Effects of Chemical Surface Modification of Carbon Black on Vulcanization and Mechanical Properties of Styrene-Butadiene Rubber Compound

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SBR 컴파운드의 가황 및 기계적 성질에 미치는 카본블랙 표면의 화학적 개질의 영향

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ABSTRACT: To see the effect of chemical surface modification, the carbon black surfaces were treated with three types of chemicals (KOH, H_3PO_4, and benzene). Vulcanization and mechanical properties of a styrene-butadiene rubber (SBR) were investigated depending on the chemical treatments. The surface free energy increased considerably with the treatments by both the acid (HCB) and base (KCB), but only a slight increase was observed for benzene treatment(BCB). The BCB showed the highest level of the London dispersive component. The vulcanization reaction was found to be faster in the order of KCB-SBR〉BCB-SBR〉VCB-SBR(virgin) 〉HCB-SBR. The difference in minimum and maximum torque of rheocurve, representing the degree of crosslinking, was found to be higher for the BCB-SBR compared to those of VCB-SBR, KCB-SBR, and HCB-SBR. The BCB-SBR and KCB-SBR showed the improved tensile and dynamic mechanical properties. A linear relationship was found to exist between the London dispersive component of surface free energy and mechanical properties.

요 약 : 카본블랙의 화학적 표면개질에 따른 영향을 조사하기 위해 3종류 화학약품(KOH, H_3PO_4, 벤젠)을 이용하여 카본블랙 표면을 처리하였으며, 이를 함유한 스티렌-부타디엔 고무(SBR)의 가황특성과 기계적 특성을 조사하였다. 산(HCB)이나 염기(KCB)로 표면 처리할 경우 표면 자유에너지의 증가가 관찰된 반면, 벤젠(BCB)의 경우 미세한 증가만이 관찰되었다. London 비극성 성분은 BCB가 가장 높았다.

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각 표면처리 카본블랙을 함유한 SBR 컴파운드의 가황반응의 빠르기는 KCB-SBR〉 BCB-SBR〉
VCB- SBR(무처리)〉 HCB-SBR의 순으로 나타났다. 일반적으로 가교도를 나타내는 가황곡선상의
최대토오크와 최소토오크의 차이는 VCB-SBR, KCB-SBR, HCB-SBR에 비해 BCB-SBR이 높은
값을 나타내었다. BCB-SBR과 KCB-SBR의 경우 인장특성과 동적기계적 특성이 증진되었다. 표
면자유에너지 중 London 비극성 요소와 기계적 특성간에는 비례관계가 있음이 확인되었다.

Keywords : rubber, carbon black, surface modification, vulcanization, mechanical property.

I. Introduction

For most rubber products including tire, they must be reinforced with carbon black to improve the end-use performance associated with the increased modulus and ultimate properties. The carbon black affects strongly the various physical and chemical properties of rubbers depending on the loading level, particle size, structure of aggregated-particles, and interaction with elastomer. Although there has been an extensive study on the carbon black reinforcement of rubbers,[1~7] no systematic study has been made on the surface modification of carbon black by chemical treatment. Manna et al.[8] have shown that the surface modification of fillers by coupling agents resulted in an improvement of the filler-matrix interactions. Akovali and Ulken[9] have suggested that the mechanical properties such as tensile strength can be improved by the surface modification of carbon black with a plasma polymerized polystyrene. Recently, Park et al.[10~12] have treated the carbon black surfaces with strong polar (acid and base) and nonpolar chemicals, and measured the surface free energy in terms of the London dispersive and specific components based on a contact angle measurement of sessile drop method.[13] They have found that the London dispersive component is closely related to the mechanical properties of rubber compounds.

In this study, as an extension of former works[10~12] the chemical modification effect was extended to a different rubber, styrenebutadiene rubber (SBR), especially in terms of the cure characteristics, and tensile and dynamic mechanical properties. An attempt was made to correlate the surface free energy information with the mechanical properties.

II. Experimental

1. Materials and Sample Preparation

A styrene-butadiene rubber (SBR-1500, bound styrene: 23.5%, *cis-1,4*: 17%, *trans-1,4*: 68%, *1,2-vinyl*: 15%, Kumho Petrochemical Co., Korea) was selected as a rubber in this study. A carbon black of N-220 type (Lucky Carbon Black Co.) was selected as a reinforcing agent, and the loading level was fixed to 50 phr. In order to impregnate the polar functional groups on the carbon black surface, the carbon blacks were immersed for 24 hours in three different solutions of 0.1 N H_3PO_4, C_6H_6, and 0.1 N KOH. Prior to use the treated carbon blacks, they were extracted in acetone at 80℃ for 2 hours and washed several times in distilled water to remove the residual chemicals, and dried in a vacuum oven at 90℃ for 12 hours.[10~12] *N-t-butyl-2*-benzothiazol-sulfenamide(TBBS) and sulfur were selected as the

Table 1. Compounding Formulations

Ingredients	Loading (phr)
SBR-1502	100
Carbon black (N-220)	50 (type varied)[1]
ZnO	5
Stearic acid	2
Accelerator[2]	1
Sulfur	2

[1]VCB: virgin, KCB: KOH-treated, BCB: benzene-treated, and HCP: H_3PO_4-treated carbon blacks.
[2]*N-t*-butyl-*2*-benzothiazole sulfenamide

cure system. The remaining additives were selected with typical grades in rubber industry. Compound recipes are summarized in Table 1.

Mixing of compound ingredients except curatives was performed using an internal mixer (82BR, Farrel Co. USA) at about 150℃ for 6 minutes according to the procedure described in ASTM D3184. The curatives were added using a two-roll mill (M8422AX, Farrel Co. USA) at about 100℃ for 3 minutes, and the mixed compound was removed from the mill in the sheet form. The rubber sheets of about 2 mm in thickness were pressed and vulcanized using an electrically heated press (Carver 2518, USA) at 145℃ for a given period of time determined by a torque rheometer (R-100, Monsanto, USA).

2. Determination of Surface Free Energy

Fowkes[14] suggested that the surface free energy of a solid, γ_s^L, is expressed as the sum of two
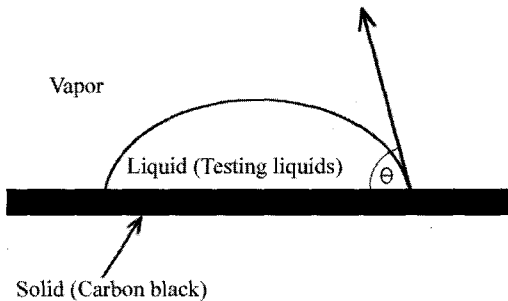

Figure 1. A sessile drop of a wetting liquid on carbon blacks.

Table 2. Surface Free Energy Characteristics of Wetting Liquids at 20℃

Surface free energy	Water	Diiodom-ethane	Ethylene glycol	Glycerol
γ_L^L (mJ/m^2)*	21.8	50.4	31.0	33.9
γ_L^{SP} (mJ/m^2)**	51.0	0.38	16.7	29.8
γ_L (mJ/m^2)***	72.8	50.8	47.7	63.7

*London dispersive component
**Specific component
***Surface free energy

components: dispersive London, γ_s^L and specific, γ_s^{SP}, components. The surface free energy of a solid can be obtained by measuring the contact angle formed between the solid and liquid of known surface free energy characteristics. In this work, the surface free energy of carbon black was determined at 20 ± 1℃ using a sessile drop method[13] (Rame-Hart Goniometer), as shown in Fig. 1 Four different wetting liquids: distilled water, diiodomethane, ethylene glycol and glycerol were selected. The basic characteristics of surface free energy of the liquids are given in Table 2. The surface free energy characteristics of carbon blacks before and after surface treatments was calculated from the slope and intercept of the following relation:[11,14~16]

$$\frac{\gamma_L(1+\cos\theta)}{2\sqrt{\gamma_L^L}} = \sqrt{\gamma_s^{SP}} \times \sqrt{\frac{\gamma_L^{SP}}{\gamma_L^L}} + \sqrt{\gamma_s^L} \qquad (1)$$

where γ_L, γ_L^L, and γ_L^{SP} are surface free energy, London dispersive, and specific components of liquids, respectively. And γ_s^L and γ_s^{SP} are the London dispersive and specific components of surface free energy of carbon blacks, and θ is the contact angle. The detailed calculation procedure was described elsewhere.[10~12]

3. Cure Behavior and Mechanical Property

The cure characteristics of mixed rubber compounds was measured at 145℃ using a torque rheometer (R-100, Monsanto, USA) with a frequency of 100 cycles/min and ±1.5 arc. Hardness was measured using a springtype hardness tester (Shore Durometer A-2 type) according to the procedure of ASTM D2240. For measuring tensile properties, the dumbbell-shaped specimens were cut from the vulcanized rubber sheets. Stress-strain curves were obtained using a tensile tester (Instron 6021, USA) at room temperature and at a cross-head speed of 500 mm/min according to the procedure described in ASTM D412. The dynamic mechanical properties were measured over a wide temperature

range from -70 to 70℃ using a dynamic mechanical analyzer (GABO Qualimeter, Eplexor-150, Germany). The dynamic frequency and deformation were set to be 11 Hz and 0.1%, respectively, and the measurement was performed by the procedure described in ASTM D2231.

III. Results and Discussion

1. Surface Free Energy

As suggested by Fowkes,[14] the surface free energy of a solid, γ_s, is expressed as follows:

$$\gamma_s = \gamma_s^L + \gamma_s^{SP} \qquad (2)$$

where γ_s^L the dispersive component due to the London interaction and γ_s^{SP} is the specific component due to the Debye and Keesom interactions, hydrogen bonding, and other polar interactions. The free surface energy and their components, determined by equation (1), of the carbon blacks before and after surface treatments are summarized in Table 3. The surface free energy was considerably enhanced when the carbon blacks were treated with the acid (HCB) and base chemicals (KCB), mainly due to the increase of their specific component, γ_s^{SP}. The observed increase of specific component was explained by the formation of polar (acidic or basic) surface oxide groups on the carbon black surfaces during the corresponding surface treatments.[10] However, only a slight increase in surface free

Table 3. Surface Free Energy Characteristics of Carbon Blacks Investigated at 20℃

Surface free energy	VCB	KCB	BCB	HCB
γ_L^L (mJ/m²)*	13.0	15.0	21.1	2.51
γ_L^{SP} (mJ/m²)**	11.0	21.5	4.11	34.2
γ_L (mJ/m²)***	24.0	36.5	25.6	37.4

*London dispersive component
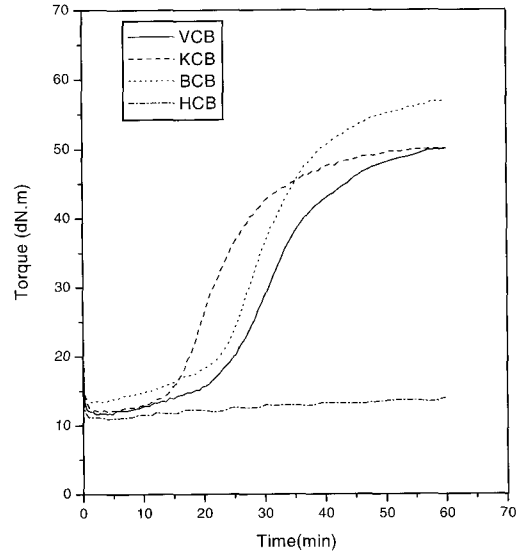**Specific component
***Surface free energy

Figure 2. Rheocurves of SBR compounds containing virgin(VCB) and treated carbon blacks (KCB, BCB, and HCB) at 145℃.

energy was observed for the benzene-treated carbon black (BCB). In view of the London dispersive (nonpolar) component, the BCB showed the highest level due to its nonpolar nature and the HCB the lowest level among the surface-treated carbon blacks.

2. Cure Characteristics

In the previous study,[12] the cure behavior of butadiene rubber (BR) based on the DSC study was found to be strongly affected by the type of chemical surface treatments, i.e., the acid treatment showed a considerable delay in vulcanization reaction and increase of corresponding activation energy, while the base treatment showed the reversed trend. Now, a similar attempt was made for the styrene butadiene rubber (SBR) matrix using a cure rheometer. Fig. 2 shows the cure behavior of SBR compound at 145℃ depending on the type of surface treatments, and the cure properties are summarized in Table 4. No detectable vulcanization reaction occurred in the case of strong acid treated-SBR compound, HCB-SBR, under the employed vulcanization conditions: 145℃ and 60 minutes in this work. The vulcanization

Table 4. Cure Characteristics of SBR Compounds

Compound	M_H[1] (dN.m)	M_L[2] (dN.m)	$\triangle M$[3] (dN.m)	t_2[4] (min)	t_{90}[5] (min)
VCB-SBR	50.39	11.67	38.72	13.75	45.88
KCB-SBR	50.39	12.02	38.37	13.23	37.92
BCB-SBR	57.09	13.30	43.79	12.05	44.23
HCB-SBR	13.99	10.69	3.3	-	-

[1,2]Maximum and minimum torque
[3]Difference between maximum and minimum torque
[4,5]Consumed times for rubber compound to be vulcanized
2 and 90%, respectively based on torque

reaction was found to be considerably accelerated in the case of strong base treatment, KCB-SBR, and to be similar in view of cure times based on t_{90}, but to be considerable higher in view of torques than those of no treatment, VCBSBR. To compare the cure rate in more detail, the conversion ratio, χ_t, at a given time t was defined by the following equation based on the rheocurves shown in Fig. 2:[17]

$$\chi_t = \frac{M_t - M_L}{M_H - M_L} \quad (3)$$

where M_H and M_L are maximum and minimum torque, and M_t is torque at a given time, t. The calculated conversion ratio is re-plotted as a function of cure time in Fig. 3. The conversion of vulcanization reaction at the given condition was found to be faster in the order of KCB-SBR〉 BCB-SBR〉 VCB-SBR〉 HCB-SBR. For instance, the required time for 50% conversion was estimated to be 22 minute for KCB-SBR, 29 minute for BCB-SBR, and 31 minute for VCB-SBR. It was well known that the reactivity in the accelerated-sulfur vulcanization reaction increased with increasing the basicity, while it rather decreased with increasing the acidity in the rubber compound.[18-20]

It should be noted here that the minimum and maximum torque, M_L and M_H, and the difference between them, ΔM ($=M_H - M_L$), were found to be higher for BCB-SBR compared to those of VCB-SBR, KCB-SBR, and HCB-SBR, as shown in
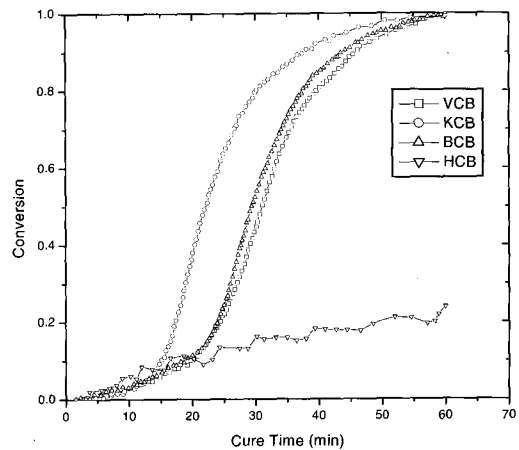

Figure 3. Conversion ratio of vulcanization reaction of SBR compounds containing virgin (VCB) and treated carbon blacks(KCB, BCB, and HCB).

Table 4. The increase in M_L and ΔM is related to the increase in viscosity and degree of crosslinking, respectively.[17] Since the same type of carbon black was equally loaded, the bound rubber formation depends only on the secondary structure of aggregate or agglomerate and the surface activity of carbon blacks.[21] According to the previous TEM observation of chemical surfacetreated carbon black, the BCB structure tended to form smaller agglomerate and to show a better dispersion than that of VCB.[12] Moreover, the London dispersive component was found to be the highest for BCB indicating the improved dispersion of carbon black into the rubber matrix. The improved dispersion property strongly indicates the increased bound rubber formation.[21] Generally, the increase in bound rubber formation results in increase of both the viscosity and crosslinking density.[21] Thus, the observed increase in M_L and ΔM might be explained, at least by part, by the increase of bound rubber formation. There is further systematic study to confirm the observed phenomena.

4. Mechanical Properties

The mechanical properties of carbon blackfilled rubber compound have been known to be strongly

affected by the interfacial interaction between the carbon black and rubber phase.[17] Since the surface of carbon black is chemically modified in this work, the interfacial interaction, that is one of the key parameters to mechanical properties, is expected to be changed to a certain degree depending on the type of treatments. To understand the mechanical reinforcement behavior of the surface modified carbon blacks, tensile properties including hardness and dynamic mechanical properties were investigated for three rubber compounds: VCB-SBR, KCB-SBR, and BCB-SBR. In the case of HCB-SBR, it was impossible to compare the properties due to the lack
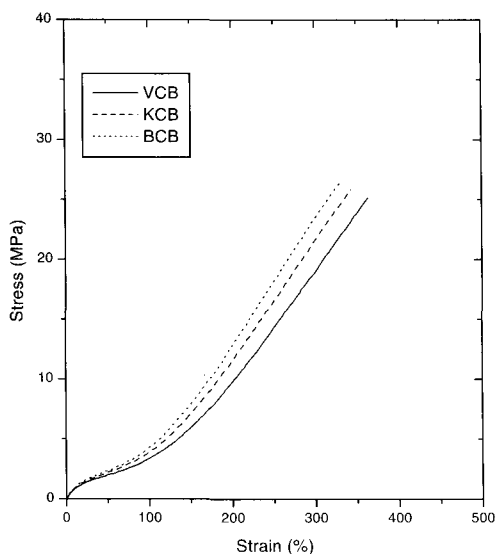
of vulcanization as shown in Fig. 2.

Fig. 4 shows the stress-strain curves, and their main properties are summarized in Table 5. The BCB-SBR showed the highest improvement in terms of hardness, modulus and tensile strength. A similar result was found for carbon black-filled polybutadiene (BR) compound.[11] The observed improvement seems to be lined with the increase in torque difference, $\Delta M (= M_H - M_L)$, in the rheocurves in Table 4. In the previous section of surface free energy measurement, it was found that the London dispersive component of surface free energy (or surface tension) of carbon black considerably increased, while specific (or polar) component decreased with the treatment using the nonpolar benzene. This strongly indicates that the interaction between carbon blacks is reduced in the case of BCB-SBR, and that between rubber and carbon black is rather increased to give rise to a better dispersion. Only a slight improvement in tensile properties was observed for KCB-SBR. The London dispersive component of KCB increased slightly. Thus, the improvement in tensile properties for BCB-SBR and KCB-SBR seems to be responsible to the improved
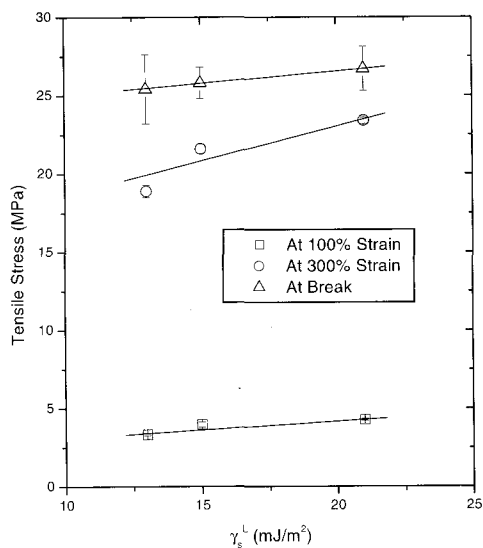

Figure 4. Stress-strain curves for SBR compounds containing virgin(VCB) and treated carbon blacks(KCB and BCB).

Table 5. Tensile Properties of SBR Compounds

Properties	VCB-SBR	KCB-SBR	BCB-SBR
Hardness (Shore A)	70	73	75
Stress (MPa) at 50% Strain	1.98±0.03	2.22±0.04	2.34±0.03
at 100% Strain	3.33±0.07	3.97±0.16	4.27±0.06
at 200% Strain	9.63±0.15	11.6±0.3	12.8±0.2
at 300% Strain	18.9±0.4	21.6±0.3	23.4±0.2
Tensile Strength (MPa)	25.4±2.2	25.8±1.0	26.7±1.4
Elongation at break (%)	377±28	349±10	342±17

Figure 5. Dependence of tensile properties on the London dispersive component of surface free energy of carbon blacks.

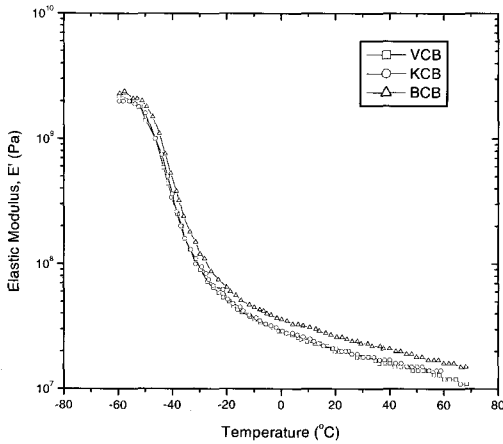**Figure 6.** Elastic modulus, E, versus temperature for SBR compounds containing virgin (VCB) and treated carbon blacks(KCB and BCB).

Figure 7. Tan δ versus temperature for SBR compounds containing virgin(VCB) and treated carbon blacks(KCB and BCB).

dispersion of carbon black into the rubber matrix leading to a higher bound rubber formation. To support the explanation, several essential properties were plotted in Fig. 5 as a function of the London dispersive component of surface free energy described in Table 3.[2] Linear lines could be drawn for all cases. This strongly indicates that the London dispersive component of surface free energy determined by a separate physicochemical method[11,14~16] could be a useful parameter to predict the tensile strength of carbon black-filled rubber compounds.

Fig. 6 and 7 shows the elastic modulus, E, and tan δ determined from a dynamic mechanical analyzer under the conditions of 11 Hz and 0.1% dynamic strain amplitude. As found in the results of tensile modulus, the BCB-SBR showed the highest elastic modulus throughout the temperature ranges investigated, possibly due to a tighter interaction between the carbon black and rubber, as shown in Fig. 6. In the case of tan δ, the peak height at the glass transition temperature was lowered slightly, and tan δ values in the temperature range from -20 to 70℃ were slightly higher for BCB-SBR than those of KCB-SBR and VCB-SBR.
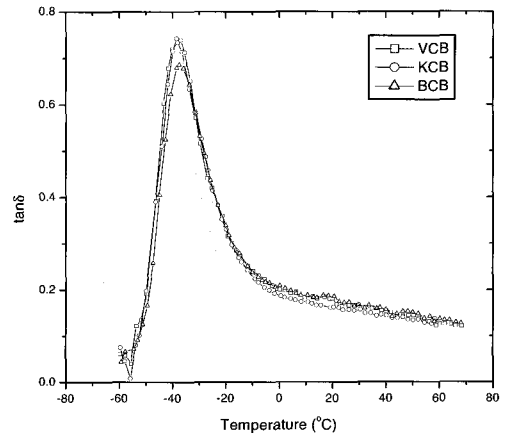
Ⅳ. Conclusions

This work reported the effects of chemical surface treatments of carbon blacks on the cure characteristics, tensile properties, and dynamic mechanical properties of a styrenebutadiene rubber. The surface free energy was considerably enhanced when the carbon blacks were treated with acid (HCB) and base chemicals (KCB), mainly due to the increase of the specific component, while only a slight increase was observed for benzene-treated carbon black (BCB). The BCB showed the highest level of the London dispersive component and HCB the lowest level. The cure behavior was strongly affected by the type of chemical surface treatments, i.e., the vulcanization reaction of SBR compounds containing various surface-modified carbon blacks was found to be faster in the order of KCBSBR BCB-SBR VCB-SBR HCB-SBR. The difference in minimum and maximum torque, representing the degree of crosslinking was found to be higher for BCB-SBR compared to those of VCB-SBR, KCB-SBR, and HCB-SBR. The BCB-SBR and KCB-SBR showed the improved tensile and dynamic mechanical properties. A linear relationship was found between the London dispersive component of surface free energy and mechanical properties.

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