

Effects of Carbon Black Content and Vulcanization Type on Cure Characteristics and Dynamic Mechanical Property of Styrene-Butadiene Rubber Compound

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Abstract : The influences of carbon black loading and cure type on the cure characteristics including kinetics and dynamic mechanical properties were investigated for a styrene-butadiene rubber (SBR). The rate constants of accelerated sulfur vulcanization reaction at three different temperatures were determined using a cure rheometer, and they were compared with those from the direct measurement of sulfur concentration. The strain softening behavior under dynamic deformation, known as the Payne effect was also discussed depending on the carbon black loading and cure type.

Introduction

Rubbers must be reinforced with carbon black for most applications 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. There has been an extensive study on the carbon black reinforcement of rubbers.¹⁻¹⁵ The carbon blacks physically absorb rubber molecules to their surfaces,^{5,6} or occlude them in internal voids⁷ which results in a partial immobilization of the rubber and an apparent increase in filler volume. They also form an agglomerated inter-particular structure⁵⁻⁸ which may be associated with specific elastic properties and a continuous breakup and rearrangement, finally leading to a strong nonlinear viscoelastic behav-

ior.^{6,8}

For most rubber products including tire, a high elasticity and frictional properties as well as a high load bearing performance is required. For this purpose, rubbers should be vulcanized using various cure systems, notably an accelerated sulfur cure system.¹⁶ The accelerated sulfur cure system forms the various crosslink structures: mono-, di-, and polysulfide networks, depending on the accelerator type, ratio of accelerator to sulfur, vulcanization temperature, and time, as well as the carbon black loading.¹⁷ It has been widely studied on the effect of cure system on the general properties of rubber compounds.¹⁸⁻²³ However, little attention has been made on the effect of the carbon black loading and type of cure system on the cure kinetics of rubber compounds.

In this study, the cure characteristics including cure kinetics and dynamic mechanical properties of a styrene-butadiene rubber (SBR) were investigated depending on the carbon black loading and

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three types of vulcanization. The rate of vulcanization as well as the activation energy was calculated based on the rheographs from a typical cure rheometer in rubber industry, and it was compared with that based on the direct determination of sulfur concentration.

Experimental

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%, Korea Kumho Petrochemical Co.) was selected as a rubber in this study. A carbon black of N-234 type (Lucky Carbon Black Co.) was selected as a reinforcing agent, and the loading level was varied from 40 to 70 phr with an increment of 10 phr. *N*-*t*-butyl-2-benzothiazol sulfenamide (TBBS) and sulfur were selected as the cure system, and three types of vulcanization: conventional (CV, TBBS: 0.7 phr, sulfur: 2.25 phr), semi-efficient (SEV, TBBS: 1.85 phr, sulfur: 1.35 phr), and efficient (EV, TBBS: 3.50 phr, sulfur: 0.6 phr) were employed to see the effect of cure type. The remaining additives were selected with typical grades in rubber industry. Compound recipes are summarized in Table I.

Mixing of compound ingredients except curatives was performed using an internal mixer (82BR, Farrel Co. USA) at about 150°C 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°C for 3 minutes.

Determination of Bound Rubber. The mixed compounds were extracted for 7 days in

n-decane at room temperature using a glass filter cage. The solvent was renewed after 3 days. The samples were dried for 24 hrs in air at room temperature, and then for another 24 hrs in a vacuum oven at 105°C. The bound rubber content was calculated using the following relation from the measured weight of the specimen:⁵

$$R_B = \frac{W_{cg} - W\left(\frac{m_c}{m_c + m_p}\right)}{W\left(\frac{m_p}{m_c + m_p}\right)} \times 100 \quad (1)$$

where W is the weight of the specimen, W_{cg} is the weight of carbon black and gel, m_c is the weight of carbon black in the compound, and m_p is the weight of rubber in the compound.

Determination of Free Sulfur. The completely vulcanized rubber specimen at 140°C was extracted by the same procedure described in previous bound rubber determination to extract the free sulfur that was not participated in vulcanization reaction. The sulfur content in the solvent was determined with a sulfur determinator (LECO SC-432, USA).

Determination of Properties. The cure characteristics was measured at four temperatures: 140, 150, 160, and 180°C using a torque rheometer (MDR 2000, Monsanto, USA) with a frequency of 100 cycles/min and ± 1.5 arc. The dynamic mechanical property of completely-vulcanized rubber specimens at 160°C was determined using a dynamic mechanical analyzer (GABO Qualimeter, Eplexor-150, Germany) at 30°C and at a frequency of 11 Hz. The dynamic strain amplitude was varied from 0.2 to 8% to see the Payne effect.

Table I. Compound Formulations Investigated

(Unit: phr)

Ingredients	4CV	4SEV	4EV	5CV	5SEV	5EV	6CV	6SEV	6EV	7CV	7SEV	7EV
SBR1500 ^a	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	3	3	3	3	3	3	3	3	3	3	3	3
Stearic Acid	1	1	1	1	1	1	1	1	1	1	1	1
Carbon Black ^b	40	40	40	50	50	50	60	60	60	70	70	70
Sulfur	2.25	1.35	0.60	2.25	1.35	0.60	2.25	1.35	0.60	2.25	1.35	0.60
NS ^c	0.7	1.85	3.50	0.7	1.85	3.50	0.7	1.85	3.50	0.7	1.85	3.50

^aStyrene-butadiene rubber: 23.5% styrene.

^bN234 type.

^c*N*-*t*-butyl-2-benzothiazole sulfenamide.

Results and Discussion

Cure Characteristics. The effect of carbon black loading on the cure characteristics of SBR compound vulcanized with semi-efficient (SEV) cure system was examined at 160°C by the Monsanto rheometer, and the results are given in Figure 1. The minimum and maximum torque, M_L and M_H , and the difference between them, ΔM ($=M_H-M_L$), increased with increasing the carbon black content. Moreover, the torque increase with time was faster for highly-loaded rubber compounds, representing a faster vulcanization reaction. The increase in M_L is in line with the well-known behavior of viscosity increase with the addition of carbon black. The torque difference, ΔM is generally related to the degree of crosslinking.^{24,25} Thus, the observed increase in ΔM with increasing carbon black loading can be attributed, at least by part, to the increase of total crosslink density in the rubber compounds. One plausible explanation for such a possibility of the increased crosslink density is that when the carbon black is added and mixed prior to the addition of curatives, which is the typical mixing procedure in the rubber industry, as well as in the present study, some of rubber molecules is bounded into the surfaces of agglomerated carbon black particles,

leading to a formation of, so called, "bound rubber".¹ If the curatives are then added into the carbon black master batch, they will disperse preferentially in unbounded rubber phase rather than in bounded one, possibly due to the immobilization of bounded rubber molecules during mixing procedure of curatives. Thus, the relative concentration of curatives in the unbounded rubber phase will be higher for the highly-loaded rubber compounds with carbon black. To support this explanation, the bound rubber content was measured for the rubber compounds having different carbon black level, and it was plotted against the ΔM , as shown in Figure 2. As can be seen, a linear relation was found between the ΔM and bound rubber content.

It has been known that the cure characteristics as well as the properties of the rubber vulcanizates strongly depend on the vulcanization type employed.¹⁸⁻²³ Figure 3 shows the rheographs of three rubber compounds having 50 phr of carbon black, but having different cure system: conventional(CV), semi-efficient(SEV), and efficient vulcanization(EV). The minimum torque, M_L , was not affected by the vulcanization type. But, the overall rate of vulcanization was found to be in the order of SEV > EV > CV. It has been known

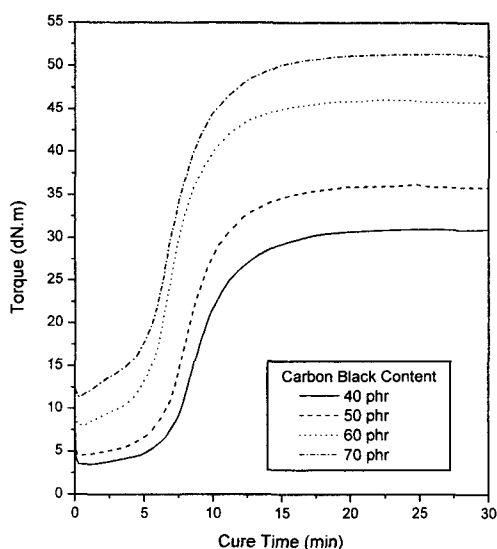


Figure 1. Effect of carbon black content on the rheographs of SBR compound at 160 °C.

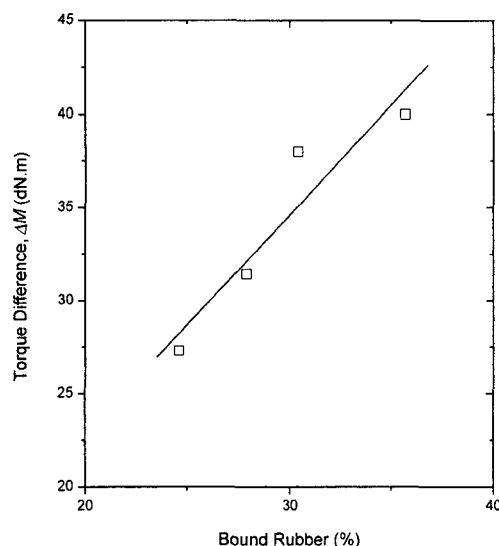


Figure 2. Relation between the torque difference, ΔM (M_H-M_L) from Figure 1 versus bound rubber of SBR compounds containing different carbon black levels.

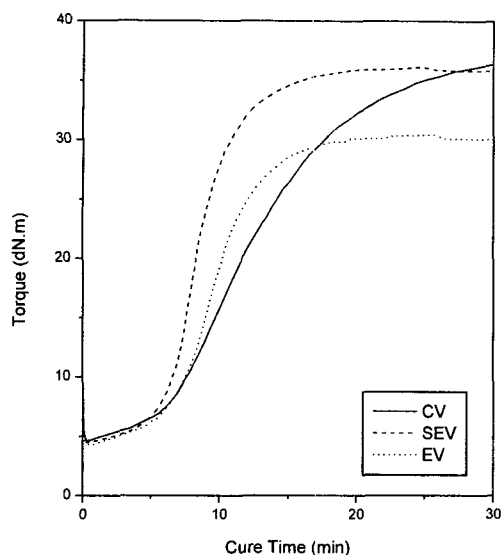
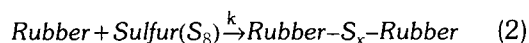


Figure 3. Effect of cure type on the rheographs of SBR compound at 160 °C; CV: conventional, SEV: semi-efficient, and EV: efficient cure type.

that the SEV is a compromised vulcanization form to produce, in structural terms, a vulcanizate containing a balance of monosulfidic crosslinks at a defined optimum cure state.^{16,26}

Vulcanization Kinetics Using Cure Rheometer. The accelerated sulfur cure of rubber can be assumed to follow the first-order kinetics,²⁷



where k is the rate constant under the cure accelerator acting as catalyst. Since the relative concentration of sulfur to rubber is usually small, the rate of vulcanization reaction can be assumed to be proportional to sulfur concentration alone, as given by:²⁷

$$\ln \frac{[S_i]}{[S_0]} = -kt \quad (3)$$

where $[S_0]$ is the initial sulfur concentration and $[S_i]$ is that after a time t . The sulfur concentration terms in equation (3) has been successfully replaced by the torque increase in cure rheometer as follows:^{24,25}

$$\ln \left(\frac{M_H - M_L}{M_H - M_t} \right) = kt \quad (4)$$

where M_i is the torque at a time t , and M_L and M_H are the minimum and maximum torque, respectively. Since the initial and final torque changes in the rheometer generally are lower than those in the middle, M_i values of 20 and 60% torque change were chosen to estimate the rate constants in this work. The rate constant, k , was determined at four different temperatures based on the equation (4) for all the rubber compounds investigated in this study, and the results are summarized in Table II. It was found that the rate constant slightly increased with increasing the carbon black content, as can be expected from the rheocurves in Figure 1. Moreover, the rate constant

Table II. Rate Constant and Activation Energy of Rubber Compounds during Vulcanization Reaction at 140, 150, 160, and 180 °C

Compound	Rate Constant ($1000 \times \text{sec}^{-1}$)				Activation Energy (kJ/mol)
	140 °C	150 °C	160 °C	180 °C	
4CV	1.671(1.588) ^a	1.660	3.098	9.938	73.9
4SEV	2.925(3.344)	4.528	9.952	24.99	85.8
4EV	2.555(3.614)	4.055	6.006	19.51	79.1
5CV	1.769(1.965)	1.951	3.273	10.63	73.0
5SEV	3.220(3.802)	5.363	8.562	26.93	82.7
5EV	2.781(3.541)	4.371	6.690	20.81	78.5
6CV	2.185(1.748)	2.243	3.675	12.33	70.9
6SEV	3.919(3.835)	6.330	10.47	36.47	87.4
6EV	3.695(3.812)	5.745	4.979	28.83	77.2
7CV	2.707(1.734)	2.668	4.358	16.78	74.9
7SEV	4.445(3.922)	8.241	11.14	45.75	89.2
7EV	4.606(3.817)	6.980	9.815	37.75	82.0

^aValues obtained from equation (3) based on the sulfur concentration.

increased considerably with increasing the temperature. The type of vulcanization also affected the rate constant, i.e., it was found to be in the order of $SEV > EV > CV$ regardless of carbon black level, as found previously in the rheometer curves. This may be explained by the fact that SEV as well as EV contains much higher weight ratio of accelerator to sulfur, and they have relatively higher possibility of faster sulfur crosslinking reaction with rubber than the CV. However, it is not clear whether the obtained rate constant based on the equation (4) can give a representative value or not. Thus, another set of experiment was made for the determination of free sulfur in the rubber compound after the completion of vulcanization reaction at 140°C. The rate constant was calculated based on the equation (3), and they are shown in parenthesis of Table II for a comparison to the values based on rheographs. A fairly good agreement was found between them, although the two methods for obtaining the rate constant were quite different. Thus, it can be concluded that the cure kinetic values from rheocurves are reasonably acceptable.

As a further step to obtain the apparent activation energy, the equation (4) was combined with the Arrhenius dependence of rate constant, and the final equation can be given by:²⁸

$$\frac{E_a}{R} = \ln \left(\frac{\ln \frac{(t_{60}-t_{20})_\beta}{(t_{60}-t_{20})_\alpha}}{\frac{1}{T_\beta} - \frac{1}{T_\alpha}} \right) \quad (5)$$

where $(t_{60}-t_{20})_\alpha$ and $(t_{60}-t_{20})_\beta$ are time lags for the torque change from 20 to 60% at temperatures T_α and T_β , respectively. Figure 4 shows the Arrhenius plots. The activation energy was calculated from the slope, and the results are summarized in Table II. As can be seen, the activation energy, E_a , of SEV and EV were slightly higher than that of CV.

Dynamic Mechanical Properties. Figure 5 shows the variation in storage modulus, E' , depending on the dynamic strain amplitude. As can be expected, the storage modulus decreased with increasing the dynamic strain amplitude. This has been known as the Payne effect.^{2,29,30} The difference $\Delta E'$, that is $E'_o - E'_\infty$, where E'_o is the

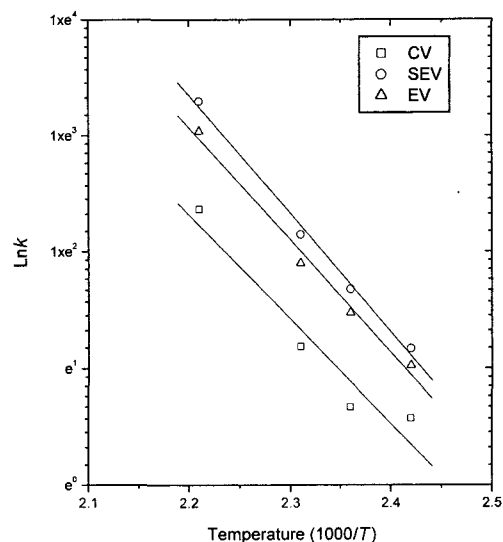


Figure 4. Typical Arrhenius plot of the SBR compounds containing 60 phr of carbon black for three different vulcanization types.

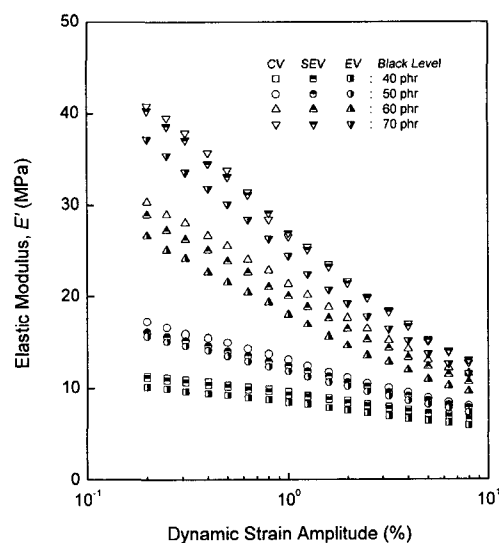


Figure 5. Plot of elastic storage modulus, E' , of SBR compounds as a function of dynamic strain amplitude at 30°C and at 11 Hz.

storage modulus at low strain (0.2%) and E'_∞ is the storage modulus at high strain (8%), is believed to be due to the breakdown of structure of the filler-filler networks.^{4,31} The difference $\Delta E'$ was found to be a linear relation with carbon black content, as shown in Figure 6. The cure system

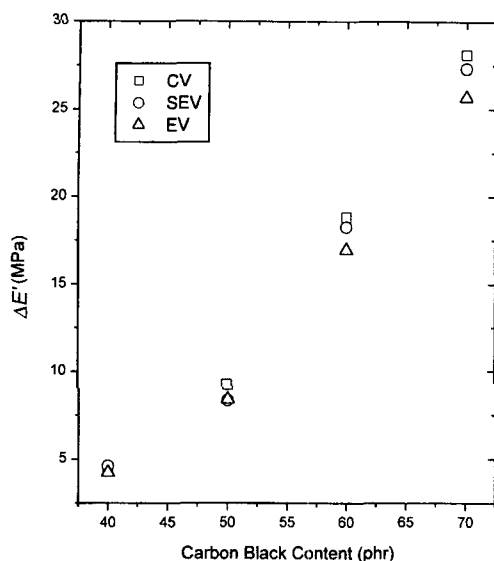


Figure 6. Difference in elastic modulus, $\Delta E'$ as a filler-filler interaction factor versus carbon black loading.

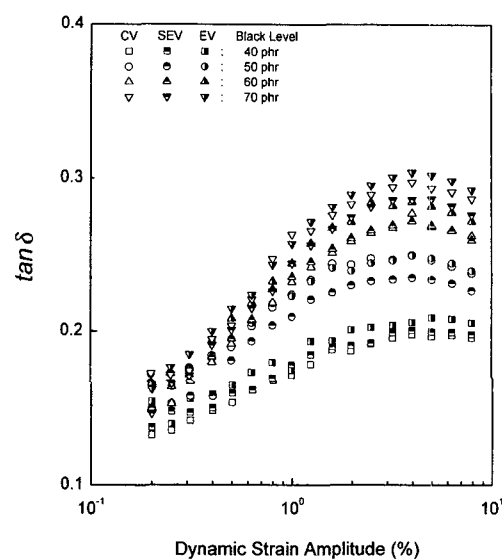


Figure 8. Plot of $\tan \delta$ of SBR compounds as a function of dynamic strain amplitude at 30 °C and at 11 Hz.

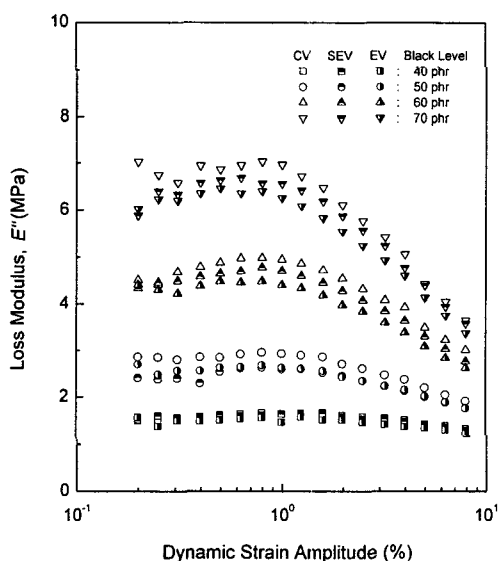


Figure 7. Plot of loss modulus, E'' , of SBR compounds as a function of dynamic strain amplitude at 30 °C and at 11 Hz.

employed here also slightly affected the dynamic moduli. For instance, the dynamic modulus, as well as its difference at each carbon black level was in the order of CV > SEV > EV. This seems to be responsible for more stable nature of monosul-

fidic crosslink, which is the major type in EV, than the polysulfidic one, which is the major type in CV, against the applied dynamic straining.

Figures 7 and 8 show the loss modulus, E'' and $\tan \delta$ as a function of dynamic strain amplitude. As can be seen, the stronger Payne effect was observed for more highly-loaded rubber compounds. This indicates that the hysteretic energy loss corresponding to the breakdown of filler-filler network increases with increasing carbon black loading. It should be noted here that the $\tan \delta$ value showed the maximum at around 5% of dynamic strain amplitude regardless of both carbon black loading and cure system employed. It has been reported that the network of carbon black particles held by van der Waals force is destroyed above 5 or 6% dynamic strain amplitude.³¹

Conclusions

This work reported the effects of carbon black loading and cure type on the cure characteristics and dynamic mechanical properties of a styrene-butadiene rubber (SBR). In the cure characteristics, the minimum and maximum torque, and its difference increased considerably with increasing

the carbon black content. The rate constant of accelerated sulfur vulcanization reaction based on the rheocurves from a rheometer agreed fairly well with that from the direct determination of sulfur concentration in the rubber compounds. The strain softening behavior under dynamic deformation, known as the Payne effect became clearly noticeable, as the carbon black loading was increased. Although the effect was relatively weak, the cure type affected the Payne effect as well.

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