HNBR rubber (Hydrogenated acrylonitrile-butadiene rubber, Zetpol-2010, JEON, Japan). The reinforcing material was carbon nanofiber (Amine-CNF) whose surface was modified with amine groups. Carbon nanofibers were commercially purchased from Carbon Nanotech Co. (Pohang, Korea). Carbon black, a reinforcing agent, was used in domestic OCI (Oriental Chemical Industry, Korea) product at Semi Reinforcing Furnace (SRF) grade. Di-octyl-phthalate (DOP), a chemical product from LG, was used as a vulcanizing agent. To improve compression set and heat resistance by maximizing vulcanization effect of the matrix and reinforcing material, peroxide vulcanization type material rather than sulfur vulcanization type one was selected. ZnO

(Zinc oxide, Hanil Chemical, Korea) as metal oxide and Perkadox 14-40 (di-(2-t-butylperoxy-isopropyl) benzene, Akzo Nobel, Netherlands) as peroxide vulcanizing agent were used. TAIC 50 (Co-agent, Triallyl isocyanurate, Tokyo, Japan) was used as a co-vulcanizing agent.

2.2. Preparation of Specimen

A 1.6 L Banbury mixer (BS-B16S, Bongshin Casting & Machinery Co., Ltd.) with a rotor speed of 44 rpm in tangential type was used in this study. The speed ratio of each roll in the Roll Mill (two roll mill, Daewoong Machinery, Korea) was 1:1.2 and the number of revolutions of the front roll was set at 19 rpm. In both Banbury mixer and Roll Mill experiments, the mixing process was carried out in two steps. In the first step of the experiment using the internal mixer, carbon black (matrix) CMB (carbon master batch) was prepared by mixing metal oxide (reinforcing material) and vulcanizing agent in the internal mixer for 10 minutes at initial temperature of 50°C and final temperature of 100°C. In the second step, FMB (final master batch) was prepared by mixing CMB, vulcanizing agent, and Co agent for 2 minutes in the internal mixer. Mixing ratios are shown in Table 1. Specimens for final evaluation were prepared by applying pressure to FMB prepared to evaluate physical properties of Tc90 which was 90% cure time appropriate for each composite material at 160°C in a Hot press (DAE LIP IRON WORK CO. Korea).

2.3. Cure Behavior and Physical Properties

To investigate cure characteristics of blended composite materials, the maximum, minimum torque

Table 1: Recipe for HNBR Rubber / Amine-CNF Blends

Contents	100/0	100/1	100/3	100/5	100/7	Remark
HNBR	100	100	100	100	100	Zet 2010
Carbon nanofibers	0	1	3	5	7	Amine-CNF
Carbon black	60	60	60	60	60	SRF
Oil	20	20	20	20	20	DOP
Metal oxide	5	5	5	5	5	ZnO
Vulcanizing agent	4	4	4	4	4	Perkadox14-40
Co agent	3	3	3	3	3	TAIC-50
Total	192	193	195	197	199	

(T_{max} , T_{min}) and scorch time (ts_2 , sec) including initial rubber cure time and optimal cure time (tc_{90} , sec) were measured using an oscillating disk rheometer (ODR 2000, Kunwha Engineering, Korea) after setting cure temperature from 180 °C to 3 °C.

Tensile test was carried out at room temperature with a rate of 500 mm/min to measure tensile strength, elongation, and modulus (tensile stress at 100% elongation). Hardness of rubber was measured using a Spring Type A Hardness Tester (JIS A, Japan). For aging of vulcanized rubber caused by heating, changes in physical properties were measured after heating at 150 °C for 168 hours. For oil resistance, changes in physical properties were measured after specimens were stored in ASTM NO. 3 oil at 130 °C for 168 hours. To evaluate compression set (uniaxial compression test), specimens were prepared in a cylindrical shape with thickness of 12.7 ± 0.5 mm and diameter of 29.0 ± 0.2 mm, They were then left at 130°C and -40°C for 22 hours [12-14].

3. RESULTS AND DISCUSSION

3.1. Surface Modification Process of Carbon Nanofibers

After adding sulfuric acid and nitric acid, surfaces of carbon nanofibers were modified with carboxyl groups using a stirrer. Additives such as ethanol and amine were then added to prepare these amine-modified carbon nanofibers. The synthesis mechanism and SEM (scanning electron microscope) images of amine-CNFs are shown in Figure 1.

3.2. Cure Characteristics

As shown in Table 2, with increasing blend ratio of aminated carbon nanofibers to HNBR, the cure rate did

not show the tendency but the ts_2 time was decreased. In addition, the viscosity of composite materials was not consistent, but T5 showed the tendency similar to ts_2 . In the Rheometer, the cure curve was not flat, but was steadily ascending. The tc_{90} time, which was generally referred to as a proper crosslinking time, varied depending on the test measurement time. The tc_{90} time was not consistent but the content of carbon nanofibers was low. Thus, the effect on the viscosity of composites may not be significant. However, since the crosslinking density (T_{max} - T_{min}) of the rubber composite materials was increased with addition of 7 phr of the aminated carbon nanofibers, it suggests that the surface modified carbon nanofibers affect the crosslinking of the rubber composite materials.

3.3. Mechanical Characteristics

Hardness, tensile strength, elongation, and 100% tensile stress of specimens prepared by adding 1~7 phr of aminated carbon nanofibers as reinforcing materials to HNBR rubber, the matrix, were measured. As shown in Figure 2, physical properties were almost the same or slightly improved until 1~5 phr of aminated carbon nanofibers were added. Amphiphilic carbon nanofibers showed almost the same or slightly improved physical properties up to 1 ~ 5 phr. However, tensile strength of composite material added with 7 phr of aminated carbon nanofibers was improved by about 15% in comparison with composite material not added with such nanofibers. Elongation shown in Figure 3 revealed almost the same improvement effect as tensile strength while hardness was only slightly increased. In addition, 100% tensile stress shown in Figure 4 revealed the same improvement effect on physical properties as tensile strength. In the case of 7 phr of carbon nanofibers, such improvement was

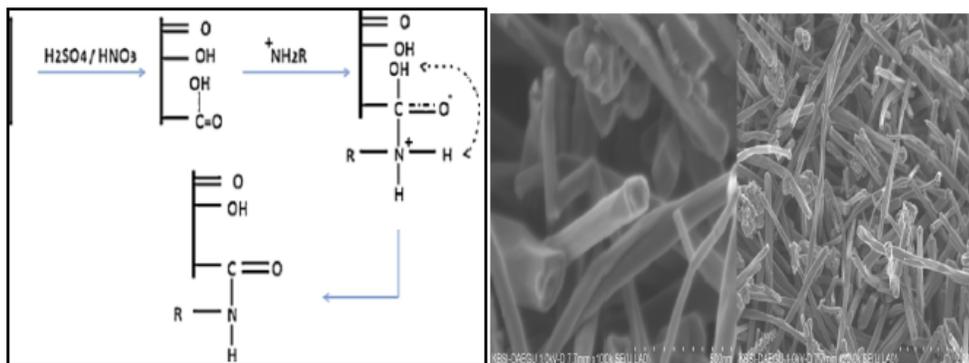


Figure 1: (a) Synthesis mechanism of amine-CNFs from Carbon nanofibers, (b) SEM images of amine-CNFs.

Table 2: Cure Characteristics of Virgin HNBR/Amine-CNF Blends

Items		100/0	100/1	100/3	100/5	100/7	Remark
ODR 180℃ X 6분	Tmax(N.m)	31.8	37.6	36.3	32.6	47.6	
	Tmin(N.m)	2.3	2.2	3.7	3.9	4.3	
	TC90(sec)	159	141	143	164	165	
	Ts2(sec)	74	77	83	85	87	
Mooney viscosity	ML121℃(Vm)	60.4	66.4	64.3	62.6	68.4	
	T5(sec)	19:07	23:40	28:02	31:11	35:04	

(Note) - Tmax: maximum torque, Tmin: minimum torque Tc90: 90% vulcanization time, ts2: scorch time at ODR
 - ML121℃: M, viscosity L, Rotor size large, T5: scorch time at Mooney viscosity.

caused by increased bonding strength between the matrix and reinforcing material. It might be associated with an increase in crosslinking density described in the crosslinking behavior.

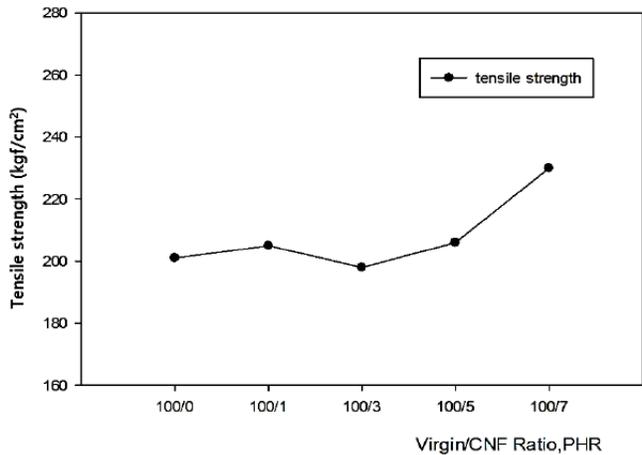


Figure 2: A graph of basic properties of tensile strength depending on the ratio of NH₂-CNFs.

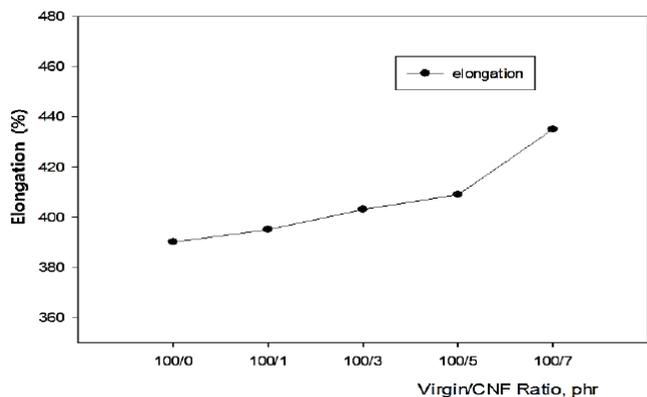


Figure 3: A graph of basic properties of elongation depending on the ratio of NH₂-CNFs.

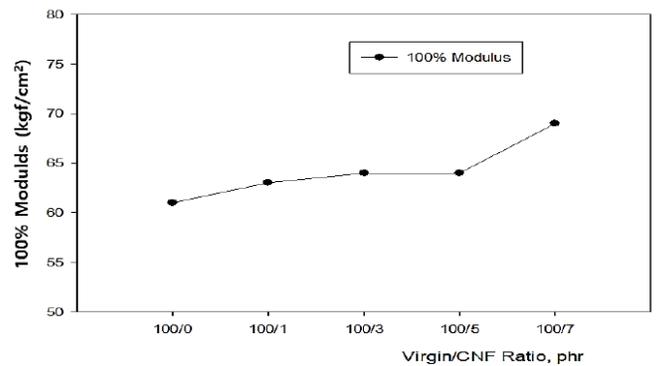


Figure 4: A graph of basic properties of modulus depending on the ratio of NH₂-CNFs.

3.4. Heat Resistance

To test heat resistance of composite materials added with aminated carbon nanofibers, physical properties were measured after they were left at a constant temperature for a fixed time. They were then compared with their initial mechanical properties. Figures 5 and 6 show changes in tensile strength and elongation after heated aging test at 150 °C, respectively. Changes in tensile strength and elongation were gradually improved with increasing amount of aminated carbon nanofibers. The reason was that bonding strength between the matrix and reinforcing material was increased due to amine group as a surface modifier of the carbon nanofiber, thus increasing heat resistance.

3.5. Oil Resistance and Compression Set

HNBR rubber is the matrix of composite materials. It belongs to rubber with good oil resistance and elasticity. In order to evaluate changes of physical properties when various amounts of aminated carbon nanofibers are added, resistance to ASTM No. 3 oil

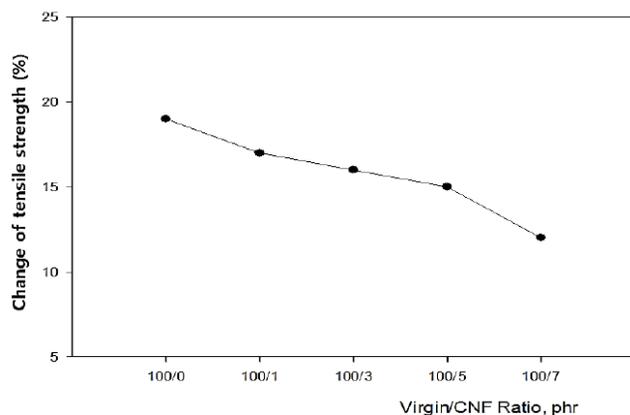


Figure 5: Changes of tensile strength after heated aging test.

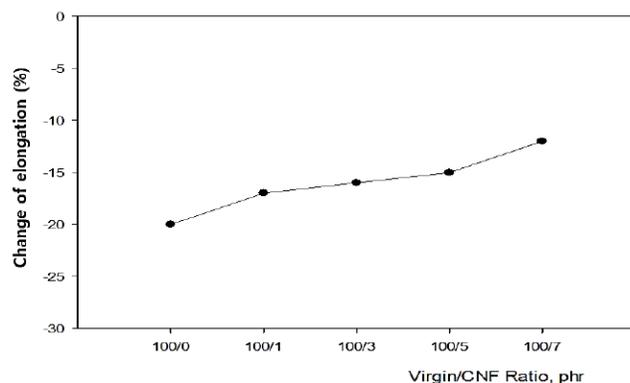


Figure 6: Changes of elongation after heated aging test.

and compression sets at high temperature of 130 °C and low temperature of -20 °C were measured for 22 hours. Oil resistance was measured by exposing specimens to a fluid at a regulated temperature for regulated time by ASTM. Changes in mechanical properties and volume were measured before and after exposing the specimen to evaluate oil resistance of the material. In this experiment, changes of mechanical properties and volume were measured after specimens were exposed to oil at 130 °C for 168 hours based on specification of automobile parts. They were then compared with properties before exposure. Results are shown in Table 3.

As shown in Table 3, composite materials added with 5 phr of aminated carbon nanofibers exhibited slight improvement in physical properties compared to those without such addition. However, when they were added with modified carbon nanofibers, physical properties of specimens were improved. Up to 5 phr of aminated carbon nanofibers did not affect the increase in crosslinking density of composite materials. However, with increasing contents of carbon nanofibers, the bonding of molecular chains was increased to become hard. Thus, penetration of oil was

decreased, thus decreasing changes of physical properties.

On the other hand, in order to measure residual strain caused by heat compression of crosslinked rubber used for dynamic compression or shear stress, compression sets at high temperature and low temperature were tested. Results are shown in Table 4. As a result of the test at high temperature, physical properties were improved as shown in results of oil resistance. In addition, amine group as a surface modifier of carbon nanofibers improved the crosslinking density of composite materials, thus improving the elasticity of these composite materials. Changes of basic properties at low temperatures were the same, suggesting that aminated carbon nanofibers did not affect the elasticity of composite materials at low temperature.

4. CONCLUSION

In this study, the rubber composite materials were prepared by blending various ratios of aminated carbon nanofibers as the reinforcing material with HNBR rubber. We measured basic physical properties, heat resistance, oil resistance, and compression set. As a result, the following conclusions were obtained.

The amine group used as a surface modifier in carbon nanofiber which was the reinforcing material diffused into HNBR rubber matrix, and played a role of promoting the crosslinking of the composite materials. With increasing contents of carbon nanofibers, the crosslinking density was increased. Functionalized carbon nanofibers were added to the HNBR matrix to reinforce physical properties and the molecular bonding became strong. As a result, mechanical properties were improved with increasing the contents. The modulus was also improved due to reinforcement of the bond between the reinforcing material and rubber matrix.

In addition, the molecular chain breakage of the composite materials caused by external heat increased the crosslinking density of the matrix to improve heat resistance due to the effects of amine groups which were surface modifiers of carbon nanofibers when the contents of reinforcing materials were increased. The oil resistance and compression set were improved with increasing contents of functionalized carbon nanofibers. In particular, 7 phr or more showing high crosslinking density showed improvement in physical properties. At low temperature, there was no effect of aminated carbon nanofibers on the physical properties of composite materials.

Table 3: Oil Resistance of Virgin HNBR/Amine-CNF Blends

Items		100/0	100/1	100/3	100/5	100/7	Remark
Oil resistanceNo.3 x 130°C x 168 hr	ΔHs(pts)	-5	-4	-4	-4	-3	
	ΔTs(%)	-5.5	-4.3	-4.1	-3.8	-3.0	
	ΔEb(%)	-4.3	-3.9	-3.7	-3.6	-2.9	
	ΔV(%)	+3.7	+3.4	+3.5	+3.4	+2.7	

* ΔHs: change of hardness; ΔTs: change of tensile strength; ΔEb: change of elongation; ΔV: change of volume.

Table 4: Compression set of Virgin HNBR/Amine-CNF Blends

Item		100/0	100/1	100/3	100/5	100/7	Remark
Compression set(%)	130°Cx22 hrs.	17	16	15	14	10	
	-40°Cx22 hrs.	24	23	22	23	23	

Therefore, on the basis of improvement in various physical properties of rubber composite materials prepared in this study, the optimum mixing ratio of aminated carbon nanofibers to the composite materials is thought to be 7 phr within the measurement range.

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