

Chemical Surface Treatment of Carbon Black to Enhance Interfacial Adhesion Between Elastomer and Carbon Black

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화학적 표면처리에 따른 카본블랙/고무 복합재료의 접착력 증가

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ABSTRACT : In this work, the effect of chemical treatments on the carbon blacks as-received has been studied in the context of surface, adsorption, microstructure properties, and physical surface free energetics. As an experimental result, the basic chemical treatment leads to an increase in the either dispersive or specific component without significant change the pH and specific surface area. While, acidic chemical treatment do significantly change the surface and adsorption properties, and microstructures of the carbon blacks. In particular, the result given by basic chemical treatment shows an increase of the London dispersive component of the surface free energy which is a major parameter in evaluating the dispersion or specific surface area of the carbon blacks studied. This is probably a major role in evaluating the dispersion the carbon blacks, which are reinforced in elastomer matrix in a composite system.

요약 : 본 연구에서는, 화학적 표면처리에 따른 카본블랙의 표면, 흡착, 그리고 미세구조의 성질과 물리적 표면 자유에너지를 고찰하였다. 실험적 결과를 통하여, 염기성 용액으로 표면 처리한 경우 pH와 비표면적의 변화 없이 표면 자유에너지의 비극성 또는 극성요소의 증가를 가져왔다. 반면에 산성 표면처리의 경우에는 표면특성, 흡착성질과 미세구조의 큰 변화를 확인하였다. 특히, 염기성 처리된 카본블랙은 비극성이나 비표면적의 중요한 인자로 표면 자유에너지의 London 비극성 요소의 증가를 볼 수 있었다. 이는 카본블랙/고무 복합재료에 있어서, 카본블랙이 강화재의 역할 뿐 아니라 분산력 발달에 중요한 역할을 담당하고 있기 때문으로 사료된다.

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I. Introduction

Carbon black is economically one of the most important active fillers for technical products made from elastomer. Its wide range of applications is filler to modify the mechanical, electrical and optical properties of the medium in which it is dispersed. It is also well known that carbon black has been largely used as a reinforcing agent for pneumatic tire industry.^{1,2}

The reinforcement of elastomers by particulate fillers has been studied in depth in numerous investigations, and it is generally accepted that this study is, to a large extent, dependent on polymer and filler properties, and processing.²⁻⁴

Among the methods very much in use to modify the surface characteristics of fillers, the grafting of functional molecules or polymers have largely a place of choice. Recently, Manna *et al.*⁵ have shown that the modification of the surface of fillers by coupling agents results in an improvement of the filler/matrix interactions.

While, it is noted that good mechanical properties and long durability of the composites depend greatly on the reinforcing agent-rubber matrix interfacial adhesion, since the stress transferred from the matrix to the reinforcing agent would require strong adhesion at the interfaces of the constitutive elements rather than a high cohesive density.^{4,6} In addition, the degree of adhesion at interfaces of a solid depends on the surface energy, active functional groups, energetically different crystallite faces, and so on.⁷⁻⁹ Wu¹⁰ reported that

surface free energies of semicrystalline solid were strongly related their crystalline structure. His data suggested that the transcrystallized polymer surfaces might have very high surface free energy due to increase of surface cohesive density. Van Oss *et al.*¹¹ found that the contact angle of liquid on polar polymer film was due to the electron acceptor-donor force oriented polymer molecules.

In this work, we studied surface free energy that applied to above method for carbon black. And one of the most important properties of carbon black is the specific surface area which can be largely studied in the adsorption behavior of a solid surface. In the context of the adsorption studies, the surface treatment may significantly influence the physical properties of carbon black, including polar acidic, polar basic, and nonpolar characteristics. For this purpose, the objective of the present work is to study the effect of chemical treatment on the property changes of adsorption, microstructure, and surface free energy of carbon black surfaces.

II. Experimental

1. Materials and sample preparation

Virginal carbon blacks denoted in UCB (namely, N220) were supplied by LG Chem. Co. of Korea. The samples denoted in HCB and KCB were prepared with 0.1 N H₃PO₄ and 0.1 N KOH in order to impregnate the polar functional groups on the carbon blacks, respectively. Prior to use following analysis, the residual chemicals were removed by

Soxhlet extraction in acetone at 80°C for 2 h. Finally, the carbon blacks were washed several times with distilled water and dried in a vacuum oven at 90°C for 12 h.

2. Surface properties

To assess the acid and base character of carbon black after surface treatment, the pHs of the carbon blacks were determined in slurry and boiling method according to the ASTM D 1512. The used carbon was prepared by placing 5 g of the carbon black in to 50 ml of deionized water contained in a 100 ml beaker. Two drops of acetone and a magnetic stir bar were added to the mixture to facilitate dispersion of the carbon black sample. The beaker was covered with a watch glass and was boiled. The pH measurement was taken after 2 min equilibration period, and three readings per sample were taken.

The acid value (A.V.) and base value (B.V.) of the carbon black surfaces were determined by Boehm's method.¹² In the case of acid value measurement, about 0.1 g of the sample were added to 100 ml of 0.1 N NaOH solution and shaking it for 24 h. Then, the solution was filtered through membrane paper and titrated with 0.1 N HCl solution. Likewise, the base value was determined by converse titration.

The specific surface areas of the carbon blacks studied were measured by N₂-gas adsorption at 77K with automated adsorption apparatus (Micromeritics, ASAP 2400). Prior to each analysis, the blacks were outgassed at 298K for 6 hrs to obtain a residual pressure of less than 10⁻³ torr.

The effects of oxidation on the morphology (particle size, shape, distribution, surface area, and

structure) of carbon black prior to compaction were ascertained by electron microscope transmission (TEM, Jeol JEM-1200EX) inspection. In this work, the carbon black particle is defined as that part of the carbon black agglomerate comprising before and after surface treatments. Suspensions of carbon blacks in water were prepared by dipping the suspensions in an ultrasonicator for 5 min.

3. Surface free energy measurement

Contact angles were measured using the sessile drop method¹³ on a Rame-Hart goniometer. About 5 μl of wetting liquids on the specimen made from carbon composite support was used for each measurement at 20°C. Reading within 5 s of drop formation was taken for the critical surface tension. And more than ten drops were tested for each of the carbon black surfaces studied.^{14,15} For this work, surface free energy (or surface tension) and London dispersive and specific (or polar) components for the wetting liquids are shown in Table 1. The testing liquids used were deionized water and diiodomethane.

Table 1. Surface Free Energy Characteristics of Testing Liquids, Measured at 20°C

	γ_L^L (mJ.m ⁻²)	γ_L^{SP} (mJ.m ⁻²)	γ_L (mJ.m ⁻²)
Water	21.8	51.0	72.8
Diiodomethane	50.42	0.38	50.8

III. Results and Discussion

1. Surface analysis

Fig. 1 shows the adsorption behaviors of the carbon blacks before and after chemical treatments.

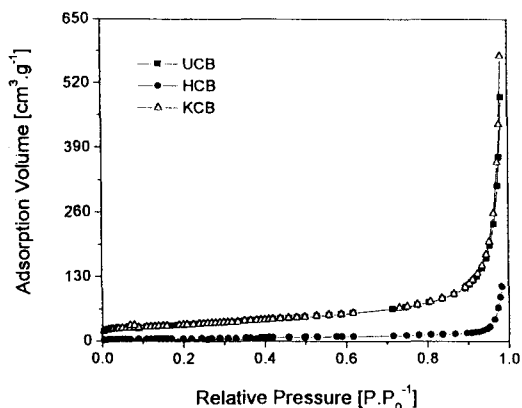


Fig. 1. Dependence of the relative pressure on the volume of N_2 gas adsorbed at 77K of carbon blacks studied.

Table 2. Results of Surface and Adsorption Values of the Virgin and Treated Carbon Blacks

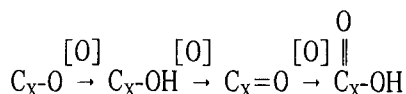
	pH	Acid value ($\text{meq}\cdot\text{g}^{-1}$)	Base value ($\text{meq}\cdot\text{g}^{-1}$)	S_{BET} ($\text{meq}\cdot\text{g}^{-1}$)
UCB	7.0	50	70	118
HCB	2.6	110	13	18
KCB	7.1	70	90	118

As a result, it can be seen that the adsorption behavior of carbon black treated by basic solution (KCB) is similar to that of carbon black untreated.

The results of surface and adsorption properties of the carbon blacks before and after treatments are listed in Table 2. It reveals that the chemical treatments do significant change in pH, acid-base values, and specific surface area (S_{BET} ,¹⁶) of the carbon blacks studied. As expected, acidic and basic treatments on carbon black lead to the increases of acid and base values, respectively. This seems to a consequence of the effective surface organic functional groups deposited in the surface of the carbon blacks after surface treatments.

While, it is accepted¹⁷ that at low process tem-

perature below 800°C , the surface functional groups of carbon are less stable and then develop acidic group, such as hydroxyl, carbonyl and carboxyl groups. On the other hand, when the process temperature is higher than 800°C , the surface functional groups are more stable and increase the basic oxide, such as pyrone and chromene groups. As a result, the pH, base surface value, and specific surface area of the HCB sample show an immense decrease as compared with UCB. This result indicates that the strong acid-base reaction between basic carbon black and acidic chemical solution makes increasing of micropore blockage of carbon black and aggregate of the HCB which were heated at very high temperature (industrially manufactured at 1400°C , here). A similar expected behavior is given in the case of the polar basic (KCB) treatments on the carbon blacks in which slight changes of the pH, acid and base values, and specific surface area are listed in Table 2. This is that the chemical structure of the surface groups identified on carbon blacks suggests that oxidation occurs predominantly in a stepwise manner:⁸



The TEM images illustrated by the texture of carbon black specimens are shown in Fig. 2 which can be easily agreed with the above results of surface and adsorption properties. The diameters of all carbon blacks studied in these micrographs are almost between 10 and 60 nm. It is shown that in the case of HCB, the aggregates vary in shape from the individual spheroidal particles that are

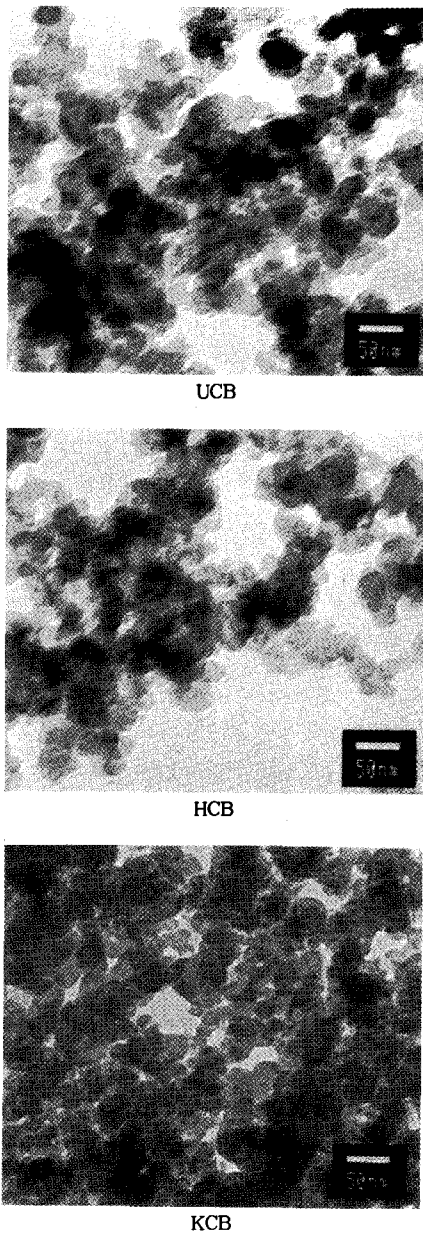


Fig. 2. TEM image on the aggregates of the virgin and treated carbon blacks.

found in carbon blacks to the more clustered, but those of KCB are well dispersed.

2. Surface free energy

In order to obtain more detailed information about the physical properties of carbon black surfaces before and after chemical treatments, an analysis of the surface free energy is evaluated in the physical energetic studies divided by two components. The London dispersive, γ_S^L , and specific (or polar) components, γ_S^{SP} , of surface free energy of carbon blacks studied (subscript, S) are determined by measuring the contact angle of a variety of testing liquids (subscript, L) having known their London dispersive and specific components of surface free energy, as seen in Table 1. And γ_S^L and γ_S^{SP} can be solved according to the method based on the propositions of Owens-Wendt and Wu.^{14,15,18}

$$\gamma_S^L = \frac{1}{4} \left[\frac{(1 + \cos \theta_1) \gamma_{L1} \cdot (\gamma_{L2}^{SP})^{\frac{1}{2}} - (1 + \cos \theta_2) \gamma_{L2} \cdot (\gamma_{L1}^{SP})^{\frac{1}{2}}}{(\gamma_{L1} \cdot \gamma_{L2}^{SP})^{\frac{1}{2}} - (\gamma_{L2} \cdot \gamma_{L1}^{SP})^{\frac{1}{2}}} \right]^2 \quad (1)$$

$$\gamma_S^{SP} = \frac{1}{4} \left[\frac{(1 + \cos \theta_2) \gamma_{L2} \cdot (\gamma_{L1}^L)^{\frac{1}{2}} - (1 + \cos \theta_1) \gamma_{L1} \cdot (\gamma_{L2}^L)^{\frac{1}{2}}}{(\gamma_{L1} \cdot \gamma_{L2}^{SP})^{\frac{1}{2}} - (\gamma_{L2} \cdot \gamma_{L1}^{SP})^{\frac{1}{2}}} \right]^2 \quad (2)$$

where subscripts 1 and 2 respectively represent water and diiodomethane, or conversely.

Table 3 shows the results of surface free energies (or surface tensions) and their London dispersive and specific components of the carbon blacks before and after surface treatments. As a result, both acid and base treatments on carbon black can increase the surface free energies, which are mainly due to their specific components, γ_S^{SP} . These

Table 3. Results of Surface Free Energy and Their Components of the Virgin and Treated Carbon Black Specimens

	γ_s^L (mJ.m ⁻²)	γ_s^{SP} (mJ.m ⁻²)	γ_s (mJ.m ⁻²)
UCB	31	32	63
HCB	28	51	79
KCB	35	43	78

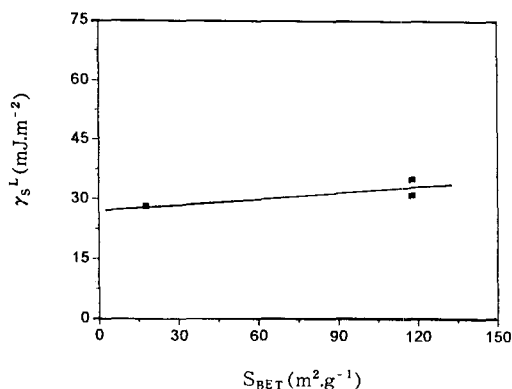


Fig. 3. Dependence of the London dispersive component of surface free energy on the specific surface area of the carbon blacks studied.

specific component increases of the surface free energy can be attributed to the polar acidic and basic surface oxide groups on carbon blacks after acidic and basic chemical treatments, respectively.

Meanwhile, it is noted that the London dispersive component of the surface free energy is largely dominated by the surface area, whereas the specific components is influenced on the surface activity which is related to the surface functional groups.^{7,19} At this time, a good agreement can be obtained between S_{BET} and London dispersive component of the surface free energy of carbon blacks studied, as seen in Fig. 3 in which S_{BET} increases in increasing the γ_s^L .

IV. Conclusion

It is thus concluded that basic chemical treatment of carbon blacks leads to an increase in the either dispersive or specific component without significantly changing the pH, acid and base values, and specific surface area. While, the polar acidic chemical treatment do significantly change the surface and adsorption properties, and microstructures of the carbon blacks. As an experimental result, increasing of London dispersive component of the surface free energy is a major parameter in evaluating the dispersion or specific surface area of the carbon blacks studied.

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