Kinetics of Sulfur Vulcanization of NR, BR, SBR, and Their Blends Using a Rheometer and DSC

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SYNOPSIS

The relationship between vulcanization reactivity and chemical structure was studied using a rheometer and DSC for natural rubber (SMR 5CV), butadiene rubber (BR 01), styrene–butadiene rubber (SBR 1501), and their blends. The overall rate of the vulcanization was SBR > BR > NR. This was the same trend as the number of allylic hydrogens in the statistical repeat unit of the rubber used. Because the corresponding rate constant for an allylic hydrogen was very similar regardless of the rubbers, it was found that the vulcanization condition for a compounded rubber could be predicted by comparing the number of allylic hydrogens. The activation energy of the vulcanization was calculated for each rubber also. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The rubbers for tire manufacture must have high elasticity and frictional properties as well as a high load bearing property. Conforming to these needs, the rubbers are vulcanized at different conditions with various materials. The reactivity of sulfur vulcanization and the physical properties are affected by the chemical structure, molecular weight, and conformation of the base elastomers.[1,2] The sulfur vulcanization with unsaturated rubbers occurs through complicated radical substitution in the forms of mono-, di-, or polysulfide bridges and sulfur containing intracyclization with the polymer molecules. The crosslink density and distribution affect the physical properties and the stability on aging and are dependent on the accelerator type, the ratio of accelerator to sulfur, reaction temperature, and time.[3]

Because the vulcanization rate of the rubber is closely related to the productivity of tire manufacture, it is desirable to increase the rate by raising temperature. However, at higher temperature, the

effectiveness of sulfur crosslinks is lower with a sacrifice of the physical properties caused by the dissociation of sulfur bonds and rubber chains.[4-6] Thus, the reactivity was controlled by additional amounts of sulfur and accelerator instead of raising temperature. The increase of sulfur addition leads to increases in crosslink density and the ratio of polysulfide linkage, causing a decrease in the stability on aging.[7] With the increase of accelerators, the effectiveness of sulfur vulcanization having mono- and disulfide linkages is improved to give stability on aging, but the dynamic properties are decreased instead. Accordingly, it is important to set up optimum conditions of vulcanization as a compromise between productivity and the quality of the tire.[8,9]

There are many methods to estimate the reactivity of vulcanization. Rheometers give information on the scorch safety and optimum cure time from the torque–time curve reflecting the degree of vulcanization. DSC measures the enthalpy and peak temperature of vulcanization to estimate the reactivity between rubber and sulfur. The enthalpy is mainly related to the sulfur content.[10] Because the characteristics of vulcanization depend upon rubbers, accelerators, and the reaction conditions, it is tedious and costly to obtain the correct evaluation of the vulcanization. Although efforts on the study

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of reactivity and physical properties according to the chemical structure of rubber have been done, it is still difficult to predict reactivity accurately due to the lack of a systematic explanation of the reaction characteristics.

This work reports on the relations between vulcanization reactivity and chemical structure, and on the determination of sulfur vulcanization conditions in rubber compounded for a tire using a rheometer and DSC for natural rubber (SMR 5CV), butadiene rubber (BR 01), styrene–butadiene rubber (SBR 1501), and their blends. Apparent activation energies for the vulcanization of rubbers were calculated and compared to explain the vulcanization reactivity of the rubbers.

EXPERIMENTAL

Materials

SMR 5CV, SBR 1501, and BR 01 were used without treatment. SMR 5CV consists of more than 98% cis-1,4-polyisoprene. SBR 1501 contains 23.5% bound styrene. The chemical structure of butadiene in the SBR consists of 68% trans-1,4, 17% cis-1,4, and 15% 1,2-butadiene. BR 01 has more than 98% cis-1,4-polybutadiene. Commercial additives, such as carbon black (N330), sulfur, zinc oxide, stearic acid, N-1,3-dimethylbutyl-N'-phenyl-phenylenediamine (Kumanox 13), and N-t-butyl-2-benzothiazolesulfenamide (TBBS) were also used without purification.

Sample Preparation

Rubber mixing was done according to ASTM D3194. Formulations are shown in Table I. As can be seen,

only types and blend ratios of rubber were changed. The antioxidant (0.2 phr) Kumanox 13 (Korea Kumho Petroleum Chemicals) was used to minimize the physical property changes during the mixing and curing process. Because the temperature is increased over 140°C by the friction in the mixing process of rubber and carbon black, the processibility becomes worse due to the formation of crosslinks when highly reactive accelerator and sulfur are exposed to heat. Thus, curatives were added in the second stage at a relatively low temperature to prevent the scorch problem.

Rubbers were preblended for 30 s at 105°C in a Banbury mixer (Farrel 82BR) at 40 rpm. Then carbon black and all additives except for sulfur and accelerator were mixed with the preblend for more 2.5 min. The first step was finished after further mixing of the preblended rubber for 1 min, and the final temperature of the compound was ca. 150°C. Then the rubber compound obtained in the first step was finally mixed with sulfur and accelerator at 100°C for 2 min. The compounding was ended after milling for 1 min on an open mill at 100°C.

Rheometer and DSC

A Monsanto rheometer (MDR 2000) was used at a frequency of 100 cycles/min and ±1.5 arc for the vulcanization temperatures of 140, 160, and 180°C to obtain the torque–time curve from which the apparent activation energy was calculated.

Using a DSC (Perkin–Elmer Series 7), the calorimetric runs were all made at different scan rates of 5, 10, 20, and 40°C/min for all compounds under nitrogen atmosphere. At each scan rate, the calorimeter was calibrated with an indium standard.

Table I   Formulations for Rubber Compounds

Materials	A	B	C	D	E	F	G	H	I
NR (SMR 5CV)	100	65	35		65	35			
SBR 1500		35	65	100				65	35
BR 01					35	65	100	35	65
C/B (N330)	50	50	50	50	50	50	50	50	50
ZnO	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2
A# oil	5	5	5	5	5	5	5	5	5
Kumanox 13	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
TBBS	1	1	1	1	1	1	1	1	1
Sulfur	2	2	2	2	2	2	2	2	2

RESULTS AND DISCUSSION

Reactivity of Sulfur Vulcanization

The vulcanization occurred by a free radical reaction initiated with accelerator. The accelerator has an — S — N — bond for which the dissociation energy is 35 kcal/mol, that can be easily dissociated by the heat of vulcanization process over 140°C to produce — S• and •N — radicals. These radicals attack elemental sulfur with comparatively weak bonds rather than rubber chains to generate a sulfur radical, — S_x•. The sulfur radicals attack allylic and benzylic hydrogens in the rubber to make crosslinks. This is simply explained by comparison of the related bond dissociation energies of sulfur, and allylic and benzylic hydrogen which are 54, 77, and 77.5 kcal/mol, respectively. Hereafter, in referring to allylic hydrogen we mean allylic and benzylic hydrogen because they have nearly the same dissociation energy. Because it is easier to thermally split the lower energy bond, the accelerator first initiates sulfur radicals that react with rubber molecules, successively.

An accelerator can be activated by zinc stearate that is produced from stearic acid and zinc oxide by heat during the mixing process and forms a complex with the accelerator to promote radical generation.[11–15] The activated accelerator complex forms a higher active complex with sulfur that provides a polysulfide link to the rubber molecule. This polysulfide reacts further to form mono-, di-, and cyclic sulfide bonds during vulcanization via dissociation, recombination, and rearrangement of the sulfur linkages. These various types of sulfur linkages affect the rubber properties and tire performance.[16–18]

In general, the reactivity of hydrogen in a carbon chain becomes higher in order of primary < secondary < tertiary carbon, because of the difference of stabilization of the corresponding radicals via hyperconjugation.

Hydrogens of allyl and benzyl groups are much more reactive than that of tertiary carbon due to the resonance stabilization. Because NR, SBR, and BR have many allylic hydrogens, sulfur radicals can react with the allylic hydrogen much easier than with any other hydrogens in the rubber molecules. Thus, the vulcanization rate depends upon the number of allylic hydrogens.

Statistical repeat units of NR, BR, and SBR have 7, 4, and 3.3 allylic hydrogens, respectively. Accordingly, NR has higher reactivity than the others.

To compare the reactivity of rubbers with the corresponding numbers of allylic hydrogens, various samples were prepared for NR, BR, SBR, and the blends of NR/BR, NR/SBR, and SBR/BR having the ratios of 35/65 and 65/35 in each.

Vulcanization Rate from Rheometer

It was shown that the increase in the rheometer torque is directly related to the crosslink density.[19] Assuming that vulcanization follows first-order kinetics, the kinetic expression for vulcanization can be shown in terms of torque as

$$\ln\left(\frac{M_h - M_l}{M_h - H_t}\right) = kt, \qquad (1)$$

where M_t is the torque at a time t; and M_l and M_h represent the minimum and the maximum torque, respectively; and k is the rate constant for the vulcanization. Because the rate in the first stage reflects the character of the main forward reaction kinetically, M_t values of 25 and 45% torque change were chosen to estimate the rate constants in this work. A combination of the Arrhenius equation and eq. (1) gives the convenient eq. (2) for the apparent activation energy using rheometer isotherms at different temperatures.

$$\frac{E_a}{R} = \ln\left[\frac{\ln\left(\frac{(t_{45\%} - t_{25\%})_\beta}{(t_{45\%} - t_{25\%})_\alpha}\right)}{1/T_\beta - 1/T_\alpha}\right] \qquad (2)$$

where $(t_{45} - t_{25})_\alpha$ and $(t_{45\%} - t_{25\%})_\beta$ are the time lags for the torque change from 25 to 45% at temperatures T_α and T_β, respectively. The torque curves are obtained at 140, 160, and 180°C for each sample of the blends in Table I.

Rheographs are shown in Figure 1 for NR, BR, and SBR at 140, 160, and 180°C. Using the rheographs and eq. (1), the rate constants are estimated and tabulated in Table II.

The overall rate of vulcanization was in the order SBR > BR > NR. This is the same trend as predicted from the number of allylic hydrogens in the statistical repeat unit of the rubber used. The rate constants are divided by the number of allylic hydrogens to find the corresponding rate constant as in Figure 2. From the result, each allylic hydrogen has a very similar rate constant regardless of the rubber. This implies that the sulfur crosslink is controlled by the allyl groups in the rubbers. Thus, if the chemical structure of the rubber used is known,
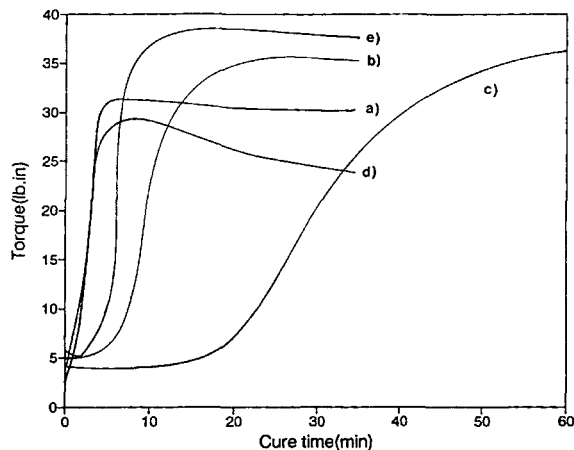
Figure 1 Rheograph of NR, BR, and SBR at various temperatures: SBR at (a) 180°C, (b) 160°C, and (c) 140°C; (d) NR at 160°C; and (e) BR at 160°C.

it may predict the reactivity and conditions for the vulcanization of a compound.

As shown in Figure 1, the maximum torque of SBR, M_h, decreases with increasing temperature. This comes from the decrease of effectiveness in the crosslink by intramolecular cyclization of sulfur bonds becoming pendant after breaking the sulfur crosslinks at higher temperature. At an early reaction stage, the forward reaction to become a crosslink may be predominant, but side reactions, like sulfur bridge breaking and cyclizing, become active at the last stage. As the side reactions increase with temperature, the maximum torque can be lower at higher temperature as the results for SBR show in Figure 1(a–c).

Comparing (b), (d), and (e) in Figure 3, NR with a high content of allylic hydrogens shows more rapid

Table II Rate Constant of Rubber Compounds at 140, 160, and 180°C by Rheometer

Sample	Rate Constant ($1000 \times k$,s^{-1})			Activation Energy (kJ/mol)
	140°C	160°C	180°C	
A	1.497	4.848	18.62	97.89
B	1.039	3.593	13.76	100.3
C	0.804	2.818	11.75	104.1
D	0.561	2.089	8.391	105.1
E	1.099	3.920	15.43	102.6
F	0.931	3.306	12.73	101.5
G	0.745	2.802	10.32	102.1
H	0.676	2.451	9.853	104.0
I	0.712	2.698	10.39	104.1
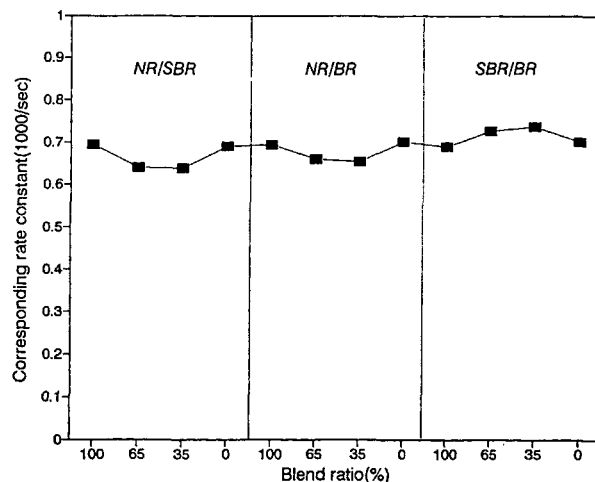
Figure 2 Corresponding rate constant per unit allylic hydrogen for various rubber compounds.

curing and a high reversion effect. Because all allylic hydrogens are not used for crosslinking, the remaining allyls may provide sites to be radicals, which a cause dissociation of sulfur crosslinks. Thus, NR can show a higher reversion effect than BR and SBR. Because BR has more allylic hydrogens than SBR, BR may have an easier reversion effect than SBR at the same cure conditions.

Using eq. (2), the activation energies are tabulated in Table II. Typical Arrhenius plots are shown in Figure 3 to estimate the activation energy.

The apparent activation energy of NR is lower than BR and SBR, bringing about easier reaction. This is consistent with the allylic hydrogen content.
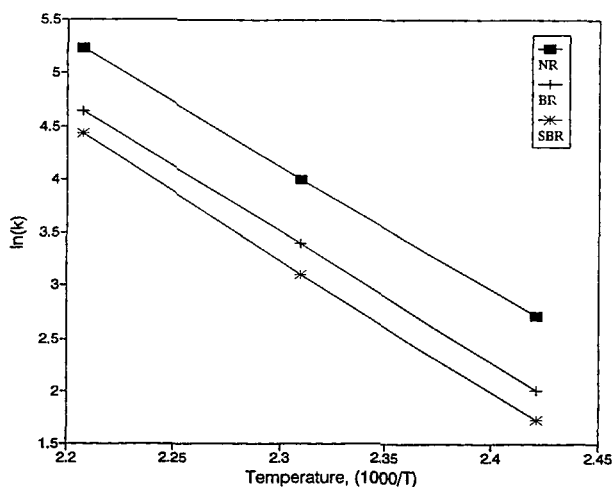

Figure 3 Arrhenius plot for NR, BR, and SBR obtained from the rheographs.

Table III   Peak Temperature and Enthalpy for Rubber Compounds Measured by DSC

Sample	Peak Temp. (°C) and Enthalpy (J/g) at Various Scan Rates by DSC				Activation Energy (kJ/mol)
	40°C/min	20°C/min	10°C/min	5°C/min	
A	207.4 (12.2)	192.9 (10.6)	180.8 (9.03)	168.7 (8.50)	94.69
B	210.6 (17.5)	197.3 (14.2)	185.2 (10.9)	174.1 (10.0)	102.3
C	214.7 (17.8)	201.8 (15.1)	190.9 (11.3)	178.5 (11.0)	105.1
D	219.0 (14.6)	206.8 (12.4)	193.8 (9.28)	183.0 (7.79)	107.6
E	208.0 (18.0)	192.8 (14.5)	182.1 (12.9)	170.1 (11.0)	97.16
F	209.4 (14.5)	195.7 (12.1)	184.4 (11.2)	172.1 (9.20)	99.42
G	211.9 (14.4)	199.2 (13.6)	186.5 (8.66)	175.3 (8.25)	102.6
H	216.0 (19.9)	202.7 (17.1)	191.4 (12.9)	180.0 (12.6)	106.3
I	214.6 (17.8)	201.9 (15.4)	189.9 (14.3)	178.0 (10.3)	103.8

Vulcanization enthalpies are in parentheses.

Vulcanization Kinetics Using DSC

A DSC thermogram is the net result of all reactions occurring within the temperature range of interest. When a rubber compound is heated, many reactions occur competitively; thus, it is very difficult to measure the enthalpy for a specific reaction. The sum of all the reactions during vulcanization is the overall exotherm for sulfur levels encountered in practical formulations. The vulcanization enthalpy is linearly proportional to the initial sulfur content. Although the addition of accelerator moves the thermogram to a lower temperature, the overall enthalpy is independent of accelerator level.[10] It can be correlated to the total enthalpy, ΔH, from the thermogram to
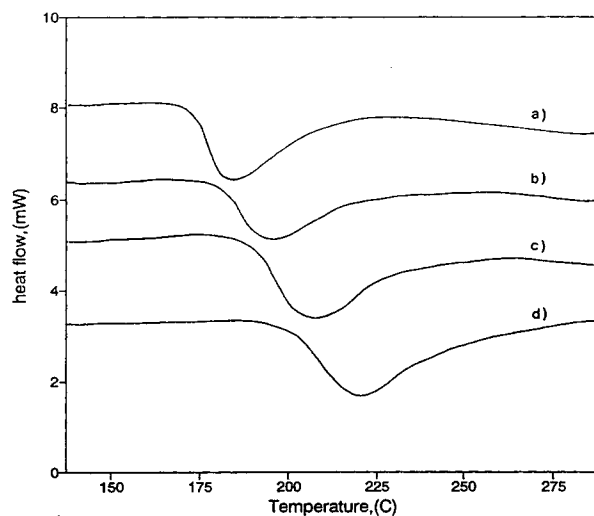

Figure 4   DSC thermograms of SBR for various scan rates: (a) 5°C/min, (b) 10°C/min, (c) 20°C/min, and (d) 40°C/min.

the vulcanization kinetics in terms of degree of vulcanization, α, which is the ratio of $H_p/\Delta H$ where H_p is heat released up to time t, assuming that the vulcanization is a first-order reaction.[20]

$$\frac{d\alpha}{dt} = k(1 - \alpha). \tag{4}$$

In eq. (4), the time variable can be changed to temperature difference using a scan rate, $\beta = \dfrac{dT}{dt}$, together with the Arrhenius equation for the rate constant,

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln k_0 - E_a/RT + \ln(1 - \alpha). \tag{5}$$

This equation represents the theoretical shape of the DSC thermogram. The activation energy can be estimated from the slope of $\ln (\beta\, d\alpha/dT)$ versus the $1/T$ plot. DSC exotherms for all samples in Table I are obtained using scan rates of 5, 10, 20, and 40°C/min. The numerical results are listed in Table III. The typical exotherms for SBR are shown in Figure 4. They show that the peak temperature is increased by ca. 12°C for doubling of the scan rate. As the heat transfer of rubber is slower than the scan rate, apparent temperature is higher than the true reaction temperature. Scan rate affects the enthalpy by 2 J/g higher when the rate is doubled.

Assuming that $d\alpha/dT$ in eq. (5) is nearly constant at the peak temperature, regardless of the scan rate, eq. (5) simply reduces to the following Kissinger equation,[21]
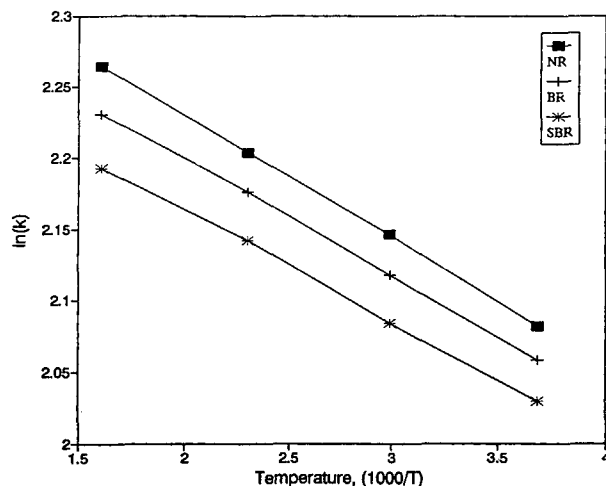
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Figure 5 Arrhenius plot of NR, BR, and SBR by DSC.

$$\ln \beta = Z - E_a/RT_p, \qquad (6)$$

where T_p is the peak temperature.

The activation energy is estimated from the Kissinger plot as shown in Figure 5 using the data from Table III. The results are consistent with the results from the rheometer.

CONCLUSIONS

This work reports on the relationship of the structure of a rubber and the vulcanization reactivity using a rheometer and DSC. The vulcanization rate of a rubber increases proportionally to the number of allylic hydrogens in the statistical repeat unit. Because each allylic hydrogen has a common corresponding vulcanization rate, it is easy to predict the reaction conditions for a compounded rubber by comparing the number of allyl groups. The higher the content of allylic hydrogen, the lower the overall apparent activation energy is in the vulcanization. Because NR has a higher number of allylic hydrogens, implying that it is more easily attacked by a sulfur radical during the vulcanization, this rubber shows a high vulcanization rate in the early stage

of the reaction. These results are consistent regardless of the experimental methods. The rubbers having higher reactivity also show comparatively higher reversion.

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