

Effect of Fluorination on Electrical Behaviors of Carbon Blacks-filled HDPE Polymeric Switch

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Electrical properties of a fluorinated carbon black (CB)-filled high-density polyethylene (HDPE) polymeric switch were investigated as a function of fluorination pressure at 0.1 ~ 0.4 MPa. From the FT-IR results, the absorption spectra of the fluorinated CB show an absorption band at 1400 ~ 1000 cm^{-1} for $\nu_{\text{C-F}}$ and the peak intensity increased with increasing fluorination pressure. Also, the analysis of XPS spectra of the fluorinated CB indicated that fluorine content increased with increasing fluorination pressure. Meanwhile, the surface free energy of the fluorinated CB decreased with increasing fluorination pressure. Consequently, the increase of fluorine contents of CB made a disappearance of negative temperature coefficient (NTC) behavior of the polymeric switch, which was probably due to the reduction of CB reaggregation after melting point of the HDPE, resulted from the decreasing of London dispersive component of the surface free energy for CB particles.

Key Words: Electrical properties, Carbon blacks, High density polyethylene, Polymeric switch, Fluorination

Introduction

The distribution of conductive fillers, such as carbon blacks (CB), carbon fibers (CF), graphites (GP), metal powders, *etc.*, into a semi-crystalline polymer matrix can obtain conductive polymer composites. Some conductive polymer composites are called positive temperature coefficient (PTC) materials because they can exhibit PTC behavior. The main feature of PTC materials is that they exhibit a sharp increase of resistivity near the melting region of the polymer matrix. PTC materials are sometimes followed by a negative temperature coefficient (NTC) effect after the melting temperature (T_m) of the polymer matrix.¹⁻³ The presence of the NTC effect has an adverse influence on the application of PTC materials, such as shielding materials, self-heating plastics, antistatic products, electromagnetic radiation absorbing materials, *etc.* because of the instability of conductivity. Therefore, it is an important matter to consider how we can eliminate the NTC effect.^{4,5}

Generally, chemical crosslinking or radiation crosslinking can result in more stable conductive behavior in these materials. However, chemical crosslinking is limited in application because it always takes place above the melting temperature of the composites. On the other hand, radiation crosslinking is not dependent on temperature, and hence can be carried out below the melting temperature (T_m), usually at room temperature. In addition, the radiation crosslinking of CB-filled composites can also provide good reproducibility of resistance if the temperature is cycled up to or above the T_m of the polymer.⁶⁻⁸ However, radiation crosslinking is a high cost method with complexly radiation equipment.

Surface modification techniques are widely used, because they have many advantages such as low cost, simple equipment, and short work time. The most commonly used surface modification techniques involve chemical treatment, electrochemical treatment, photoirradiation or phototreatments with ionized gases, *i.e.*, microwaves, radiofrequency, glow discharge plasmas, and direct fluorination with fluorine gas.⁹⁻¹⁴ Among

these, the physical properties and chemical reactivities of organic molecules or carbon materials can be dramatically affected by fluorination. The high ionization potential of fluorine and its relatively low polarizability imply very weak intermolecular interactions, low surface energies, and low refractive indexes for perfluorocarbon.¹⁵

Fluorinated CB has recently been fabricated as a new class of reinforcing or conducting fillers. Reacting CB with elemental fluorine *via* proprietary processes can adjust both surface energy and electrical conductivity of CB adjusted due to a layer with strong carbon-fluorine (C-F) bonds at the surfaces.¹⁶ The main objectives of this work, thus, are to investigate the PTC and NTC phenomena of fluorinated CB-filled HDPE composites at a fluorination pressure of 0.1-0.4 MPa. The changes in surface properties of fluorinated CB are investigated using X-ray photoelectron spectroscopy (XPS) and contact angle measurements.¹⁷

Experimental

Materials. The polymer matrix used was high-density polyethylene (HDPE, density 0.967 g/cm^3 , number average molecular weight 30000, melt index 0.35 g/10 min supplied by Honam Petrochem. Co. of Korea) and carbon blacks (HIBLACK-420B, average particle size 24 nm, Di-butyl phthalate (DBP) absorption 153 cc/100 g, specific surface area 88 m^2/g supplied by Korea Carbon Black Co.) were used in this study.

Sample preparation. CB was subjected to fluorination in different conditions. The fluorination reaction was performed in a batch reactor made of nickel with an outer electric furnace. The fluorine pressure was 0.1 ~ 0.4 MPa and the nominal reaction time was 10 min at room temperature. The nanostructured CB-filled HDPE polymeric switch was prepared using an internal mixer for 20 min at 160 °C. Materials were taken out of the mixer, and then compression-molded at 180 °C into 1 mm thickness using the hot-press, and drawn out to cool at room temperature. The samples were cut into pieces to measure

Table 1. London dispersive (γ_L^L) and specific (γ_L^{SP}) components of surface free energy (γ_L) of wetting liquids (subscript: L), measured at 20 °C

Wetting liquids	γ_L	γ_L^L	γ_L^{SP}
Water	72.8	21.8	51
Diiodomethane	50.8	50.42	0.38

[unit: mJ/m²]

electrical resistivity in the thickness direction of the CB-filled HDPE polymeric switch.

Characterization and measurements. The occurrence of surface chemical reaction on the CB surfaces was investigated. Infrared spectra of the ion beam irradiated CB were measured with Fourier transform infrared spectroscopy (FT-IR, Digital FTS-80, Bio-Rad). The X-ray, a photoelectron spectroscopy (XPS) measurement of CB surfaces, was performed using a VG Scientific ESCA LAB MK-II spectrometer equipped with an Mg-K α X-ray source. The base pressure in the sample chamber was controlled in the range of 10⁻⁸ to 10⁻⁹ torr. Contact angles of fluorinated CB were measured using the sessile drop method on a Rame-Hart goniometer. About 5 μ L of wetting liquid was used for each measurement at 20 °C, and more than 10 drops were tested for each of the fluorinated CB. The testing liquids used were deionized water and diiodomethane. For this work, the surface tension and the components for the wetting liquids are shown in Table 1. The change of surface of fluorinated CB was examined using a scanning electron microscope (SEM, JEOL JSM-840A).

In order to measure the volume resistivity of the CB-filled HDPE polymeric switch at room temperature and progressively elevated temperatures, we connected the heating electrode of the insulating resistance tester to a programmed temperature controller. The composites were cut into circular pieces with 1 cm diameter, and the electrical resistivity was measured by the four-probe method with a digital multimeter in the thickness direction of the specimens. Copper paste and conductive binder were used to ensure good contact of the sample surface with the electrodes of the conduction tester. PTC intensity is defined as the ratio of the maximum resistivity (ρ_{max}) to the resistivity at room temperature (ρ_{RT}) calculated from the temperature dependence of composite resistivity, as shown in Equation (1).¹⁸

$$PTC \text{ intensity } (I_{PTC}) = \rho_{max} / \rho_{RT} \quad (1)$$

Results and Discussion

Electrical properties. To begin with, CB-filled HDPE conductive composites are studied for the correlation of CB contents and resistivity. Figure 1 shows the plots of volume resistivity of the CB/HDPE polymeric switch according to the temperature. It can be seen that the volume resistivity of the polymeric switch increases as it responds to the increase of temperature to below the T_m of the polymeric switch, and then steeply decreases as temperature increases above T_m . The NTC is shown above T_m . Nowadays it has been accepted that the PTC effect is due to the volume expansion of HDPE polymer,¹⁹ yet some investigators have provided a detailed

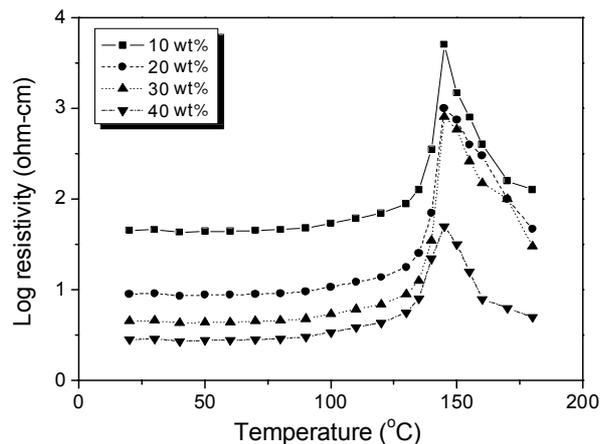
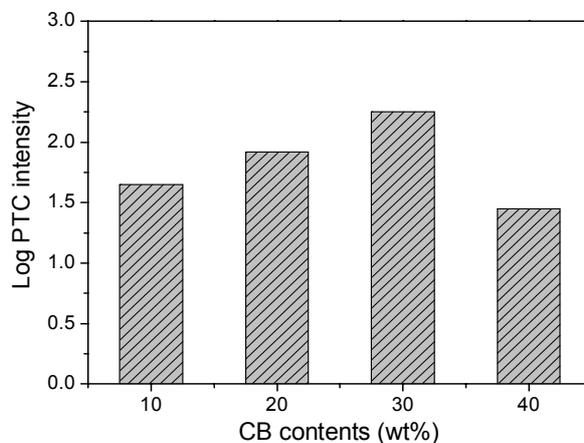
**Figure 1.** PTC curves of CB/HDPE polymeric switch as a function of CB content.**Figure 2.** PTC intensity of CB/HDPE polymeric switch as a function of CB content.

illustration of the PTC effect. However, it is not widely agreed that the NTC effect is due to the reaggregation of CB particles, although some investigators have proposed this point of view.^{20,21} Obviously, dynamic factors, such as van der Waals interaction, have been considered as main factors to cause a reaggregation of CB particles.

Figure 2 shows the PTC intensity of the polymeric switch as a function of CB content. As expected, the CB content can significantly influence the PTC intensity of the polymeric switch; though the 10 wt% CB-filled polymeric switch has the highest value of ρ_{max} , the ρ_{RT} is relatively highly increased compared to other polymeric switches, resulting in decreasing the PTC intensity. It is widely reported that the conducting polymer composites shows a good PTC effect when the CB content is more than the critical content. And, the resistivity of the conducting polymer composites decreases at their percolation threshold and maintains low values after percolation. Under the present experimental conditions, the percolation threshold is about 30 wt% CB content, as shown in Figure 1. Therefore, the 30 wt% CB-filled HDPE polymeric switch exhibits the highest PTC intensity.

Surface properties. Figure 3 shows the FT-IR results of fluorinated CB. As a result, the carboxyl/ester group (C=O) at 1632 cm⁻¹, hydroxyl group (O-H) at 3450 cm⁻¹, and carbon-

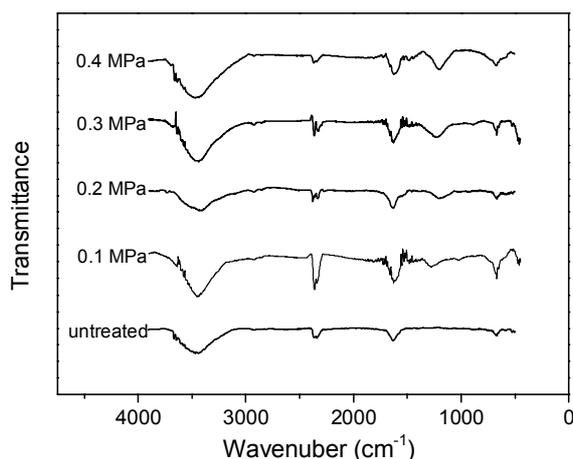


Figure 3. FT-IR spectra of fluorinated CB as a function of fluorination pressure.

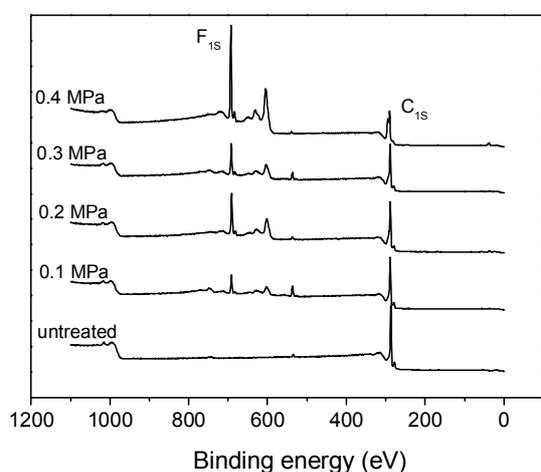


Figure 4. XPS survey spectra of fluorinated CB as a function of fluorination pressure.

fluorine group (C-F) at $1400\text{--}1000\text{ cm}^{-1}$ are observed at the fluorinated CB. Moreover, the fluorinated CB has a higher C-F peak intensity than that of the untreated CB; the peak intensity of the C-F group increases with the increase in the fluorination pressure.

It is well known that XPS has been used as a powerful analytical technique to evaluate compositions of the CB. XPS analysis was, therefore, performed in order to obtain information about the surface composites (up to a sample depth of about 10 nm).²² The broad scan XPS spectra of fluorinated CB is shown in Figure 4, which is C_{1s} and F_{1s} XPS analysis curves of fluorinated CB, measured at different fluorination pressures. Noticeable changes are observed with respect to the starting materials after fluorination. Binding energy (E_b) of the band assigned to graphitic carbon (C-C), undergoes a slight shift ($0.01\text{--}0.1\text{ eV}$) towards lower E_b because of a lowering of the Fermi level (E_F) and a subsequent decrease of the energy gap between the C_{1s} core level and E_F . In the C_{1s} spectra, the peak intensity decreases with increasing fluorination pressure. Also, the component (C=O) (with $E_b = 286.83 \pm 0.06\text{ eV}$) is also connected with non-fluorinated C in the position of C-F bonds. The slight shift from (C-C) arises from the weak

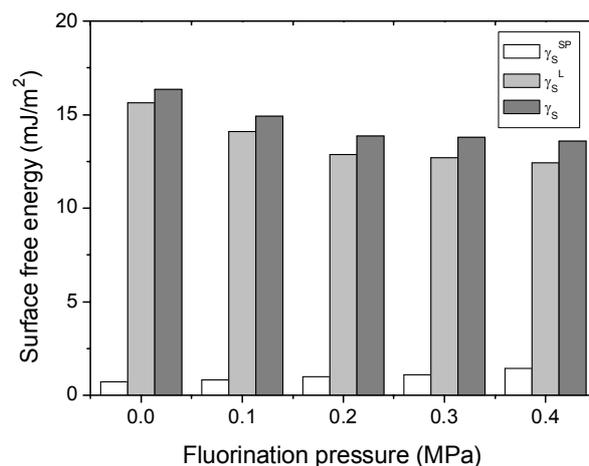


Figure 5. Surface free energy of fluorinated CB as a function of fluorination pressure.

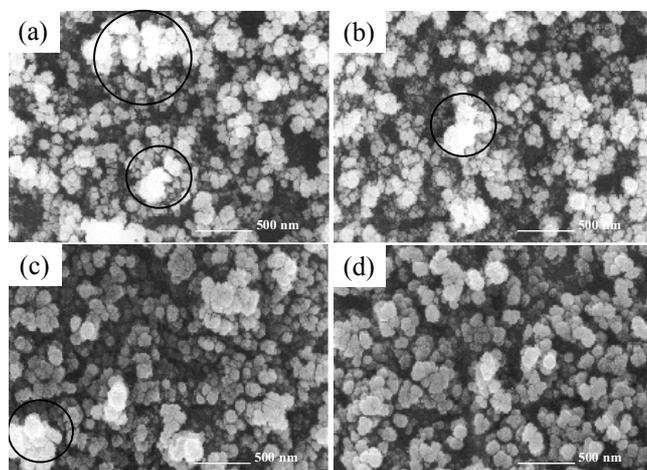


Figure 6. SEM pictures of CB/HDPE polymeric switch as a function of fluorination pressure.

excess of positive charge, which is located on these atoms because of the presence of neighboring F. Since the work of Mallouk and Bartlett,²³ it has been known that the graphene layers are associated with a physical type E_b , which lies ca. $287.75 \pm 0.06\text{ eV}$ (component $C_{1s}\text{HO-C=O}$) in C_{1s} spectra. In the F_{1s} spectrum the physical component occurs at $E_b = 686.13 \pm 0.05\text{ eV}$. That is, two components at $687.10 \pm 0.03\text{ eV}$ (CF_1) and at $686.13 \pm 0.04\text{ eV}$ (CF_2) in the F_{1s} spectra are assigned to physical $C-F_x$ ($1 \leq x \leq 2$) groups that present on the surface of the CB or at structural defects. Consequently, by increasing the amount of fluorination on the surface, the content of carbon decreases, whereas the relative amount of $C-F_x$ increases with increasing fluorination pressure.

Figure 5 shows surface free energy²⁴⁻²⁶ of fluorinated CB as a function of fluorination pressure. The surface free energy of fluorinated CB decreases with increasing fluorination pressure. The higher result for fluorine content on the CB surfaces appears with decreasing of the surface free energy. In other words, it seems that the polar part of the surface free energy increases at higher degrees of fluorination with increasing fluorination pressure. The nature of the C-F bonding is affected mainly by the fluorine content and the fluorination temperature.

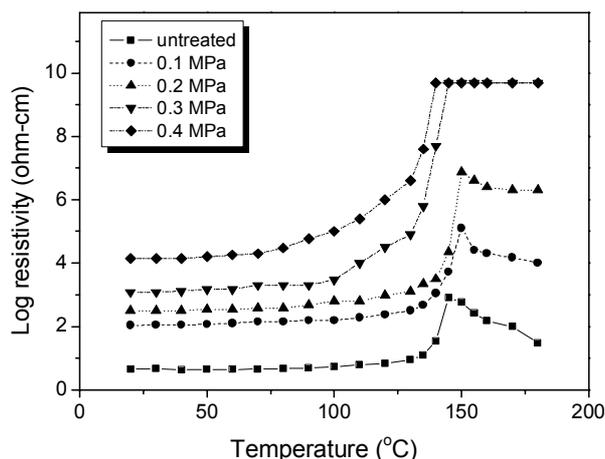


Figure 7. PTC curves of fluorinated CB/HDPE polymeric switch as a function of fluorination pressure.

The decrease in the dispersive component (γ_s^L) of the surface free energy may be caused by the destruction of the graphitic character of the CB surface due to fluorination.²⁷ The γ_s^L values are usually assumed to be fairly independent of the method of surface modification of the carbon materials.²⁸ It is assumed that the specific component (γ_s^{SP}) reflects the essential surface characteristics of carbon or the partial graphitized carbon framework of the particles. In contrast, we observe a distinct dependence of the values of the fluorine content on the CB surfaces. When a certain amount of fluorine is present on the CB surfaces, the amorphous part of the surface is eliminated; therefore, the amount of graphite must decrease, in accordance with the results of surface analysis.^{29,30}

Figure 6 shows the SEM pictures of the fluorinated CB. Although untreated CB has some CB particle clusters due to their tendency to agglomerate. But, fluorinated CB shows a decrease of CB particle clusters. This is likely due to the decrease of mutual attraction between the CB particles, which results from the decreased surface free energy of the CB particles.

PTC/NTC behaviors. The resistivity of fluorinated CB/HDPE polymeric switches as a function of temperature is shown in Figure 7. The resistivity of the polymeric switch increases abruptly near the crystalline T_m of the HDPE, due to the thermal expansion of the HDPE matrix. As the temperature further increases, the untreated CB/HDPE polymeric switch does not show the PTC effect but rather strong NTC behavior, because the CB is easily reaggregated above T_m of the HDPE. This consequently results in the formation of a new path and a conductivity increase, giving rise to the NTC effect. However, the fluorination of CB leads to a disappearance of NTC behavior in the CB/HDPE polymeric switch, probably due to the reduction of mutual attraction between the CB particles at T_m of the HDPE, resulting from decreasing the surface free energy of fluorinated CB particles.⁹

Conclusions

In this study, fluorinated CB was used to reduce the NTC phenomenon of CB-filled high-density polyethylene (HDPE)

composites. FT-IR and XPS results showed that the fluorinated CB had higher C-F peak intensity than that of the untreated CB and that the peak intensity of the C-F group increased with increasing fluorination pressure. As shown in the contact angle and SEM results, the surface free energy of fluorinated CB decreased with increasing fluorination pressure. The higher the fluorine content on the CB surfaces, the lower the surface free energy. It seemed that the polar part of the surface free energy increased at higher degrees of fluorination with increase of fluorination pressure. SEM photographs of fluorinated CB showed a decreasing of CB particle clusters. This was probably due to the decrease of mutual attraction between the CB particles. Therefore, it was concluded that the introduction of fluorine on CB surfaces led to a disappearance of NTC behavior of the CB/HDPE composites, which was probably due to the reduction of CB reaggregation above the melting point of the HDPE, resulting from decreasing the surface free energy of CB particles.

References

- Donnet, J. B.; Voet, A. In *Carbon Black: Physics, Chemistry, and Elastomer Reinforcement*; Marcel Dekker: New York, 1976.
- Candau, F.; Ottewill, R. H. In *An Introduction to Polymer Colloids*; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1990.
- Park, S. J.; Kim, H. C.; Kim, H. Y. *J. Colloid Interface Sci.* **2002**, *255*, 145.
- Narkis, M.; Ram, A.; Stein, Z. *J. Appl. Polym. Sci.* **1984**, *29*, 1639.
- Farid, E. T. *Eur. Polym. J.* **2002**, *38*, 567.
- Yang, H. H.; Piao, J.; Chen, X. *Radia. Phys. Chem.* **1993**, *42*, 135.
- Park, S. J.; Kim, J. S. *J. Colloid Interface Sci.* **2000**, *232*, 311.
- Al-Saleh, M. H.; Sundararaj, U. *Carbon* **2009**, *47*, 2.
- Park, S. J.; Kim, J. S. *J. Colloid Interface Sci.* **2001**, *244*, 336.
- Park, S. J.; Kim, B. J.; Lee, Y. S.; Cho, M. J. *Int. J. Hydrogen Energy* **2008**, *33*, 1706.
- Pandey, K. K. *Polym. Degrad. Stab.* **2005**, *90*, 9.
- Gao, L.; Zhai, J.; Yao, X. *Appl. Surf. Sci.* **2009**, *255*, 4521.
- Park, S. J.; Sohn, H. J.; Hong, S. K.; Shin, G. S. *J. Colloid Interface Sci.* **2009**, *332*, 246.
- Park, S. J.; Seo, M. K.; Rhee, K. Y. *Mater. Sci. Eng. A* **2003**, *356*, 219.
- Sen, K. D.; Jorgensen, C. K. In *Electronegativity*; Springer-Verlag: New York, 1987.
- Watanabe, N.; Nakajima, T.; Touhara, H. In *Studies in Inorganic Chemistry: 8. Graphite Fluoride*; Elsevier Science Publisher: New York, 1988.
- Seo, M. K.; Park, S. J. *J. Colloid Interface Sci.* **2009**, *237*, 330.
- Luo, S.; Wong, C. P. *International Symposium on Advanced Packaging Materials*, 1999.
- Matsushige, K.; Kobayashi, K.; Iwami, N.; Horiuchi, T.; Shitamori, E.; Itoi, M. *Thin Solid Films* **1996**, *273*, 128.
- Chatterjee, S.; Sengupta, K.; Maiti, H. S. *Sens. Actuators B* **1999**, *60*, 155.
- Luo, Y.; Wang, G.; Zhang, B.; Zhang, Z. *Eur. Polym. J.* **1998**, *34*, 1221.
- Ishiki, T.; Okino, F.; Hattori, Y.; Kawasaki, S.; Touhara, H. *Carbon* **1997**, *35*, 716.
- Bartlett, N.; Mallouk, T.; Okino, F.; Rosenthal, G.; Verniolle, J. *J. Fluor. Chem.* **1983**, *23*, 409.
- Fowkes, F. M. *J. Phys. Chem.* **1962**, *66*, 382.
- Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.
- Kaelble, D. H.; Uy, K. C. *J. Adhesion* **1970**, *2*, 66.
- Bismark, A.; Thahan, R.; Spriner, J.; Schulz, A.; Klapötke, T. M.; Zell, H.; Michaeli, W. *J. Fluor. Chem.* **1997**, *84*, 127.
- Park, B. J.; Park, S. J. *J. Mater. Sci. Lett.* **1999**, *18*, 373.
- Donnet, J. B.; Bansai, R. C.; Wang, M. J. In *Carbon Black: Science and Technology*, 2nd ed.; Marcel Dekker: New York, 1993.
- Park, S. J.; Seo, M. K.; Nah, C. *J. Colloid Interface Sci.* **2005**, *291*, 229.