

# Solid-State $^{13}\text{C}$ -NMR and Equilibrium-Swelling Studies of Filled, TBBS-Accelerated Sulfur Vulcanization of Natural Rubber

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Received 2 September 1997; accepted 8 December 1997

**ABSTRACT:** The effective network chain density ( $\nu_e$ ) and the density of the chains between sulfurizations ( $2[\text{S}]_{\text{chem}}$ ) for natural rubber vulcanized with *N-t*-butyl benzothiazole sulfenamide (TBBS) in different levels of HAF-HS (N347) carbon black were determined by equilibrium swelling and solid-state  $^{13}\text{C}$ -NMR measurements, respectively. The proportion of the intermolecular crosslinks over a whole range of sulfurized products ( $Ec$ ) for the gum stock was estimated by the comparison of the chemical network chain density ( $\nu_{\text{chem}}$ ) calculated from  $\nu_e$  using Mullins's approach with  $2[\text{S}]_{\text{chem}}$ .  $Ec$  increases with cure, reaches a maximum at an optimum cure state ( $t_{90}$ ), and decreases during an overcuring. It was observed from the NMR results that the total amount of chemical sulfurization reactions occurring in the rubber is almost independent of the level of carbon black loading. Based on the assumption that the amount of the intermolecular crosslinking reactions is also constant with the carbon black content, the amount of physical crosslinks ( $\nu_{\text{ent}}$ ) in filled formulations was determined by subtracting the estimated  $\nu_{\text{chem}}$  from the  $\nu_e$ . The linear relationship obtained from the plot of the  $\nu_{\text{ent}}$  at the optimum cure state ( $t_{90}$ ) as a function of carbon black content postulates that the physical adsorption plays a major role in the polymer-filler interactions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1391–1399, 1998

**Key words:** NMR; vulcanization; carbon black; polymer-filler interaction

## INTRODUCTION

Many previous studies attempted to explain the basis of the complex reinforcing effects of particulate fillers on rubber matrices. The reinforcement effects have been attributed to molecular interactions of the rubber and the filler. Dannenberg investigated the reinforcement effects of fillers by swelling the rubber matrices.<sup>1</sup> For an elas-

tomer vulcanizate, the number of effective network chains per unit volume of rubber ( $\nu_e$ ) can be determined from the equilibrium swelling behavior and has been interpreted using the statistical network theory of the thermodynamics of swelling.<sup>2</sup> Kraus and Dugone observed that, apparently, the amount of crosslinking in the rubber network increases with the volume fraction of carbon black and expressed these results as reflecting the increased amount of rubber adsorbed on the carbon black.<sup>3</sup> They also investigated the magnitude of the reinforcement of carbon black by considering the differences in the effective network chain densities of the unfilled and filled vulcanizates.<sup>4</sup> However, they concluded that the

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Contract grant sponsors: National Science Foundation; The Yokohama Rubber Co.

*Journal of Applied Polymer Science*, Vol. 70, 1391–1399 (1998)  
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**Table I** Natural Rubber Formulations

Material	Formulation			
	#1	#2	#3	#4
Natural rubber (SMR-CV60)	100.0	100.0	100.0	100.0
TBBS (Santocure <sup>®</sup> NS) <sup>a</sup>	0.75	0.75	0.75	0.75
Sulfur	2.38	2.38	2.38	2.38
Carbon black (N347)	0.00	15.00	30.00	50.00
Zinc oxide	5.00	5.00	5.00	5.00
Stearic acid	3.00	3.00	3.00	3.00

<sup>a</sup>®, Registered trademark of Monsanto Chemical Co.

contributions of the filler to crosslinking does not quantitatively represent the number of filler-to-rubber linkages since this contribution depends on the degree of cure, the vulcanization system, and the filler particle or aggregate shape.<sup>5</sup> Berry and Cayre concluded that the network chain densities obtained from the swelling measurements should be regarded merely as a convenient index of the tightness of the gel and the extent of the polymer–filler interactions, since no distinction can be made between those chains formed by direct attachment of the rubber molecules to the filler particles and those which arise by a crosslinking reaction taking place between the rubber chains already attached to the particles.<sup>6</sup> This ambiguity arises from the fact that the network chain densities obtained from the swelling measurements reflect not only the effects of rubber-to-rubber chemical linkages but also the physical effects including rubber-to-filler interactions and the chain entanglements.

There have been many attempts to relate the densities of elastically effective strands in an unfilled vulcanized rubber network to the amount of chemical and physical crosslinkages.<sup>7–12</sup> However, due to the complex nature of the polymer-to-filler interactions, no convenient expression for the filled rubber network has been proposed.

Solid-state <sup>13</sup>C-NMR is a useful tool to identify and quantify the chemical products occurring in vulcanization reactions. Usually, an elastomer well above its glass transition temperature has high-frequency motions which average the dipolar interaction in the sample and the line widths of the NMR spectra are narrow. Therefore, a high-resolution spectra can be obtained for both gum and filled formulations in the solid state.<sup>13–15</sup> By applying a single-pulse method using MAS and HPPD without CP, quantitative results can be

obtained. The total amount of the sulfurization products can be estimated by integrating all corresponding peaks on the spectra.<sup>16–19</sup> Although the <sup>13</sup>C-NMR method can distinguish the sulfurized structures with different carbon sites on the backbone and their sulfur ranks, the main disadvantage of this approach is an inability to distinguish the effectiveness of the particular sulfide structures on the elastic properties. Thus, to understand the complex features of the rubber network structures, the combined use of chemical and physical (swelling) approaches is desirable.

In this study, the efficiency of the intermolecular crosslinking over the whole range of sulfurization reactions for the unfilled natural rubber formulation and the filler-reinforcement effect in terms of the physical entanglement density for the filled natural rubber formulations are discussed via the results of the <sup>13</sup>C-NMR and equilibrium swelling experiments.

## EXPERIMENTAL

SMR-CV60 controlled-viscosity natural rubber was sulfur-vulcanized using four conventional formulations containing 0, 15, 30, and 50 phr of HAFHS-grade carbon black (N347) along with *N*-*t*-butyl benzothiazole sulfenamide (TBBS) and the other auxiliary agents (see Table I). Each formulation was cured at 140°C to constant cure stages of 10% (*t*10), 50% (*t*50), and 90% (*t*90) of the maximum rheometer torque (*t*100 – *t*0). An oscillating disk rheometer, a Monsanto ODR-2000, was run to determine the cure times to those cure levels for the individual formulations. Uncured and overcured samples were also prepared, each of which corresponds to cure times of 0 and 120 min. The experimental details for the

vulcanization process and the resulting products were reported in the preceding paper by the present authors.<sup>14</sup> The Rubber Chemical Division of the Monsanto Chemical Co. (Flexsis America) supplied all samples for this study. Twenty samples prepared were then characterized by equilibrium-swelling measurements and <sup>13</sup>C solid-state NMR.

### Equilibrium-swelling Measurements

The network chain density of the vulcanized products was determined by equilibrium-swelling measurements performed in benzene. A small piece (~ 0.1 g) of the rubber sample was soaked in the solvent in a glass vial with a stopper and left in the dark for 48 h. The samples were removed, blotted dry with a paper towel, placed in a clean stoppered vial, and weighed. The samples were dried for 48 h in a vacuum oven at ambient temperature and then reweighed to obtain the weight of the network gel and the amount of the imbibed solvent.

The modified Flory–Rehner equation<sup>20</sup> was used to calculate the network chain density following the method of Shelton and McDonald<sup>21</sup> and Adams and Johnson<sup>22</sup>:

$$\nu = \frac{\rho_r}{Mc} = \frac{-[\ln(1 - Vr) + Vr + \chi Vr^2]}{V_0(Vr^{1/3} - 2Vr/f)}$$

where  $\nu$  is the network chain density per unit volume of rubber (mo V cm<sup>3</sup>);  $Mc$ , the molecular weight between crosslinks;  $Vr$ , the volume fraction of rubber in the swollen vulcanizate;  $\chi$ , the Huggins interaction parameter;  $\rho_r$ , the density of the rubber;  $V_0$ , the density of the solvent; and  $f$ , the functionality of the crosslinkage. The volume fraction,  $Vr$ , was calculated from the reciprocal of the degree of swelling:

$$Vr = \frac{1}{1 + Q}$$

where

$$Q = \frac{[wt \text{ of solution in network}] \rho_r}{[wt \text{ of network}] \rho_s}$$

where  $\rho_r$  is the density of the solvent.

The values of the constants used in the above calculations were  $\rho_r = 0.93$  g/cm<sup>3</sup>,  $\rho_s = 0.879$  g/cm<sup>3</sup>,  $V_0 = 89.40$  cm<sup>3</sup>/mol, and  $f = 4$ . The

Huggins interaction parameter,  $\chi$ , was given as<sup>23,24</sup>

$$\chi = 0.41 + 0.20Vr$$

The calculation of the network chain density is based on the assumptions that the filler particles do not swell and the dependence of the interaction parameter on cure are trivial.<sup>24</sup> Swelling experiments were performed three times per sample and average  $\nu$  values were employed for the experimental data.

The effective network chain density,  $\nu_e$ , was determined from the  $\nu$  data by considering the free terminal effect in the network structure:

$$\nu_e = \nu \left( 1 - c \frac{Mc}{M} \right)$$

where  $M$  is the number-average molecular weight of the rubber and  $c$  is a constant. The  $M$  of the soluble component of the original SMR–CV-type natural rubber is  $1.8\text{--}3.7 \times 10^5$ ,<sup>25</sup> but it was decreased by the mastification done prior to the compounding. In this study, the  $M$  of  $1.3 \times 10^5$  was employed instead as the number-average molecular weight of the mastificated natural rubber molecule.<sup>26</sup> The constant,  $c$ , was reported to be 2.3 for the natural rubber systems.<sup>2</sup> For lesser vulcanized samples where the molecular weight between crosslinks is on the order of  $M$ ,  $\nu_e$  was set to zero, indicating no physically effective crosslinkages.

### Calculation of the Chemical Crosslink Density

The chemical crosslink density of the unfilled vulcanized samples was estimated by the calculation based on the Mullins's approach.<sup>2</sup> The constant,  $C1$ , in the Mooney–Rivlin equation is given from the equilibrium-swelling results, assuming that the interaction between the network chains is negligible ( $C2 = 0$ ) in the equilibrium state of the uniaxial deformation and/or the volume fraction rubber in the swollen vulcanizate is small for the nonpolar elastomer systems<sup>27</sup>:

$$C1 = \frac{\nu_e RT}{2}$$

Mullins proposed the following equation based on the comparison of the  $C1$  obtained from the equi-

librium swelling experiments and the chemical crosslink density estimated from the chemical probe for the di-*tert*-butyl peroxide-cured natural rubber<sup>2</sup>:

$$C1 = \left( \frac{\rho_r RT}{2M_{c,chem}} + a \right) \left( 1 - c \frac{\overline{M}c_{chem}}{M} \right) \\ = \left( \frac{\nu_{chem} RT}{2} + a \right) \left( 1 - c \frac{\rho_r}{M\nu_{chem}} \right)$$

Here,  $a = 0.78 \times 10^6$ , which represents the contribution from chain entanglements on the physical network properties and the latter term compensates for the free terminal effect in which  $c = 2.3$  for natural rubber. This observation was also supported by a proceeding study of the dicumyl peroxide-vulcanized natural rubber systems.<sup>22</sup> The chemical network chain density,  $\nu_{chem}$ , is then determined by solving the equation for each  $C1$  obtained from the equilibrium-swelling result,  $\nu_e$ . It has been proposed that the amount of the chain entanglement increases with the level of chemical crosslinking or cure<sup>12-29</sup> but the appropriate correlation for the natural rubber system has not been proposed. Thus, the calculation in this study was based on the assumption that the contribution of the physical entanglement is constant during the extent of the vulcanization.

### Solid-state <sup>13</sup>C-NMR Measurements

All NMR measurements were performed on a Bruker MSL 300 at a <sup>13</sup>C frequency of 75.47 MHz. Quantitative measurements were performed under a gated high-power decoupling (GHPD) pulse sequence with the recycle delay of 6 s, which has been shown to be more than five times the longest spin-lattice relaxation time,  $T1$ . The other experimental details for the NMR measurements were given in the preceding article.<sup>22</sup>

Nine peaks were detected from five kinds of sulfide structures and the concentrations of each sulfide structure were quantified by integrating the peaks. The density of the sulfurized carbons in the natural rubber backbone can be determined by quantifying the concentration of the total sulfurized structures. While <sup>13</sup>C-NMR is a powerful method for distinguishing the type and site of sulfide substitution, it cannot distinguish between effective and ineffective crosslinks.<sup>19-30</sup>

Since each sulfide bonds to two carbons on the rubber main chain, the chemical sulfurization point density per unit volume of the rubber can be defined as

$$[S]_{chem} = \frac{1}{2} \frac{I(Sx)}{I_0} \frac{\rho_r}{M_0}$$

$$I(Sx) = I(64) + I(58) + I(51) + I(45)$$

where  $[S]_{chem}$  is the chemical sulfurization point density per unit volume of rubber (mol/cm<sup>3</sup>);  $I(Sx)$ , the total peak intensity of the sulfurized structure;  $I_0$ , the average intensity of the backbone carbon;  $I(X)$ , the intensity of the peak at  $X$  ppm; and  $M_0$ , the molar mass of the isoprene unit. The density of the chains between the sulfurization points per unit volume of rubber can be then expressed as

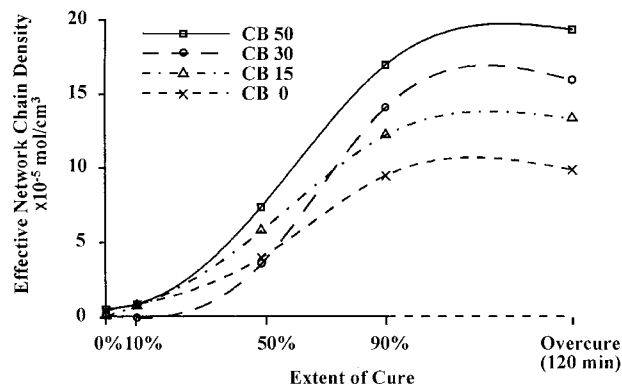
$$2[S]_{chem} = \frac{\rho_r}{M_{c,sulf}} = \frac{I(Sx)}{I} \cdot \frac{\rho_r}{M_0}$$

where  $M_{c,sulf}$  is the molecular weight between the sulfurized carbons.  $2[S]_{chem}$  is now in the same dimension as that of the network chain densities obtained by the equilibrium-swelling measurements, enabling the comparison of those two sets of data.

## RESULTS

The effective network chain densities per unit volume of rubber obtained by the equilibrium-swelling measurement ( $\nu_e$ ) for the four formulations are presented in Figure 1. They increased as the vulcanization reaction proceeded during the curing region and then became constant or slightly decreased during overcuring. The slope and the value increased with volume fraction of carbon black.

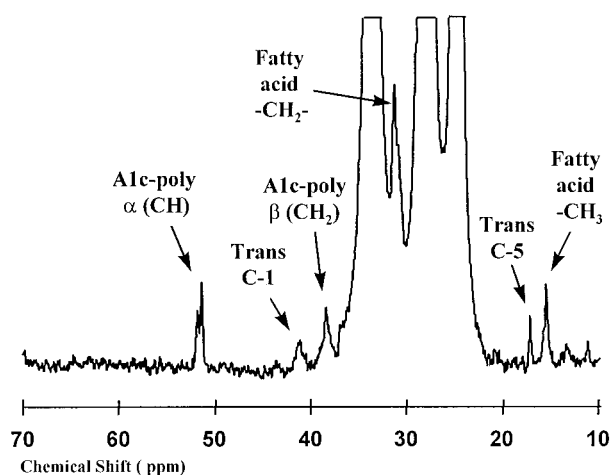
The magnified <sup>13</sup>C-NMR spectra of the aliphatic regions typical of medium and overcured filled natural rubber vulcanizates are shown in Figures 2 and 3. To quantify the density of the chains between sulfurization points ( $2[S]_{chem}$ ), the intensities of the resonances arising from  $\alpha$ -carbons of the all sulfide structures have been summed. The resonances used were the peaks at 64, 58, 51, and 45 ppm; the detailed assignment of the peaks in this particular system were previously reported by the present authors.<sup>22</sup> The



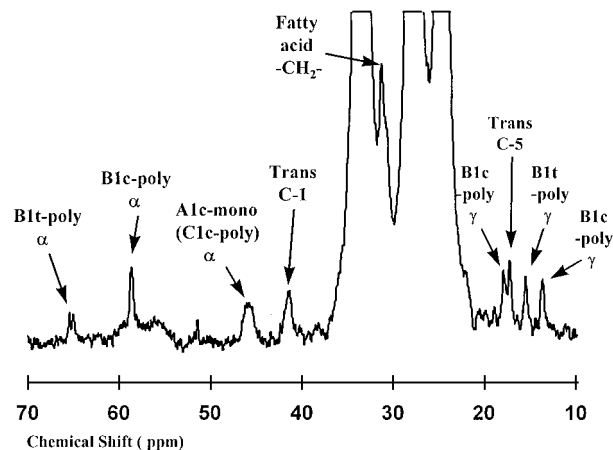
**Figure 1** Effective network chain densities per unit volume of rubber as a function of cure obtained by the equilibrium-swelling measurements for four formulations.

$2[S]_{\text{chem}}$  obtained for the four formulations are shown in Figure 4. The densities constantly increased with cure even in the overcuring and their slope and values were almost constant for all formulations with different level of carbon black loading.

The amount of chemical crosslinks ( $\nu_{\text{chem}}$ ) in the gum stock calculated from the  $\nu_e$  using Mullins's approach was compared with the  $2[S]_{\text{chem}}$  obtained by NMR (see Fig. 5). The  $2[S]_{\text{chem}}$  was larger than the  $\nu_{\text{chem}}$  for all curing stages and the difference between them was smallest at the 90% cure stage.



**Figure 2**  $^{13}\text{C}$ -NMR spectrum of natural rubber cured for 26 min (medium cure) for formulation #2.



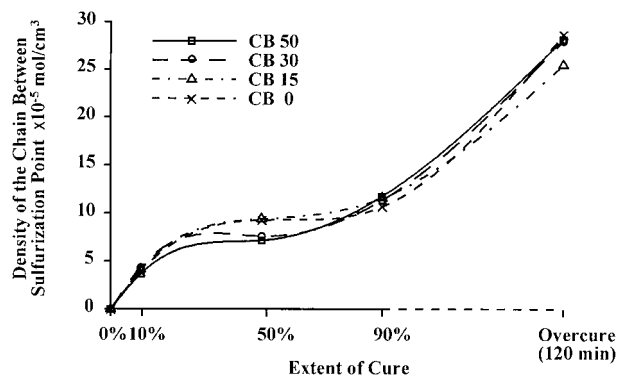
**Figure 3**  $^{13}\text{C}$ -NMR spectrum of natural rubber cured for 120 min (overcured) for formulation #3.

## DISCUSSION

### Efficiency of the Chemical Crosslinking over the Sulfurization Reactions

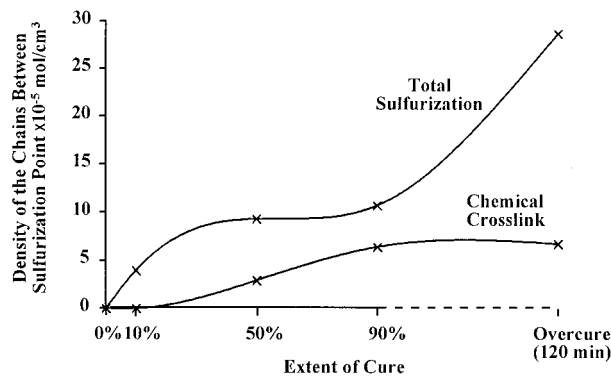
In the equilibrium-swelling measurements, the network chain density of the rubber vulcanizate ( $\nu_e$ ) can be determined from the balance between the expansion force due to the swelling in the solvent and the contraction force produced by the rubber elasticity. So, any factors influencing the network construction and its topology may affect the behavior of the rubber matrices in the solvent. Among these factors are not only the crosslinking structure due to the chemical bonding but also the physical adsorption including the entanglement of the chains and/or gel structures.

Using  $^{13}\text{C}$ -NMR analysis, the amount of the total chemical sulfurization reactions occurring at



**Figure 4** Densities of the chains between sulfurization points per unit volume of rubber as a function of cure obtained by  $^{13}\text{C}$ -NMR for four formulations.





**Figure 5** Comparison of the total amount of sulfuration and the amount of intermolecular crosslink for the unfilled formulation (#1).

the particular cure level is quantified. This result was termed the density of the chains between sulfuration points ( $2[S]_{\text{chem}}$ ). By simply considering the nature of these two chain densities, it might be assumed that  $\nu_e$  is larger than  $2[S]_{\text{chem}}$ ; however, this is not the case especially for the formulations with no or lower carbon black content. This is because the amount of the sulfurations detected in the  $^{13}\text{C}$ -NMR includes a physically ineffective accelerator complex (pendant sulfide) and cyclic and vicinal crosslink structures along with the intermolecular crosslinkages.

By utilizing the Mullins approach,<sup>2</sup> the amount of the physically effective chemical crosslinks ( $\nu_{\text{chem}}$ ) can be estimated from the equilibrium-swelling results for the unfilled formulation. Since the derivation of the  $\nu_{\text{chem}}$  by this method is based on many assumptions and uses the equation that was constructed for similar but not identical systems compared to the present system, the values obtained may not have an absolute meaning. However, it is possible to obtain some insight into the efficiency of the intermolecular crosslinking over the whole sulfuration reactions by comparing the obtained  $\nu_{\text{chem}}$  and  $2[S]_{\text{chem}}$ . The comparison of the  $2[S]_{\text{chem}}$  and the  $\nu_{\text{chem}}$  is presented in Figure 5. The efficiency ( $Ec$ ) can be expressed as

$$Ec = \frac{\nu_{\text{chem}}}{2[S]_{\text{chem}}}$$

The  $Ec$  plotted as a function of cure is shown in Figure 6.

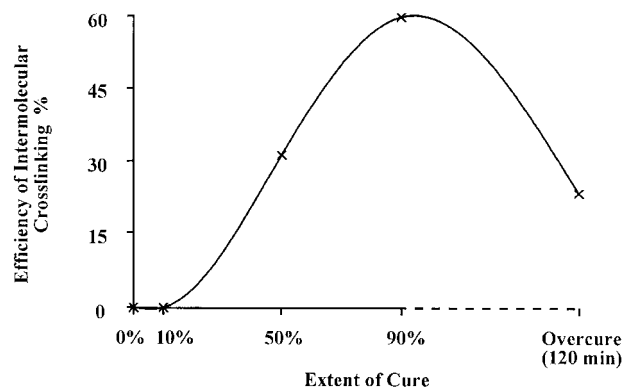
It can be seen in Figure 6 that the  $Ec$  is zero until the scorch cure ( $t_{10}$ ) increases with the cure

during the curing period and hits the maximum, 59.8%, at the optimum cure stage ( $t_{90}$ ). The  $Ec$  then decreases with time in the overcuring and drops to 23.4% at that (120-min) cure.

The calculation of  $\nu_{\text{chem}}$  in this study is based on the assumption that the amount of the physical crosslinks ( $\nu_{\text{ent}}$ ) is independent of the level of cure, but  $\nu_{\text{ent}}$  actually increases with the  $\nu_{\text{chem}}$ .<sup>12,29</sup> If this effect is accounted for in our system, the  $\nu_{\text{chem}}$  in the middle of the curing period ( $\sim t_{50}$ ) may become larger than that calculated in this study. However, it might not affect the basis of the observed trend since the  $\nu_e$  at  $t_{50}$  is almost half of  $\nu_e$  at  $t_{90}$ . Furthermore, this effect can be neglected in the overcure periods since the  $\nu_{\text{chem}}$  is almost constant in this region.

Another uncertainty in the calculation comes from the assumption that the molecular weight of the rubber hydrocarbon does not change during the vulcanization although it may change to some extent by the chain scission in the overcuring. However, the decrease in molecular weight of rubber results in the decrease in the  $\nu_{\text{chem}}$  in the overcuring, which does not change the observed trend that the  $Ec$  decreases with time in the overcure period. It was reported that the level of the chain scission in the peroxide-vulcanized natural rubber is negligible<sup>31,32</sup> and also there is no spectral evidence for the presence of the chain scission in the TBBS-accelerated sulfur vulcanization of natural rubber.<sup>14,17</sup> Thus, the effect of the change in the molecular weight on the observed trend for  $Ec$  is small.

Before scorch cure, as seen in Figure 5, only the sulfuration reaction without the interchain crosslinking occurs. The accelerator complex (pendant sulfide) is the major product in this pe-



**Figure 6** Efficiency of the intermolecular crosslinking over the whole sulfuration reactions for the unfilled formulation (#1).

riod, which reacts with the other polymer chains to form an intermolecular crosslink in the following stage.<sup>33</sup> It can be assumed that  $E_c$  approaches 100% during the latter half of the curing period, but we observed it reaches a ceiling of 59.8% at  $t_{90}$ . This can be explained by the possible remaining pendant structures and the formation of the ineffective sulfurization such as the intramolecular (cyclic sulfide) and the vicinal crosslinks. The maximum  $E_c$  is usually small in the unaccelerated sulfur-vulcanization systems and it increases with the accelerator-to-sulfur ratio in the accelerated vulcanization systems. The  $E_c$  at the moderate cure of 67% was reported for the MBT-cured model olefin system.<sup>34</sup> Thus, the maximum  $E_c$  of 59.8% obtained in the conventionally vulcanized natural rubber studied here is reasonable.

The considerable drop in the  $E_c$  in the overcure period results from a large increase in the amount of total sulfurizations with an almost constant level of the effective chemical crosslinks in this period. The sulfurization reactions proceed after the curing periods, which has been demonstrated, from the HPLC study, to be due to the existence of a high proportion of the accelerator complex (BtSH) at the onset region of overcuring and its gradual decrease with cure time.<sup>35,36</sup> Most of these reactions are considered to result in ineffective sulfides such as cyclic and vicinal crosslink structures. Under these considerations, it can be assumed that the efficiency of the chemical crosslinking over the total sulfurizations may also play a role, to some extent, on the physical properties of the end vulcanized products along with the chemical and physical crosslink densities and the effect of main-chain modifications.

### Filler-reinforcement Effect

The effective network chain density ( $\nu_e$ ) increased with the level of carbon black (Fig. 1), while the density of the chains between the sulfurization points  $2[S]_{\text{chem}}$  was almost independent of the carbon black content (Fig. 4). Considering these two trends, it can be assumed that the filler-reinforcement effect on the physical properties of the rubber vulcanizates comes from factors other than the chemical crosslinking. Unfortunately, the estimation of the  $\nu_{\text{chem}}$  using the methods mentioned in the previous sections is valid only for the unfilled formulation. However, it is possible to discuss the changes in the amount of physical crosslinks ( $\nu_{\text{ent}}$ ) induced by the carbon black

by applying an assumption that is based on the  $^{13}\text{C}$ -NMR observations.

In the  $^{13}\text{C}$ -NMR analysis, chemical species occurring in the elastomer are detectable. Carbon black itself, however, cannot be detected by the NMR measurement because of its nonprotonated structure and possible large frequency shift due to its inherent high electrical conductivity. Chemical bonding between the polymer-filler could be detected by NMR, but in our experiments, no such structure was detected, indicating that the amount of the chemical bonding of the polymer to the filler is small. There have been many arguments whether the polymer-filler interactions are governed by chemical bonding<sup>37-39</sup> or physical adsorption.<sup>40,41</sup> Presently, it is believed that the nature of this interaction is mainly physical adsorption, although chemical bonding may be possible in the case of rubbers having saturated backbones.<sup>38</sup> The present NMR results support the mechanism of physical adsorption in the natural rubber/carbon black system.

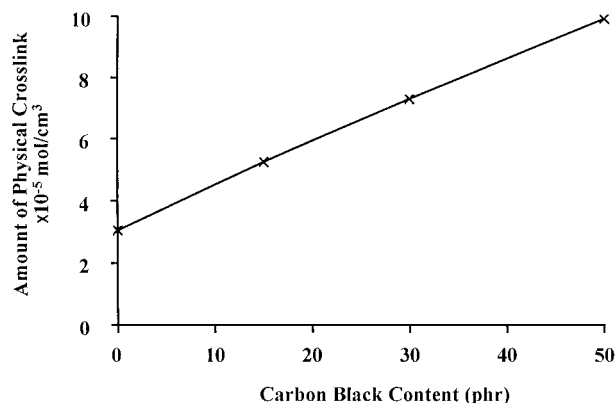
It was shown in Figure 4 that the sulfurization curves from the formulations with the carbon black contents of 0, 15, 30, and 50 phr are similar. It is clear that the total amount of the chemical sulfurization reaction occurring in the natural rubber vulcanization system is not affected by the incorporation of carbon black. The total amount of the chemical reaction may be kinetically controlled and depends primary on the thermal and mixing history of the system. Based on these facts, one can assume that the levels of the chemical crosslinkages are also constant with change in the carbon black content.

Based on this assumption, the amounts of the physical adsorption at the optimum cure state ( $t_{90}$ ) can be expressed by the following equation:

$$\nu_{\text{ent}} = \nu_e - 2[S]_{\text{chem}}E_{c_{\text{gum}}}$$

where  $\nu_{\text{ent}}$  is the physical network chain density per unit volume of rubber ( $\text{mol}/\text{cm}^3$ ). The plot of  $\nu_{\text{ent}}$  as a function of carbon black content is presented in Figure 7. A linear relationship was observed which represents the correlation between the filler-reinforcement effect and the amount of physical crosslinking.

It has been shown that the entanglement of the rubber chains plays a considerable role in the elastic properties<sup>42-44</sup> and also in the reinforcement effect of filler in rubbery matrices.<sup>45</sup> This concept has been further elaborated in terms of



**Figure 7** Estimated amount of physical crosslinks per unit volume of rubber at optimum cure state ( $t_{90}$ ) as a function of carbon black content.

the effect of the entanglement of chains on the mechanical properties of the rubbery materials.<sup>29,46,47</sup> Funt made extensive studies and concluded that both hydrodynamic interactions and chain entanglements control the reinforcement effect of filler on the rubber matrices.<sup>48</sup> The entanglement formation is observable not only between the polymer chains but also between bulk rubber and carbon gel. This observation is important to interpret the reinforcement effect since the carbon gel usually traps a considerable amount of the polymer<sup>49</sup> and the chain entanglements entrapped in the polymer can then work as additional anchors for physically effective strands.

Considering these points, the observations shown in Figure 7 are valuable in estimating the amount of polymer–filler interactions. The slope of the plot may then represent the efficiency of the reinforcement that changes depending on the surface area and/or structure of the carbon black used. Since the reinforcement effects of carbon black depend on the type of raw material, the type of the ingredients used in the formulation and the size and the nature of the carbon black, further study using the different formulation systems will reveal the value of the concepts shown in this study for the evaluation of the filler-reinforcement effect.

## CONCLUSIONS

The effective network chain density ( $\nu_e$ ) and its counterpart containing both effective and ineffective chemical sulfurizations ( $2[S]_{\text{chem}}$ ) of SMRCV60

natural rubber vulcanized with a constant amount of TBBS and four different amounts of HAF–HS carbon black were determined by the equilibrium-swelling measurements using the modified Flory–Rehner equation and solid-state <sup>13</sup>C-NMR quantitative measurements, respectively. For the unfilled formulation, the amount of chemical network chains ( $\nu_{\text{chem}}$ ) was calculated from the  $\nu_e$  based on the assumption made by Mullins and was compared with  $2[S]_{\text{chem}}$ . The efficiency of the intermolecular crosslinking over the whole range of sulfurization reactions was then evaluated by the  $\nu_{\text{chem}}$ -to- $2[S]_{\text{chem}}$  ratio ( $Ec$ ), which showed the commonly observed trend that the efficiency becomes maximum at the optimum stage of cure for the unfilled formulation.

The  $\nu_e$  for each cure state increased with the amount of carbon black while the  $2[S]_{\text{chem}}$  was almost independent of the carbon black content. The amount of physical crosslinks ( $\nu_{\text{ent}}$ ) for the four formulations was estimated based on an assumption that the amount of the chemical crosslinks is a constant proportion of the  $2[S]_{\text{chem}}$ . The  $\nu_{\text{ent}}$  at the optimum cure state ( $t_{90}$ ) increased with carbon black content, which indicates that physical adsorption plays a major role in the polymer–filler interactions. It was proposed that the plot of the  $\nu_{\text{ent}}$  at an optimum cure as a function of the carbon black content can be used to evaluate the degree of the filler-reinforcement effect.

The authors would like to acknowledge the Rubber Division of Monsanto Chemical Co. (Flexsis America) for their sample preparation. They also would like to acknowledge the support of Division of Material Research at the National Science Foundation and The Yokohama Rubber Company.

## REFERENCES

1. E. M. Dannenberg, *Ind. Eng. Chem.*, **40**, 2199 (1948).
2. P. J. Flory, N. Rabjohn, and M. C. Shaffer, *J. Polym. Sci.*, **4**, 225 (1949).
3. G. Kraus and J. Dugone, *Ind. Eng. Chem.*, **47**, 1809 (1955).
4. G. Kraus, *Rubber World*, **135**, 67 (1956).
5. G. Kraus, *Rubber World*, **135**, 254 (1956).
6. J. P. Berry and P. J. Cayre, *J. Appl. Polym. Sci.*, **3**, 213 (1960).
7. A. M. Bueche, *J. Polym. Sci.*, **19**, 297 (1956).
8. L. Mullins, *J. Appl. Polym. Sci.*, **4**, 1 (1959).
9. O. Lorenz and C. R. Parks, *J. Polym. Sci.*, **50**, 299 (1961).



10. G. Kraus, *J. Appl. Polym. Sci.*, **7**, 1257 (1963).
11. N. R. Langley, *Macromolecules*, **4**, 348 (1968).
12. F. P. Baldwin, P. Borzel, and H. S. Makowski, *Rubber Chem. Technol.*, **42**, 1167 (1969).
13. R. A. Komoroski, *Rubber Chem. Technol.*, **56**, 959 (1983).
14. M. Mori and J. L. Koenig, *Rubber Chem. Technol.*, **68**, 551 (1996).
15. S. Clough and J. L. Koenig, *Rubber Chem. Technol.*, **62**, 908 (1989).
16. G. Simon, B. Gotschmann, D. Matzen, and H. Schneider, *Polym. Bull.*, **21**, 475 (1989).
17. M. R. Krejsa and J. L. Koenig, *Rubber Chem. Technol.*, **65**, 427 (1992).
18. W. Gronski, U. Hoffmann, G. Simon, A. Wutzer, and E. Straube, *Rubber Chem. Technol.*, **65**, 63 (1992).
19. M. R. Krejsa and J. L. Koenig, *Rubber Chem. Technol.*, **67**, 348 (1994).
20. P. J. Flory, *Principle of Polymer Chemistry*, Cornell University Press, London, 1953.
21. J. R. Shelton and E. T. McDonald, *Proc. Int. Rubber Conf.*, 596 (1959).
22. E. H. Adams and B. L. Johnson, *Ind. Eng. Chem.*, **45**, 1539 (1953).
23. W. M. Saltman, *The Stereo Rubber*, Interscience, New York, 1977.
24. G. M. Bristow, *J. Appl. Polym. Sci.*, **9**, 1571 (1965).
25. A. Subramaniam, *Rubber Research Institute of Malaysia Technology Bulletin, No. 4*, Kuala Lumpur, 1980.
26. W. J. Roff and J. R. Scott, *A Handbook of Common Polymers*, CRC Press, London, 1971.
27. J. A. Brydson, *Rubber Chemistry*, Applied Science, London, 1978.
28. E. F. Cluff, E. K. Gladding, and R. Pariser, *J. Polym. Sci.*, **45**, 341 (1960).
29. W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1 (1974).
30. A. M. Zaper and J. L. Koenig, *Rubber Chem. Technol.*, **60**, 252 (1987).
31. K. W. Scott, *J. Polym. Sci.*, **58**, 517 (1962).
32. G. M. Bristow, *J. Appl. Polym. Sci.*, **7**, 1023 (1963).
33. R. H. Campbell and R. W. Wise, *Rubber Chem. Technol.*, **37**, 635 (1964).
34. L. Bateman, Ed., *The Chemistry and Physics of Rubber-like Substances*, Maclaren, London, 1963, Chap. 15.
35. A. B. Sullivan, C. J. Hann, and G. H. Kuhls, *Rubber Chem. Technol.*, **65**, 488 (1992).
36. C. J. Hann, A. B. Sullivan, B. R. Host, and G. H. Kuhls, Jr., *Rubber Chem. Technol.*, **67**, 76 (1994).
37. W. F. Watson, *Ind. Eng. Chem.*, **47**, 1281 (1955).
38. A. M. Gessler, *Rubber Age*, **94**, 750 (1964).
39. A. K. Sircar and A. Voet, *Rubber Chem. Technol.*, **43**, 973 (1970).
40. G. Kraus and J. J. Gruver, *Rubber Chem. Technol.*, **41**, 1256 (1968).
41. L. L. Ban, W. M. Hess, and L. A. Papazian, *Rubber Chem. Technol.*, **47**, 858 (1974).
42. G. Kraus and G. A. Moczygemba, *J. Polym. Sci. Part A*, **2**, 277 (1964).
43. B. M. E. Van der Hoff, *J. Macromol. Sci. Chem.*, **1**, 747 (1967).
44. T. L. Smith, *J. Polym. Sci. Part C*, **16**, 841 (1967).
45. E. A. Meinecke and M. I. Taftaf, *Rubber Chem. Technol.*, **61**, 534 (1988).
46. M. H. Wagner and S. E. Stephenson, *J. Rheol.*, **23**, 489 (1979).
47. P. G. de Gennes, *Phys. Today*, **36**(6), 33 (1983).
48. J. M. Funt, *Rubber Chem. Technol.*, **61**, 842 (1988).
49. G. Kraus and K. W. Rollmann, *J. Polym. Sci. Symp.*, **48**, 87 (1974).