

Electromagnetic Interference Shielding Properties of CO₂ Activated Carbon Black Filled Polymer Coating Materials

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Abstract

Carbon blacks could be used as the filler for the electromagnetic interference (EMI) shielding. The poly vinyl alcohol (PVA) and polyvinylidene fluoride (PVDF) were used as the matrix for the carbon black fillers. Porous carbon blacks were prepared by CO₂ activation. The activation was performed by treating the carbon blacks in CO₂ to different degrees of burn-off. During the activation, the enlargement of pore diameters, and development of microporous and mesoporous structures were introduced in the carbon blacks, resulting in an increase of extremely large specific surface areas. The porosity of carbon blacks was an increasing function of the degree of burn-off. The surface area increased from 80 m²/g to 1142 m²/g and the total pore volume increased from 0.14073 cc·g⁻¹ to 0.9343 cc·g⁻¹. Also, the C=O functional group characterized by aldehydes, ketones, carboxylic acids and esters was enhanced during the activation process. The EMI shielding effectiveness (SE) of raw N330 carbon blacks filled with PVA was about 1 dB and those of the activated carbon blacks increased to the values between 6 and 9 dB. The EMI SE of raw N330 carbon blacks filled with PVDF was about 7 dB and the EMI SE increased to the range from 11 to 15 dB by the activation.

Keywords : *Electromagnetic interference shielding, Carbon black, CO₂ activation, Poly vinyl alcohol, Polyvinylidene fluoride*

1. Introduction

All electronic and electrical devices emit electromagnetic signals which can interfere with the proper operation of either the emitting equipment or the equipments around it. Therefore, the electromagnetic interference (EMI) shielding is receiving increasing attention in electronic and communication industries because of devices becoming increasingly sensitive, dense and abundant[1]. The effect of EMI can range from degradation to interception and obstruction of the performance of electronic or electrical equipment. Therefore, an electrically conductive housing is needed to shield EMI produced from the electronic equipments[2].

There are three mechanisms for EMI attenuation: reflection, absorption and multiple reflections. The primary mechanism, reflection, requires the existence of mobile charge carriers (electrons or holes) which interact with the electromagnetic radiation. The secondary mechanism of EMI shielding is absorption. For significant absorption of the radiation by the shield, the shield should have electric and/or magnetic dipoles which interact with the electromagnetic fields in the radiation. The last mechanism of shielding is multiple reflections which requires the presence of a large surface area or interface area in the shield[3].

Composites with conducting fillers, such as metal particles, metal flakes, carbon particles and carbon-fibers,

are widely used for EMI shielding[4]. The carbon blacks with high aspect ratio have advantages in both electrical conductivity and specific surface area. Due to the desire for light weight for laptop computers, aircraft and many other devices, polymer-matrix composites are increasingly important for EMI shielding. Polymer-matrix composites containing conductive fillers are attractive for shielding due to their processability (e.g. moldability), which helps to reduce or eliminate the seams in the housing that is the shield. In addition, polymer-matrix composites are attractive in their low density[5].

The CO₂ activation process is essential to high performance carbon blacks. The physical or thermal activation process is carried out at a temperature between 800 and 1000°C in the presence of suitable oxidizing gases such as steam, carbon dioxide or any mixture of these gases[6-7]. In physical activation, the slow gasification kinetics allow gas molecules to diffuse into the carbon micropores and develop a large surface area[8-9]. Activated carbons are nowadays one of the most relevant adsorbent materials in our society and in diverse areas of human activity. Activated carbons are used in a wide range of applications, in both the gas and liquid phases, that include medicinal uses, gas storage, pollutant and odour removal, gas separations and catalysis[10]. The activated carbon blacks filled SBR rubber composites showed the much higher EMI shielding effec-

tiveness (SE) which was described by Ao[11]. The reason was that it could make more developed continuous conductive filler network in the rubber matrix due to the extremely high specific area of the carbon black after CO₂ activation.

The main focus of this work lies on characterizing the various properties of carbon blacks after CO₂ activation and their polymer composites. We tried to find out the effect of those properties of carbon blacks on the EMI SE of PVA or PVDF composites.

2. Experimental

Carbon blacks N-330 fluffy were supplied by DC Chemical. Co., Ltd. Polyvinyl alcohol (PVA, 96% hydrolyzed) was provided by Aldrich Chemical Company, Inc. Polyvinylidene fluoride (PVDF) was made by Kureha Corporation, Japan. Distilled water was used as the solvent of PVA and 1-Methyl-2-pyrrolidone (NMP, Samchun Pure Chemical Co., LTD., Korea) was used as the solvent of PVDF. The dispersant of Polyoxyethylene Nonylphenyl (NP-10, Greensoft Chem, Co., Korea) was introduced into polymer solution to disperse the carbon blacks homogeneously. The PVA solutions were made by stirring the mixture containing 10 wt% of PVA and 90 wt% of distilled water at 90°C for at least 4 h. Solution of PVDF was obtained by stirring 10 wt% of PVDF in 90 wt% of NMP at room temperature for 10 h. Carbon blacks were crushed in a mixer for 5 min. The crushed fillers (40 wt%, dry basis) and the dispersant (2 wt%, liquid) selected were introduced into the PVA or PVDF solution. The mixture was stirred at 600 rpm for 20 min by a mechanical stirrer and at 20000-40000 rpm for 3 min by a homogenizer continuously. The mixture obtained was coated into the size of 15 cm × 15 cm with the thickness of 50 μm after drying using an applicator.

The samples denoted by N330-f-CO₂ were surface mo-

dified raw N330-f carbon blacks with different yields by CO₂ activation. N330-f-CO₂ was prepared by placing raw N330-f carbon black into a horizontal cylindrical furnace (80mm diameter) under flowing nitrogen (100 ml/min). For all activations, approximately 25 g of carbon blacks were used. The furnace was purged with nitrogen for around 30 min and then, the temperature was increased to the desired activation temperatures from 950 to 1000°C at a constant rate of 10°C/min under flowing nitrogen (100 ml/min). Once the activation temperature was reached, nitrogen flow was switched to CO₂ (from 500 to 700 ml/min). Furnace temperature and CO₂ flow were kept constant for 3 h. At the end of the activation period, the sample was cooled under nitrogen (100 ml/min). Carbon blacks with various degrees of burn-off were prepared.

The BET surface area and pore size distribution of carbon blacks were characterized by physical adsorption tests with N₂ as the adsorbate at 77 K with a surface analyzer (Automatic Volumetric Sorption Analyzer, Autosorb-1, Quantachrome). Resistivity of carbon blacks was tested by a digital multi-meter (Hioki Co., HI Tester 3540) after the carbon black samples being kept under a constant pressure of 1,000 psi for about 20 min by a power press (ISE-WP 10T, Enerpac, USA). An automatic four-probe system (CMT-SR 1000N, Chang Min Tech Co.) was used for measuring the electrical conductivity of coating materials. The electromagnetic interference shielding effectiveness of the coating materials was measured using a Spectrum Analyzer (ADVENTEST R3361C).

3. Results and Discussion

Changes in surface area and pore volume during activation were monitored and controlled to produce a series of activated carbon blacks with different degrees of burn-off. Variations in surface area and pore volume with carbon

Table 1. Properties of N330-f Carbon Blacks Treated by CO₂ Activation

Sample	Yield (%)	Mesopore Volume (cc · g ⁻¹)	Micropore volume (cc · g ⁻¹)	Total pore volume (cc · g ⁻¹)	Specific surface area (m ² · g ⁻¹)
Raw N330-f	100	0.1010	0.0367	0.1377	80
N330-f-CO ₂ activation (950°C 500 sccm 3 h)	68	0.2311	0.2680	0.4991	598
N330-f-CO ₂ activation (950°C 700 sccm 3 h)	66	0.3726	0.3817	0.7543	690
N330-f-CO ₂ activation (970°C 500 sccm 3 h)	62	0.4548	0.3902	0.8450	739
N330-f-CO ₂ activation (970°C 700 sccm 3 h)	58	0.4491	0.4002	0.8493	748
N330-f-CO ₂ activation (1000°C 500 sccm 3 h)	51	0.4497	0.4415	0.8912	949
N330-f-CO ₂ activation (1000°C 700 sccm 3 h)	44	0.4513	0.4830	0.9343	1142

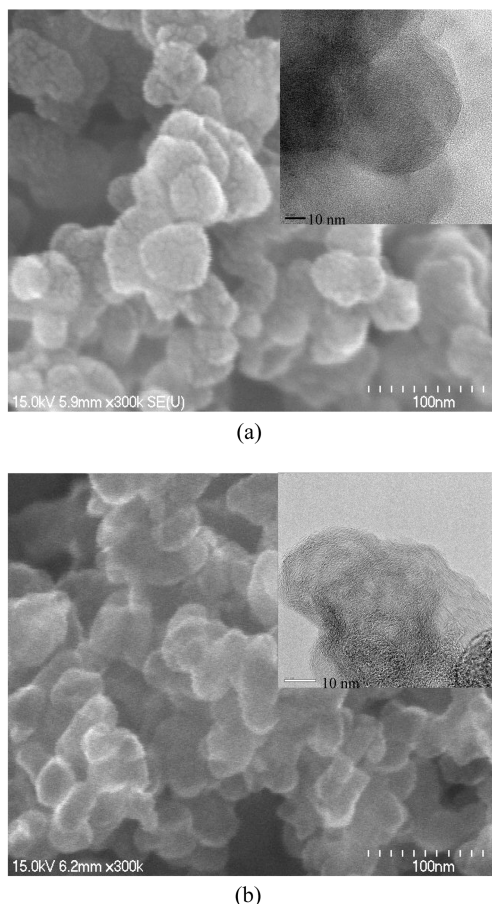


Fig. 1. SEM images and TEM images of (a) raw N330-f and (b) N330-f-1000°C-700 sccm.

burn-off during activation are normally taken as the essential characteristics of a particular activation process[12]. Mesopore, micropore volumes and specific surface areas of CO₂ activated carbon blacks are reported in Table 1. After the activation of the carbon blacks, the surface areas were in the range of 598~1142 m²/g and the total pore volumes of the activated carbon blacks were in the range of 0.50~0.93 cc·g⁻¹. The values of mesopore and micropore volumes for the activated carbon blacks indicated that their porosity was an increasing function of the degree of burn-off. In general, microporosity in carbon blacks is created by removal of solid material by an activation process. However, after the evolution of microporosity to certain optimum degree, further activation to increase the microporosity is accompanied by mesopore evolution[13]. In Fig. 1, the SEM images showed that the activated carbon blacks treated at 1000°C with 700 sccm of CO₂ gas exhibited more heterogeneous surface than the raw carbon blacks, having much different particle sizes. From the high resolution TEM images of inset, it could be seen clearly that the carbon blacks developed more pores after the CO₂ activation. It was confirmed that the carbon blacks with the higher degree of

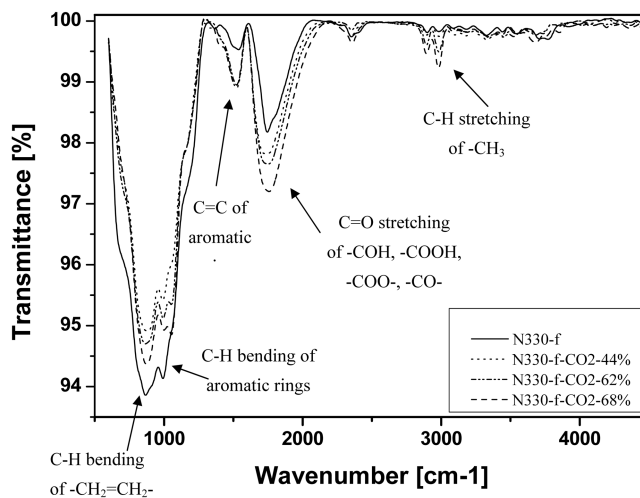


Fig. 2. ATR-FTIR spectra of N330-f before and after CO₂ activation at different conditions.

burn-off developed more pores than that with the lower degree of burn-off[11].

Surface functional groups of carbon blacks before and after CO₂ activation were shown in Fig. 2 of the ATR-FTIR spectra which were corrected by removing the spectral contributions due to atmospheric water. The strong peak at 1750 cm⁻¹ of carbon blacks before and after CO₂ activation could be seen, which indicated the presence of C=O functional groups characterized by aldehydes, ketones, carboxylic acids and esters. Generally, the temperature of activation is higher than 800°C, the basic functional groups such as pyrone and chromene could be developed which resulted in the enhancement of the C=O functional group [14]. All carbon black samples also presented two peaks at 1000 and 900 cm⁻¹. The peak at 1000 cm⁻¹ could be assigned to the C-H bending of alkenes and the peak at 900 was the C-H cm⁻¹ bending of aromatic rings in carbon blacks. The reduction of the C-H bending might be caused by the decomposition of the alkanes and aromatic rings at the high temperatures.

Table 2 showed the variations of the electrical properties of carbon blacks and their PVA and PVDF coating materials before and after the CO₂ activation. Generally, carbon black is a highly carbonaceous material typically containing more than 90% carbon with some foreign elements such as 0.4% of H, 0.7% of O and 0.6% of S. The high temperatures favor the removal of sulfur containing functional groups and the electrical conductivity of carbon blacks increases with decreasing the concentration of non-carbon elements on their surface. On the other hand, the resistivity of CO₂ activated carbon blacks decreased with the increased surface area. It was observed that the electrical resistivity of carbon blacks was strongly influenced by the structure, specific surface area, and other properties[15]. Thus the resistivity of the activated carbon blacks was lower than that of raw carbon

Table 2. Variations of the Electrical Properties of Carbon Blacks and Their Polymer Coating Materials before and after CO₂ Activation

Sample (carbon blacks 40 wt%, 50 μm)	Resistivity of carbon black (Ω·cm)	PVA		PVDF	
		Volume resistivity of coating materials (Ω·cm)	Surface resistivity of coating materials (Ω/sq)	Volume resistivity of coating materials (Ω·cm)	Surface resistivity of coating materials (Ω/sq)
Raw N330-f	0.0744	2.05 ± 0.50	394 ± 33	0.76 ± 0.02	152 ± 1.4
N330-f-CO ₂ activation (950°C 500 sccm 3 h)	0.0582	0.63 ± 0.07	118 ± 17	0.26 ± 0.02	57 ± 2.6
N330-f-CO ₂ activation (950°C 700 sccm 3 h)	0.0579	0.57 ± 0.03	114 ± 10	0.22 ± 0.01	46 ± 0.9
N330-f-CO ₂ activation (970°C 500 sccm 3 h)	0.0544	0.45 ± 0.02	91 ± 8.7	0.20 ± 0.01	40 ± 0.2
N330-f-CO ₂ activation (970°C 700 sccm 3 h)	0.0541	0.39 ± 0.04	77 ± 9.1	0.19 ± 0.01	38 ± 0.4
N330-f-CO ₂ activation (1000°C 500 sccm 3 h)	0.0539	0.35 ± 0.01	68 ± 6.4	0.17 ± 0.01	29 ± 0.8
N330-f-CO ₂ activation (1000°C 700 sccm 3 h)	0.0537	0.32 ± 0.02	64 ± 6.7	0.14 ± 0.01	24 ± 2.4

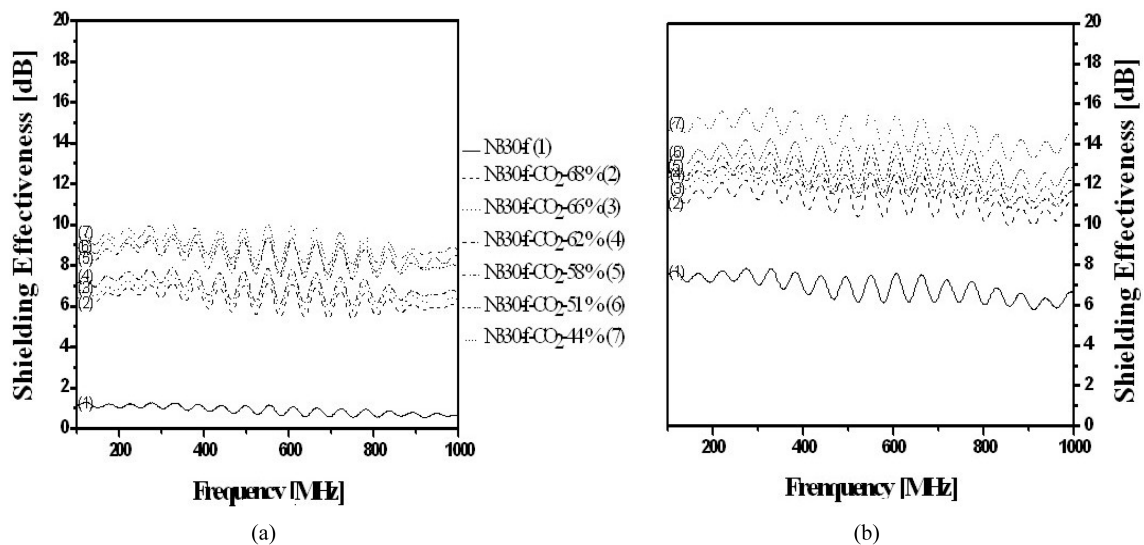
blacks.

Probst and Grivei also found that the activated carbon black had low resistivity than the other carbon blacks without activation even though the density of activated carbon black was much lower than those of the other blacks [16]. Similar to our work, since the resistivity of the samples was measured under a pressure of more than 1000 psi, the activated carbon black with high porous structure might have better contact points than the raw carbon blacks. Another possible explanation was that since the ordered carbon were removed selectively during the CO₂ activation, the crystallinity of remained carbon blacks would be higher than that of raw carbon blacks showing low resistivity. The polymer is an insulator, therefore, the electrical resistivity of carbon black/polymer coating materials reduced with the

decreased resistivity of carbon black fillers. Also it could be explained that the more complex surface structure of carbon blacks after the CO₂ activation would form a better continuous conductive filler network in the polymer matrix [11].

The EMI SE of carbon blacks filled PVA and PVDF coating materials before and after the CO₂ activation was shown in Fig. 3. The EMI SE of raw carbon black/PVA composites was about 1 dB. After the CO₂ activation, the EMI SE increased to the values between 6.4 and 9.3 dB depending on the degree of burn-off. The EMI SE of raw N330 carbon black/PVDF composites was about 7 dB and those of activated carbon black/PVDF composites increased to the range from 11 to 15 dB.

The polymer-matrix composites are increasingly important for EMI shielding due to their moldability and processability.

**Fig. 3.** EMI Shielding effectiveness of carbon blacks filled (a) PVA and (b) PVDF coating materials before and after CO₂ activation.

Since percolation theory indicates that the electrical conductivity of a composite is determined by the ability to form a conducting network[3]. The high performance for EMI shielding of carbon black-based composite is a reflection of their high conductivity and systematic organization of the polymers to form fine network. Compared to PVA, PVDF was a more efficient matrix for the EMI shielding and as the result the EMI SE of the carbon black/PVDF composites was higher than that of the PVA composites. With increasing of the degree of burn-off, the specific surface area obviously increased which caused the enhancement of EMI SE. The specific surface area and electrical conductivity of carbon blacks were important properties for EMI shielding. As the EMI fillers, large specific surface area is desirable. It was reported that filler's specific surface area was the more important factor than the filler's conductivity[2].

Low surface activity might be another reason that could enhance the EMI SE of the polymer composites. The surface activity broadly defined as the tendency of a carbon black to interact with its surroundings. It includes hydrogen content, crystallite size, oxygen content and heats of adsorption[17]. Hydrogen content is highly significant, but may only be an indicator of relative surface activity. When hydrogen is removed from a carbon black, the graphic layers are free to join together into a more continuous and inert surface microstructure. The loss of hydrogen can take place with increasing the heat treatment temperature. So, the low hydrogen content can be indicated as the low surface activity [18]. The low surface activity of carbon black results in a decreased interaction with the polymer phase, providing a developed carbon black network formation which can improve the connectivity of the carbon black/polymer composites. Although the shielding does not require connectivity, it is enhanced by the connectivity[5].

4. Conclusions

Carbon blacks were dispersed as conductive fillers in PVA and PVDF matrix, and the EMI SE of carbon black and polymer composites before and after CO₂ activation was investigated. The effect of CO₂ activation of carbon blacks has been studied by the means of surface heterogeneities including porosity, specific surface area and functional groups of carbon blacks surfaces. With the CO₂ activation, the porosity of resulting carbon blacks was turned out to be an increasing function of the degree of burn-off, resulting in an increase of extremely large specific surface areas. The surface functional groups of carbon blacks such as C=C and C=O bonds were enhanced and the C-H bending were reduced due to the decomposition of the alkanes after the

CO₂ activation, which might cause the reduction of hydrogen content and surface activity. The EMI SE of CO₂ activated carbon blacks filled PVA composite increased from 1 dB to the range of 6.4~9.3 dB. That of PVDF composites enhanced from 7 dB to the values between 11 and 15 dB. This was caused by the extremely high specific surface area of the carbon black after CO₂ activation which would be the most important factor of the EMI shielding. The reduced surface activity also could enhance the EMI SE of the carbon blacks/polymer composites.

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