Characteristics of Functionalized Carbon Nanofibers/EPDM Rubber Composite Material

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Abstract: A rubber composite material was prepared by adding various amounts of carbon nanofibers functionalized with an amine group through surface modification to EPDM (Ethylene Propylene Diene Monomer) rubber. Changes of the cure and physical characteristics of composite materials were investigated according to contents of carbon nanofibers. Basic physical properties, heat resistance, anti-freezing resistance, and compression set at high/low temperature of rubber composite materials were measured. After adding 1~7 phr of carbon nanofibers functionalized with an amine group through surface modification to EPDM rubber, various physical properties were measured. As a result, basic physical property, heat resistance, and anti-freezing resistance of rubber composite materials added with 5~7 phr of carbon nanofibers showed improved physical property the most.

Keywords: EPDM, Carbon nanofiber, Surface modification, Rubber composite.

1. INTRODUCTION

Even if materials used in various industries have excellent properties, it is difficult to industrialize them unless they have characteristics required for the products. Recently, the biggest achievement in the field of materials is the birth of composite materials and their application to all fields of industry.

The history of composite materials is relatively long. It is still growing. After ancient Egyptians made bricks by mixing straw and sand with mud of the Nile River and drying them in the Sun, they built houses using these bricks. The brick used at that time was historically the starting point of composite materials. Our ancestors mixed short-cut rice straw with mud when they built houses. These blends could be called composite materials. If only mud was used, cracks would occur due to shrinkage when it was dried. However, if cut straw was mixed with soil, cracks would not occur during drying. Even if cracks occur, the rice straw plays a role as the reinforcing material to prevent cracks from spreading. In addition, the swallow nest is made of composite materials produced by mixing clay with straw. The bow used by the Genghis Khan's army was famous as a laminated composite material.

Human beings have been mixing various kinds of materials to produce necessary functions of materials since ancient times. A composite material is a material mixing two or more kinds of materials. Conceptually, it is a material whose performance is superior while original properties are physically and chemically maintained after two or more kinds of materials are mixed [1].

Recently, many studies have been conducted on carbon fiber reinforced rubber composite (CFRR) using carbon fiber as the reinforcing material. In the present study, carbon nanofiber reinforced rubber composite (CNFRR) was prepared by using carbon nanofiber (CNF) as the reinforcing material and EPDM rubber as the matrix. We analyzed its basic physical properties and characteristics. The content of CNF showing the best physical property was also investigated.

The CNF used as a reinforcing material refers to fiber material having a carbon content of 90% or more and a thickness of less than 1 μm. It can be applied to various fields depending on its shape and microstructure. Due to hybridization bonds such as sp, sp^2, sp^3 formed when basic properties of carbon are used, the highest strength of diamond, excellent electrical and thermal conductivity of graphite or graphene, or chemically stable and biocompatible characteristics can be shown.

When carbon material having such structural characteristics is converted into nanofiber with a diameter as small as a few nanometers, the adsorption characteristic which is the function of the micropore is maximized. On the other hand, the characteristic of a large specific surface area can maximize the efficiency even when the catalyst support is applied to its surface. As the basic structure and physical properties of carbon isotopes can vary depending on the process of making the nanofiber or the starting precursor, the purpose of the material varies [2].

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EPDM used as a matrix in this study was a polymer composed of ethylene, propylene, and copolymers of dienes. It is an elastomer with excellent weathering resistance, heat aging resistance, and ozone resistance. It has excellent stability which maintains initial properties over 20 years even when it is exposed to ultraviolet rays and ozone. It has excellent stability. Due to these excellent properties, these materials are being used in a variety of applications ranging from general industrial parts to components for the aerospace industry. For example, EPDM rubber is being widely used in various fields including waterproofing materials, tires, automobile parts, wires or cables, construction in new buildings, renovated buildings, subways or tunnels, construction for reservoirs and wastewater treatment facilities, construction for ponds of golf course, and construction for indoor/ outdoor ponds [3, 4].

In this study, composite materials were prepared by adding CNFs functionalized through surface modification of EPDM rubber with an amine group at various ratios to improve adhesion to rubber. Basic properties, heat resistance, anti-freezing resistance, and compression set at high/low temperature of these composite materials were measured to investigate the content of CNFs with the best physical property as rubber composite material.

2. EXPERIMENTAL

2.1. Reagents and Materials

The matrix used in this study was virgin EPDM rubber (EPT4035, MITSUI, Japan) and the reinforcing material was carbon nanofiber modified with amine (Amine-CNFs). The reinforcement material was Korea Carbon product of Fast Extruder furnace (FEF) grade. Additives used included P-90 oil (Sechang Oil, Korea) as a plasticizer, Zinc oxide (ZnO, Hanil Zinc, Korea) and Stearic acid (S/A, LG, Korea) as activators, M and TS (Dongyang Chemical, Korea) as accelerators, and S (S, Miwon Chemical, Korea) as a vulcanizing agent.

2.2. Compositions and Preparation of Specimen

All specimens used in this study were prepared by primary mixing according to ASTM D3192. In primary mixing, a 1.6 L airtight mixer (Bongshin) was used at the rate of 44 rpm. The initial temperature was set at 40 °C and the final temperature was set at 120~130 °C. Materials were added in the following order. Carbon black was added into composite materials prepared by using virgin rubber and Amine-CNFs. Drugs were then added. They were mixed for 5 minutes. After mixing, blends were left at room temperature for 6 hours considering thermal stability of the elastic structure of the rubber. Accelerators were mixed in a two-roll mill at 80 °C for 10 minutes. Plate specimens were prepared using a flat plate type heater at 160 ℃ and pressure of 120 Kg/cm^2 in order to measure various physical properties. Plate specimens were prepared in the form of dumbbell type 3 using a specimen cutter. Table **1** shows mixing ratios of rubber materials and various additives applied in this study.

2.3. Cure Characteristics

To investigate cure characteristics of EPDM rubber and carbon nanofiber composite materials, the cure

Table 1: Recipe for Virgin EPDM / Amine-CNFs Rubber Blends

Materials	100/0	100/1	100/3	100/5	100/7	Remark
EPDM	100	100	100	100	100	EPT3045
Carbon nanofiber	-	1	3	5	7	Amine-CNF
Carbon black	60	60	60	60	60	FEF
Oil	30	30	30	30	30	P-90
Activator	5	5	5	5	5	ZnO
Stearic acid	1	1	1	1	1	S/A
Accelerator	0.5	0.5	0.5	0.5	0.5	M
Accelerator	1.5	1.5	1.5	1.5	1.5	TS
Vulcanizing agent	1.5	1.5	1.5	1.5	1.5	S
Total	199.5	200.5	202.5	204.5	206.5	

temperature was set at 160℃ using a Moving Disk Rheometer (MDR P200, Alpha technology, USA). The maximum and minimum torque (Tmax, Tmin), the optimal cure time (Tc90), the first rubber cure time, and Scorch time (ts2) were measured. In addition, Mooney scorch time (T_5) and Mooney viscosity (ML_{1+4}) of each blend were measured at 121℃ using a Mooney viscometer (Monsanto, USA).

2.4. Physical Characteristics

Tensile characteristics were measured at a rate of 500 mm/min at 25℃ using a tensile tester (Instron 10, USA) after specimens were prepared according to ASTM D-412. To investigate effects of heat, tensile characteristics were measured after dumbbell specimens for tensile test were heated at 130 °C for 168 hours in an oven exposed to air. To test resistance properties of anti-freezers most frequently used in EPDM products, water and anti-freezers were mixed at a ratio of 50:50 and then left at 115℃ for 360 hours. Changes in physical properties of anti-freezers were evaluated to measure mechanical properties. Compression set was evaluated under test conditions of 120 °C, 70 hours ~ 20 °C, 22 hours. Specimens used in the test for compression set were cylindrical with thickness of 12 mm and diameter of 29 mm. The compression set was 25% [5].

3. RESULTS AND DISCUSSION

3.1. Preparation of Surface Modified Carbon Nanofibers

After sulfuric acid and nitric acid were added, carbon nanofibers were synthesized through surface modification with carboxyl groups. Amine-CNFs functionalized through surface modification with the addition of ethanol and amine were synthesized by the mechanism shown in Figure **1**.

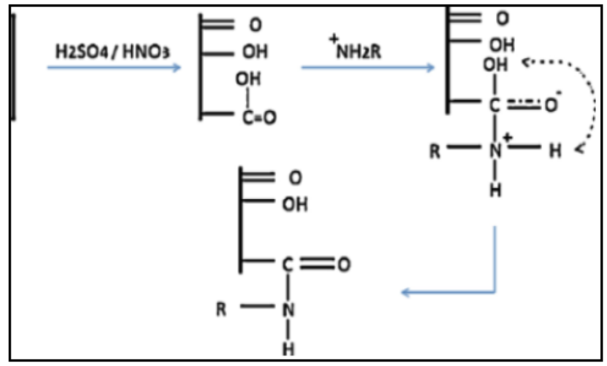

Figure 1: Synthetic Mechanism of Amine-CNFs.

3.2. Cure Characteristics of Composite Materials

Cure characteristics of mixed rubbers were examined with a Rheometer. In general, the cross-linked bond of elastomer is referred to as a bond in which two or more chains are bonded. The cross-linked polymer is known to have at least two cross-linked bonds in each chain. It can form a two-dimensional or three-dimensional network with other chains [6]. In this experiment, cure characteristics of mixed rubber were measured when Amine-CNFs were added in four ratios (1, 3, 5, and 7 phr) within the range of 1~7 phr. Measurement results are shown in Table **2**. With increasing contents of CNFs, the scorch time (Ts2) decreased. Hamed *et al*. have reported diffusion between two mixed materials during the mixing process and vulcanization reaction [7]. In this study, amine as a surface modifier of carbon nanofiber acted as a composite reinforcing material. It moved to the EPDM rubber which was the matrix to increase vulcanization reaction of composite materials. Thus, scorch time was decreased.

Table 2: Cure Characteristics of Virgin EPDM and Amine-CNFs Rubber Blends

Contents		100/0	100/1	100/3	100/5	100/7
MDR 160℃ *20min.	Tmax	15.90	16.75	16.66	19.05	20.4
	Tmin	1.04	1.12	1.48	1.90	2.0
	Tc90	8.31	9.34	10.52	9.72	10.22
	ts2	3.18	2.40	1.98	1.78	1.65
MS100℃		19.4	18.9	19.4	22.6	23.2
ML121℃ Vm/T_5		25.7/17.4	25.2/14.3	26.9/15.0	26.2/14.3	28.2/13.2

Tmax: maximum torque; Tmin: minimum torque; Tc90: 90% curing time; ts2: Scorch Time.

3.3. Physical Characteristics

Basic Properties

EPDM rubber was blended with CNFs. Hardness, tensile strength, elongation, and 100% tensile stress of composite materials were measured. With increasing contents of CNF blends, tensile strength was increased while elongation was gradually decreased. On the other hand, the hardness was almost the same. Figure **2** shows results of tensile strength measured with increasing contents of CNFs. With the addition of CNFs, the tensile strength of rubber composite materials was increased. Figure **3** shows elongation measured when materials are broken. With addition of CNFs, elongation was decreased. Figure **4** shows tensile stress after changing 100% elongation of specimens. With the addition of CNFs, the tensile stress was increased. It was thought that the bond length of composite rubber was decreased to decrease the elongation as CNFs were filled in the molecular chains. In addition, mutual interactions stably reconstructed between CNFs (reinforcement materials) while EPDM rubber (matrix) increased tensile strength when 100% elongation was changed. This is consistent with the fact that spatial arrangement of particles is stabilized or fixed to perform characteristics required for dynamic performance [8-11].

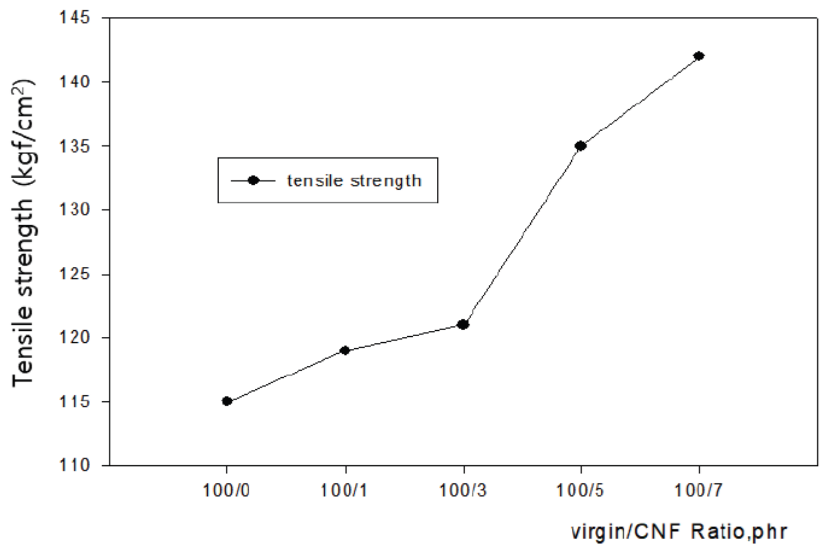

Figure 2: Basic properties of tensile strength according to the ratio of carbon nanofibers.

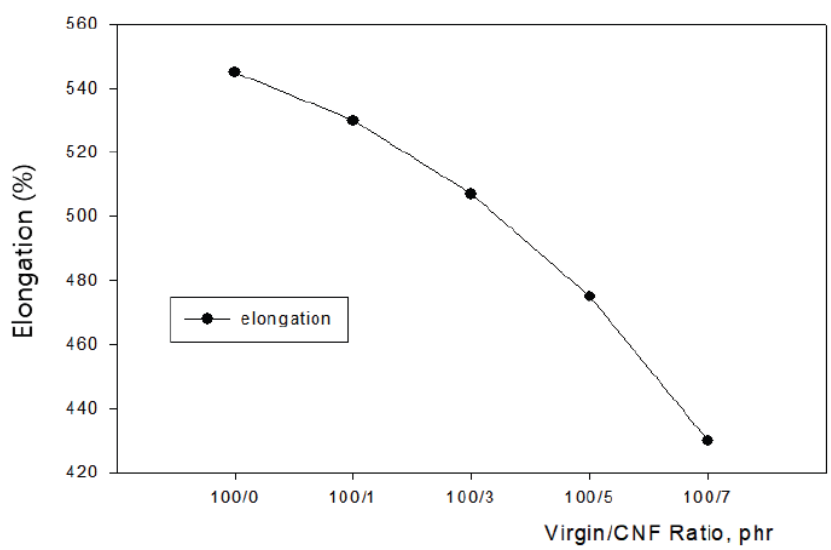

Figure 3: Basic properties of elongation according to the ratio of carbon nanofibers.

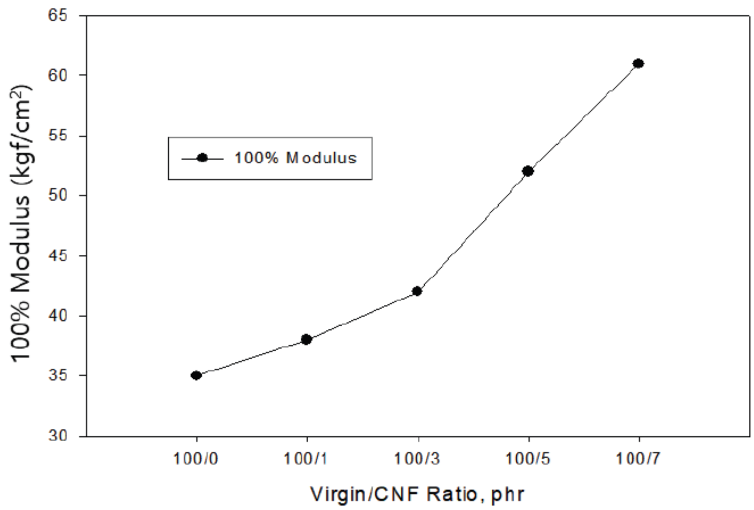

Figure 4: Basic properties of modulus according to the ratio of carbon nanofibers.

Heat Resistance

Hardness, tensile strength, and elongation of composite materials were measured after rubber specimens were aged at 130 °C for 168 hours in order to measure heat resistance characteristics of these composite materials added with CNFs. Figures **5** and **6** show changes in tensile strength and elongation, respectively. With increasing contents of CNFs, the hardness was almost not changed between before and after heat treatment. However, tensile strength and elongation showed small changes in physical properties. When compared with 100% blends without CNFs, the continuity of molecular chain of composite material was increased with the addition of CNFs. Thus, even if composite materials added with CNFs were heated, the change of tensile strength was low. Figure **6** shows change of elongation measured after heated aging test. The change of elongation in specimen fracture was small. It tended to be low compared to changes of tensile strength. The reason was that the vulcanization density of the composite material was increased by the surface modifier, amine, and the cleavage of molecular chains was improved by CNFs.

Anti-Freezing Resistance

EPDM rubber is the matrix of composite materials. It is used most frequently in anti-freezers containing ethylene glycol. Thus, the anti-freezing resistance of materials used in this study was tested. The test was carried out as below. Specimens were exposed to the fluid at specified temperature and time. Changes of mechanical properties and volume were measured to evaluate the resistance of materials against the fluid. In

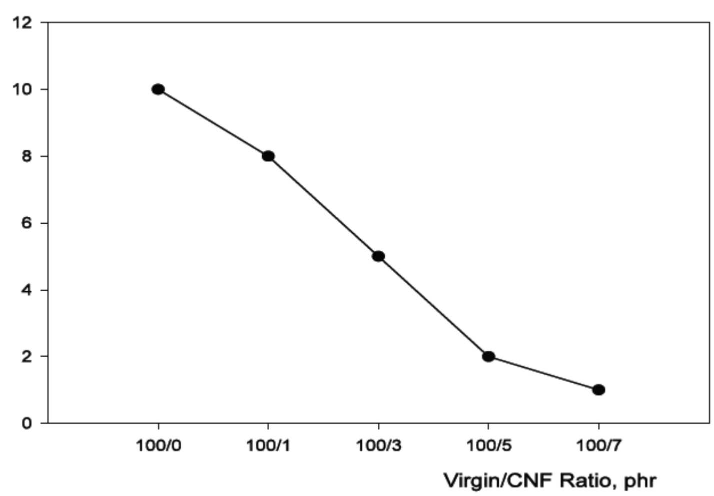

Figure 5: Change of tensile strength measured after heated aging test.

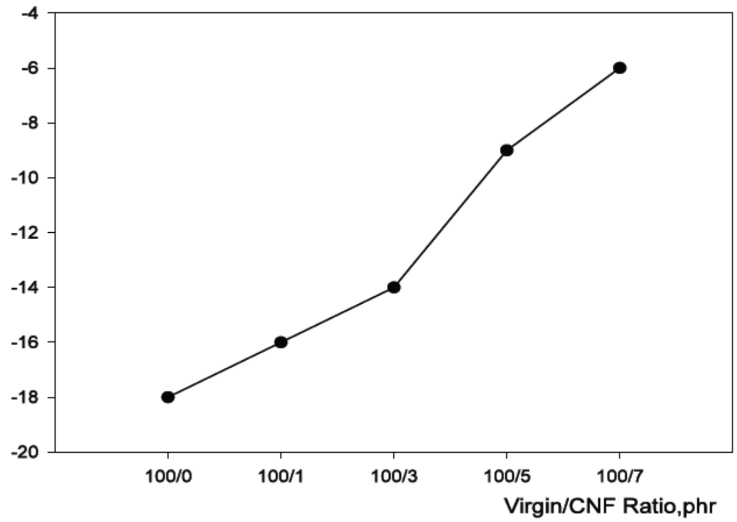

Figure 6: Change of elongation measured after heated aging test.

this experiment, specimens were exposed to the anti-freezer at 115 °C for 360 hours based on specification of automobile parts. Changes of mechanical properties and volume were measured and compared with physical properties before the exposure. Results are shown in Table **3**. According to Table **3**, physical properties of the composite materials added with 3 phr of CNFs were almost the same as those of blended materials without the addition of CNFs. However, when more than 3phr of CNFs were added, physical properties of specimens were different. The addition of up to 3 phr of CNFs did not significantly affect vulcanization density of rubber composites. However, with increasing contents of CNFs, bonds of molecular chains were increased to make strong molecular structure. Thus, the penetration of anti-freezer was decreased, resulting in changes of physical properties.

Compression Set

To measure residual deformation caused by hot compression of the vulcanized rubber frequently used in the part applied by dynamic compression or shear force, compression set test was performed at high/low temperature. Results are shown in Table **4**. As shown in results of the anti-freezing resistance test, physical properties were improved when more than 5phr of CNFs were added. The elasticity of the composite material was improved as amine group which was the surface modifier of CNFs increased the vulcanization density of the composite material. Since physical

Table 3: Anti-Freezing Resistance of Virgin EPDM and Amine-CNF Blends

Contents		100/0	100/1	100/3	100/5	100/7
Anti-freezer resistance *115℃ *360 HR	ΔHs	+4	+4	+5	+2	+1
	ΔTs	+6	+4	+5	+1	0
	ΔEb	-25	-23	-22	-17	-18
	ΔV	+2,5	+2.3	+2.3	+1.9	+1.8

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

Table 4: Compression set of Virgin EPDM and Amine-CNF Blends

Contents	100/0	100/1	100/3	100/5	100/7	Remark
120℃*70HR	35.6	33.5	33.4	27.6	26.8	unit: %
-20℃*22HR	27.8	27.7	26.5	25.8	26.4	

properties at low temperature were the same, CNFs did not affect the elasticity of the composite material at low temperature.

4. CONCLUSION

Rubber composite materials were prepared by blending virgin EPDM rubber with CNFs functionalized through surface modification using amine groups. The following conclusions were drawn based on test results obtained from basic physical properties, heat resistance, anti-freezing resistance, and compression set.

1) The amine group modified carbon nanofibers which was used as a reinforcing material on EPDM matrix were dispersed into the EPDM, which result in accelerating the vulcanization speed of the composite materials. With increasing contents of CNFs, the scorch time was shortened.

2) EPDM composite materials were made of CNFs functionalized with amine groups. When CNFs were added to the matrix, they had physical reinforcing effects to make a strong molecular bond. With increasing contents, the tensile strength was improved. Due to reinforcing effects of the tensile strength, elongation was decreased. On the other hand, the modulus was improved due to the strengthening of bond strength between the reinforcing material and the matrix.

3) Cleavage of molecular chain of composite materials by external heat was affected by the amine group which was the surface modifier of CNFs. With increasing contents of CNFs, the vulcanization density of the matrix was increased to improve heat resistance.

4) The anti-freezing resistance and compression set showed improved physical properties with the addition of 5~7 phr of CNFs because of the high vulcanization density which was similar to heat resistance. In addition, CNFs did not affect physical properties of the composite materials at low temperature.

5) The most optimal mixing ratio of functionalized CNFs against EPDM was 5~7 phr to improve physical properties of the composite material.

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