

Rice Husk Ash Filled Natural Rubber. III. Role of Metal Oxides in Kinetics of Sulfur Vulcanization

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ABSTRACT: In preceding investigations the overall rate and apparent activation energy for the vulcanization process were calculated for natural rubber compounds, assuming that vulcanization follows first-order kinetics. It was observed that the addition of white rice husk ash (WRHA) increased the rate of crosslinking and lowered the apparent activation energy more profoundly than commercial fillers, precipitated silica (Zeosil-175) and carbon black (N762), with a conventional vulcanization system. In this work, a specific model for the vulcanization process accelerated by *N*-cyclo-

hexylbenzothiazole sulfenamide was used to investigate the real role of WRHA in crosslink formation. Cure studies were carried out at 150°C, and the kinetics constants were evaluated. In relation to the other fillers, WRHA seems to develop catalytic activity, resulting in a positive effect on the specific rate of crosslink formation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1519–1531, 2003

Key words: vulcanization; rubber; activation energy

INTRODUCTION

Rice husks (RHs) are a major by-product of the rice milling industry. Efforts to utilize RHs has been handicapped by their tough, woody, and abrasive nature and their low nutritive properties, resistance to degradation, great bulk, and high ash content. The efforts over the years to make good use of RHs has resulted in minor usage, mostly in low-value applications in agriculture, such as fuel, or it is burned. Little advantage has been taken of RHs and large amounts are still being produced, causing pollution problems as a consequence of the disposal process. However, the high silicon content in RHs has largely widened the potential for its use in the past few decades.¹ The silica in RH originally exists in the amorphous form, but it becomes crystalline during combustion of the husk. Silica is used in a wide range of applications. For example, silicas are often used as fillers in rubber materials, such as tires, and they are also applied as catalyst supports and drying agents.

RH ash (RHA) contains nearly 95% silica. When burned it yields two main grades of ash, white RHA (WRHA) with high silica content and black RHA (BRHA) with low silica content. Carbon-free ash

(white ash) has opened a new dimension in concepts for its utilization during recent years² as a source of high-grade amorphous silica, which is utilized in the production of silicon.³ The formation of amorphous white ash involves controlled combustion at low temperatures.⁴ The application of RHA as a filler in plastics is relatively limited and the literature reports are mainly on polypropylene (PP).^{5–7} However, as early as the 1970s, researchers began to perform studies on RHA as a filler in rubbers.⁸

A rheometer consists of a biconical disk rotor confined in a cavity filled with raw rubber. The rotor is submitted to a small angle (usually 1° or 3°) oscillation, and the torque required to produce these oscillations is measured continuously with time. The cavity is maintained under pressure at curing temperature. As the rubber cures it stiffens, and the torque required to produce the oscillations increases. Much time has already been invested in relating these traces to the kinetics of the cure reaction in pure gum compounds. It has been shown that the observed increase in rheometer torque (or complex dynamic modulus) at a given time t (ΔL_t) is directly related to the crosslink density, particularly if the measurements are done at relatively low frequencies.⁹

In Part I of this series¹⁰ we showed that WRHA seems to accelerate the vulcanization process in natural rubber (NR) compounds in the presence of zinc oxide, whereas BRHA does not have any catalytic effect or, if it does have, it is in minor extension. In Part II of this series¹¹ carbon black (CB, type N762)

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and precipitated silica (Zeosil-175) were partially replaced by WRHA. The results allowed the conclusion that, when those replacements take place, there is indeed a catalytic effect on the vulcanization process, although it is less discernible than that occasioned by the incorporation of WRHA alone in NR compounds.¹¹

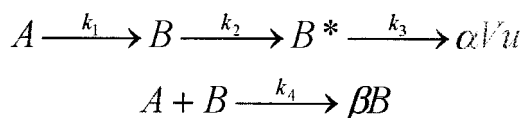
This article investigates the effect of WRHA and BRHA upon NR vulcanization by using the model developed for the study of the delay in crosslink formation when a sulfenamide accelerator is employed.¹² We again used CB and silica for comparison purposes. The different kinetic constants were calculated and the real effect of RHA was interpreted in accordance with a simple sequential reaction scheme proposed by Coran.¹²

Reaction scheme for sulfur vulcanization

In the general case, diene rubbers form not only mono-, di-, and polysulfidic crosslinks but also pendent sulfidic groups terminated by an accelerator residue, cyclic sulfides, conjugated diene and triene units, cis- and trans-isomerized olefin units, and vicinal crosslinks. Di-, and especially polysulfidic, crosslinks not only display poor thermal aging resistance but, as a consequence of their high chemical reactivity, also affect other physical properties as well. The main-chain modifications brought about by side reactions also seem to affect a given selection of properties. Some of these are probably a consequence of an increase in polarity and/or in the glass-transition temperature of the rubber. Others are the result of interruptions in the stereoregularity of the elastomer backbones, leading to a reduced tendency to crystallize.¹²

In the transformation of the initial polysulfidic network into the more complex "final" network present in the vulcanizate being prepared, two principal reactions were identified. The first is desulfuration, giving rise to crosslink shortening and eventually leading to monosulfide crosslinks. This reaction was shown to be affected by zinc complexes derived from the accelerator (or sulfur donor) and zinc compounds present in the rubber mix. The second reaction is thermal decomposition, which forms cyclic mono- and disulfides, conjugated dienes and trienes in the rubber backbone, and zinc sulfide. The balance between these two reactions was found to largely determine the type of vulcanizate network formed.¹²

The critical features of this scheme were the identification of an accelerator-terminated polysulfidic pendent group as the rubber-bound precursor to crosslinks and the postulation that the initially formed crosslinks were polysulfides, which subsequently underwent a number of competing reactions. Since the scheme was first proposed, further evidence for the existence and identity of the rubber-bound intermedi-



Scheme 1 A simple reaction scheme for the kinetics of scorch delay vulcanizates.¹³

ate was obtained, but there is as yet no general agreement on the chemical nature of the active sulfurating agent, in particular, as to whether it contains zinc.¹²

Coran model

The kinetics of scorch delay vulcanizates has not been treated in terms of elementary reactions. Such a treatment, if proven consistent with experimental observations, could greatly improve the understanding of accelerated sulfur vulcanization. It has been found that the usual simple sequential reaction scheme ($A \rightarrow B \rightarrow C \rightarrow D$, etc.) is not adequate to explain the long delay periods frequently encountered when a sulfenamide accelerator is used in sulfur vulcanization. However, it has been possible to formulate a suitable, although simple, reaction scheme, based on the results obtained from the chemical analysis of NR-sulfur vulcanizates accelerated by 2-(morpholiniothio)benzothiazole.¹³

An interesting observation from this work was that crosslink formation appeared to occur in a first-order fashion, but only after the nearly complete disappearance of the accelerator and its apparent immediate reaction products with sulfur. In the formulation of the scheme, it was thus assumed that the accelerator and its immediate reaction products with sulfur actually inhibit the formation of crosslinks. The delay period should then largely depend on the time required for the disappearance of these species.^{14,15}

The basic scheme is shown in Scheme 1, where A is the accelerator and/or its reaction products (with sulfur, Zn^{2+} , etc.); B is a precursor to crosslinks, probably polymeric; B^* is an activated form of B , probably a free radical; Vu is a crosslink; and α and β are stoichiometric adjustments. Rubber is not used in the scheme because it is considered to be in excess and of constant concentration throughout the process. The model explains the long delay periods associated with accelerators such as the thiazoles sulfenamides; if the reaction through k_4 is much faster than that through k_3 , very little crosslink formation can occur until A is essentially depleted. Both the reaction through k_4 and that through k_3 are assumed to be much faster than the reaction through k_2 . Hence, the reaction through k_2 is the rate controlling step for crosslink formation after A is completely consumed.^{14,15}

The constant k_2 can be determined from oscillating disk rheometer tracings, assuming the formation of Vu to be first order in B . It is assumed that the

progress of cure (L_t , measured by the rheometer), corresponding to any period of vulcanization (t), is proportional to the concentration of Vu. Indeed, the increases in rheometer torque readings (L_t) are found to be proportional to the crosslink density as determined by swelling test measurements; however, the constant of proportionality (between L_t and Vu_t) changes with different types of stock.¹⁴ The following equation proposed by Cotten⁹ may be used for the evaluation of k_2 :

$$\ln \left[1 - \left(\frac{\Delta L_t}{\Delta L} \right) \right] = k_2 t \quad (1)$$

where L represents the maximum increase in rheometer torque observed at full cure or at t minutes, and k_2 is the rate constant for the crosslink reaction. The first-order nature of crosslink formation is not achieved immediately upon the onset of crosslink formation. The time required for the curvature in the plot to disappear, which is the time required for crosslinking to become an unperturbed first-order reaction, is assumed to be the time t_{display} required for the depletion of A . After t_{display} , a plot of eq. (1) gives a straight line and k_2 is then the negative slope of the straight line portion of the curve.^{14,15}

From the rheometer curves, the values of k_1 and k_2 can be obtained by means of the logarithm plot and a solution for eq. (2):

$$k_1 t_{\text{display}} - \ln k_1 = k_2 t_{\text{display}} - \ln k_2 \quad (2)$$

It has not been possible to evaluate the constants k_3 and k_4 separately; however, the ratio k_4/k_3 can be estimated. This ratio, which might be called the quenching ratio, is indicative of the tendency for an accelerator, or an early reaction product therefrom, to inhibit crosslinking. After simplifying assumptions, eq. (3) may be obtained^{14,15}:

$$\frac{k_4}{k_3} = - \left(\frac{M_A U}{C_A} \right) \left(\frac{\Delta L}{\Delta L_t} \right) \ln \left[\frac{k_2 \exp(k_1 t) - k_1 \exp(k_2 t)}{k_2 - k_1} \right] \quad (3)$$

where k_4/k_3' is the quenching ratio expressed as a dimensionless ratio of second-order rate constants, M_A is the accelerator molecular weight, C_A is the concentration of accelerator expressed in parts per 100 g of rubber (phr), and U is the number of "moles" of double bonds per 100 g of rubber. The k_4/k_3' ratio indicates the abruptness of the first-order crosslink formation onset.^{14,15}

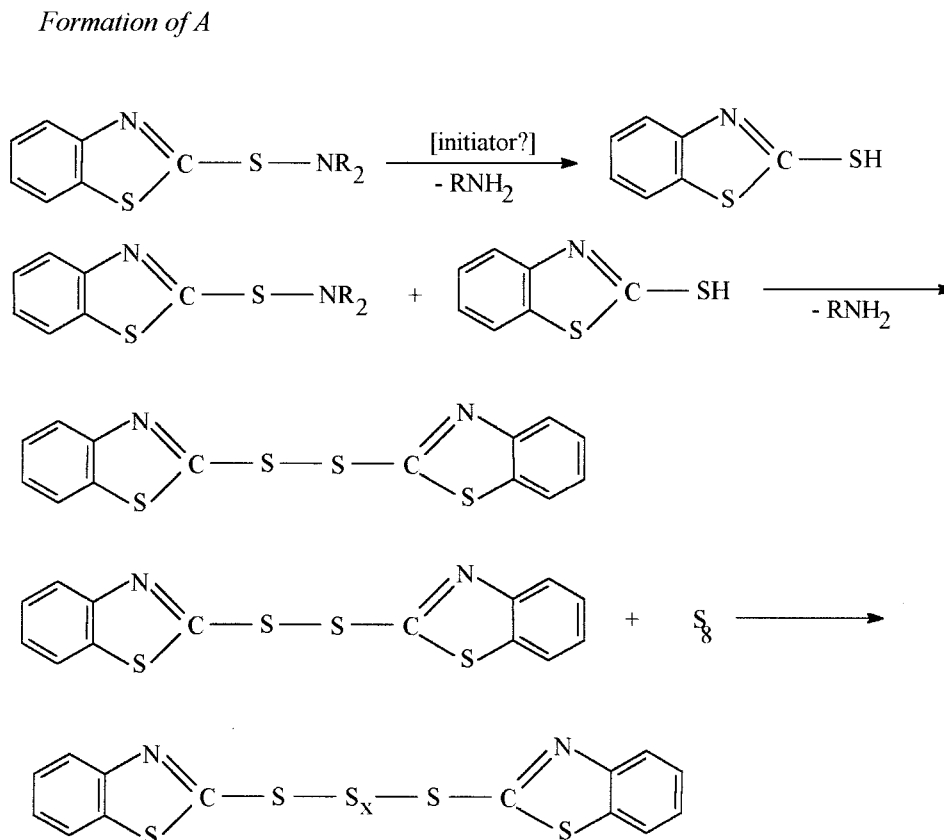
Based on the chemical analyses and kinetic studies, vulcanization with a sulfenamide accelerator can be written in more detail as shown in Scheme 2. Because the elaboration of the detailed model is based on several reactions, the treatment can be used in the study of specific stages of vulcanization. On the basis of the

model and treatment, the effects of the experimental conditions and compounding variables could be determined with respect to each of the rate constants.

The scorch delay, or induction period, is when the majority of the accelerator chemistry occurs. It should be noted that the length of the scorch delay period varies widely, depending on the accelerator. Sulfenamides have been claimed to function as accelerators by their dissociation into benzothiazolyl sulfonyl and amine radicals, which initiate the conversion of the eight-member sulfur ring into the active open chain sulfur. The initial reaction involves the decomposition of a portion of the sulfenamide accelerator. This step is likely to involve a reductive or hydrolytic (or both) cleavage of the sulfenamide ($-\text{S}-\text{N}-$) bond. The reducing agent may be elemental sulfur, thiolate, an electron-rich antidegradant, or moieties on the surface of a filler (e.g., CB). It may be mediated by zinc ions. The initiation reaction effectively liberates a quantity of amine and 2-mercaptobenzothiazole (MBT). The amine thus liberated can react with S_8 to generate an activated sulfur capable of either insertion or reduction reactions. The net changes observed in this step are the slight reduction in free sulfur and sulfenamide and the formation of MBT and amine.

During the induction step, there is a depletion of a large portion of the sulfenamide with the formation of accelerator polysulfides and disulfides, which occurs at this stage dominated by sulfur exchange reactions. The rate of sulfur-sulfenamide reaction and the stability of the intermediates seem to be the factors influencing the relative scorch delay and the acceleration rates shown by the sulfenamides. These factors are in turn determined by the basicity and the steric nature of the amine from which the sulfenamides are derived and by the sulfenamide/sulfur ratio used in the formulation. Accelerator polysulfides and disulfides formed in the induction step are depleted, liberating, most likely, 2-bisbenzothiazole-2,2'-disulfide (MBTS₂). The end of the activation period is marked by the nearly complete disappearance of the sulfenamide accelerator. After depletion of the sulfenamide, disulfides, and polysulfides, the polymer is sulfurated and crosslinked simultaneously (Scheme 2).^{16,17}

For Gradwell and McGill,¹⁸ who studied polyisoprene vulcanization with *N*-cyclohexylbenzothiazole sulfenamide (CBS), sulfur, and zinc oxide by heating in a differential scanning calorimetry (DSC) apparatus, the delayed action of the CBS accelerator is explained in terms of an exchange reaction between benzothiazole-terminated polysulfidic groups on the polymer chain and CBS to yield unreactive amine-terminated pendent groups and MBTS. MBTS reacts with sulfur to form 2-bisbenzothiazole-2,2'-polysulfides (MBTPs), which also form pendent groups. Crosslinks do not take place until all of the CBS has been consumed and pendent groups are no longer



Scheme 2 The Coran model^{14,15} for sulfenamide-accelerated vulcanization and the formation of A, B, B*, Vu, and side reactions.

deactivated. MBT is released only on crosslinking. When MBT is present in the formulation at the onset of the reaction, it will trap the released cyclohexylamine as CBS adds to the chain to form pendent groups. The MBT-amine salt participates in a reaction to regenerate MBTS, which thus will not be consumed in the vulcanization process. Zinc oxide does not react with CBS, and its role in increasing the crosslink density is attributed to its promoting crosslinking reactions between pendent groups and neighboring chains rather than intramolecular reactions, thus leading to cyclization.

EXPERIMENTAL

Materials and methods

Table I shows the formulation used to prepare the different compositions and the suppliers. The fillers were CB (N762) from Columbian Chemicals Brasil S.A., precipitated silica (Sil, Zeosil-175) from Rhodia Brasil Ltd., and the RHA supplied by Empresa Brasileira de Pesquisa Agropecuária. The ashes were milled for 5 h and sieved on a 325-mesh sieve before use.

The ashes were analyzed for chemical composition by inductively coupled plasma emission spectroscopy, and the results are shown in Table II. The particle size

distribution, surface area, and density for each of the four fillers are presented in Table III. These values were determined by using a Global Lab Image (SP0550) software package, an ASAP 2010 accelerated surface area and porosimetry system (through the Brunauer-Emmett-Teller method), and a glass pycnometer, respectively. The ASTM D 1512 method was followed to measure the pH.

Preparation of mixes and rheometry

Mixing was carried out on a two-roll mill at a speed ratio of 1:1.25 at 70°C, according to ASTM D 3182. The RHA was dried at 120°C for 24 h immediately before use. All fillers were incorporated into the NR in loadings ranging from 0 to 50 phr, and a TI-100 curometer (Tecnologia Industrial) was used at a $\pm 3^\circ$ arc. The sample history was found to influence the shape of the rheometer torque curve. Therefore, all samples were allowed to rest for 24–72 h after compounding. Torque-time curves were registered at a vulcanization temperature of 150°C. Three samples of each mix were analyzed and the rheometric data were used to calculate the different constants, according to the Coran model.

TABLE I
Typical Formulations

Material	Supplier	phr
Natural rubber	Celsoft Industrial e Comercial Ltd.	100
Zinc oxide	Reference standard reagent	3.5
Carbon black	Columbian Chemicals Brasil S. A.	0–50
Silica	Rhodia Brasil Ltd.	0–50
Rice husk ashes	EMBRAPA ^a	0–50
Stearic acid	Reference standard reagent	2.5
CBS ^b	Bann Quimica Ltd.	0.8
Aminox ^c	Uniroyal Chemical Company	2.0
Sulfur	Vetec Quimica Fina Ltd.	2.5

^a Empresa Brasileira de Pesquisa Agropecuária.

^b *N*-Cyclohexyl-2-benzothiazole-2-sulfenamide.

^c Antioxidant: low temperature reaction product of diphenylamine and acetone.

RESULTS AND DISCUSSION

The values of the optimum cure time (t_{90}), minimum torque (M_l), and maximum torque (M_h) of BRHA, WRHA, silica, and CB–NR mixes at 150°C are shown in Table IV. For the t_{90} value it can be observed that, compared to pure gum, WRHA accelerates the vulcanization process whereas BRHA and CB do not interfere in this parameter.

Fillers are known to influence the crosslinking reaction during vulcanization. In most cases the cause for retardation can be traced to the greater or lesser acidity of the filler (indicated to some extent by the pH of its aqueous slurry, Table III), which does influence the kinetics of the crosslinking reaction. Silica imparts a somewhat different behavior as the t_{90} increases with increasing amounts of filler. Silica has a number of hydroxyl groups on the surface, which results in strong filler–filler interactions, as well as adsorption of polar materials on the surface; thus, the dispersion of silica in rubber compounds is more difficult than that of CB. The highly polar surface of silica makes hydrogen bonding with polar materials possible and can lead to the adsorption of curatives by silica, thereby resulting in extension of the scorch time and reduction

TABLE II
Chemical Composition of Rice Husk Ash

Chemical Composition (%)	BRHA	WRHA
CaO	0.40	0.77
MgO	0.38	0.53
Fe ₂ O ₃	0.13	0.25
K ₂ O	1.22	1.05
Na ₂ O	0.13	0.30
Al ₂ O ₃	0.23	0.27
MnO	0.16	0.14
TiO ₂	0.01	0.01
P ₂ O ₅	0.96	1.00
SiO ₂	74.85	97.00
Loss on ignition	21.00	0.20

TABLE III
Physical Properties of Rice Husk Ash, Silica, and Carbon Black

Properties	BRHA	WRHA	Silica	Carbon Black
Mean particle size (μm)	2.5	2.2	0.018	0.054
Surface area (m^2/g)	109	17	185	30
Micropore area				
m^2/g	88.2	1.8	48.3	3.7
%	80.1	22.6	31.0	12.5
Density (g/cm^3)	1.9	2.0	2.0	1.9
pH	9.5	9.4	6.5	6.4

of ΔL (the difference between maximum and minimum torques).

In this article, the aim is the analysis of the rheographs of the gum and filled systems by using the Coran model^{14,15} to investigate the possibility of catalytic activity of the fillers. The plots of eq. (1) for the different fillers are shown in Figures 1–4 and the results of k_2 , estimated from the negative slope of the

TABLE IV
Optimum Cure Time (t_{90}) and Minimum and Maximum Torque for BRHA, WRHA, silica, and Carbon Black Filled NR Vulcanizates at 150°C

Filler Loading	Torque (dN m)		t_{90} (min)
	Min.	Max.	
0	4.9	41.6	11.9
NR-WRHA			
10	1.6	45.0	10.1
20	1.8	46.8	8.9
30	2.6	48.2	8.8
40	3.2	51.5	8.7
50	4.6	55.2	8.32
NR-BRHA			
10	2.2	47.2	11.9
20	3.1	47.6	12.2
30	3.6	48.6	12.6
40	3.9	48.8	13.6
50	4.3	49.2	13.8
NR-Carbon Black			
10	6.2	54.4	10.5
20	8.1	56.9	10.6
30	9.5	58.3	10.6
40	10.1	64.4	10.8
50	11.4	64.9	10.8
NR-Silica			
10	8.8	43.5	14.4
20	10.6	45.0	24.6
30	13.8	47.5	53.4
40	17.8	49.9	64.2
50	23.0	52.8	63.0

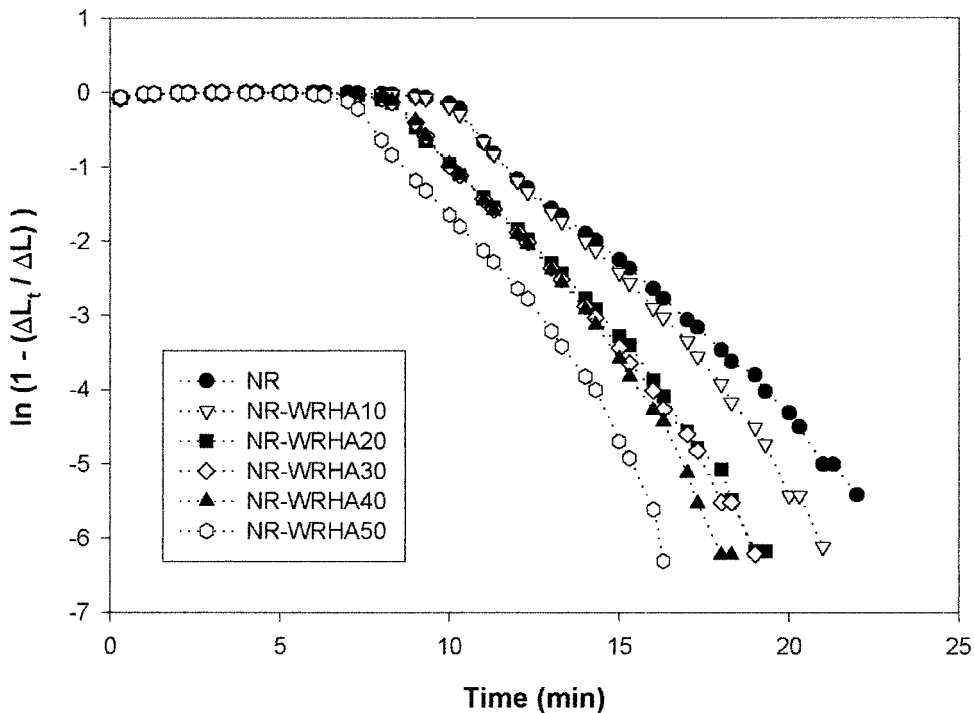


Figure 1 A plot for the estimation of k_2 for WRHA filled NR compounds at 150°C.

straight portion of the curve, are summarized in Figure 5. The $t_{display}$ required for the depletion of A (Scheme 2) and for crosslinking to become an unperturbed first-order process can also be estimated for each composition. A positive variation in k_2 has two effects: an increased specific rate for the crosslink formation and a shorter delay period.

From Figures 1 and 5 it can be noted that for the WHRA-NR compounds there is a remarkable increase in k_2 as the filler loading increases. WRHA is constituted of 97% silica, the loss on ignition is only 0.20%, and the oxide content is 19.3% larger than in BRHA (see Table II). The presence of impurities, which occur in the form of metallic oxides or silicates, and a small surface area for

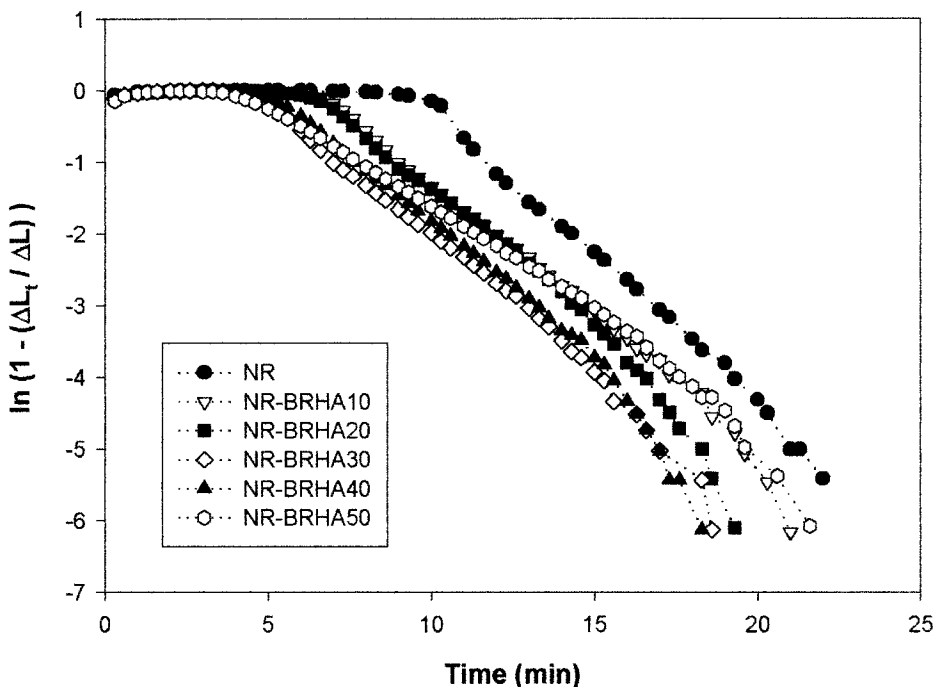


Figure 2 A plot for the estimation of k_2 for BRHA filled NR compounds at 150°C.

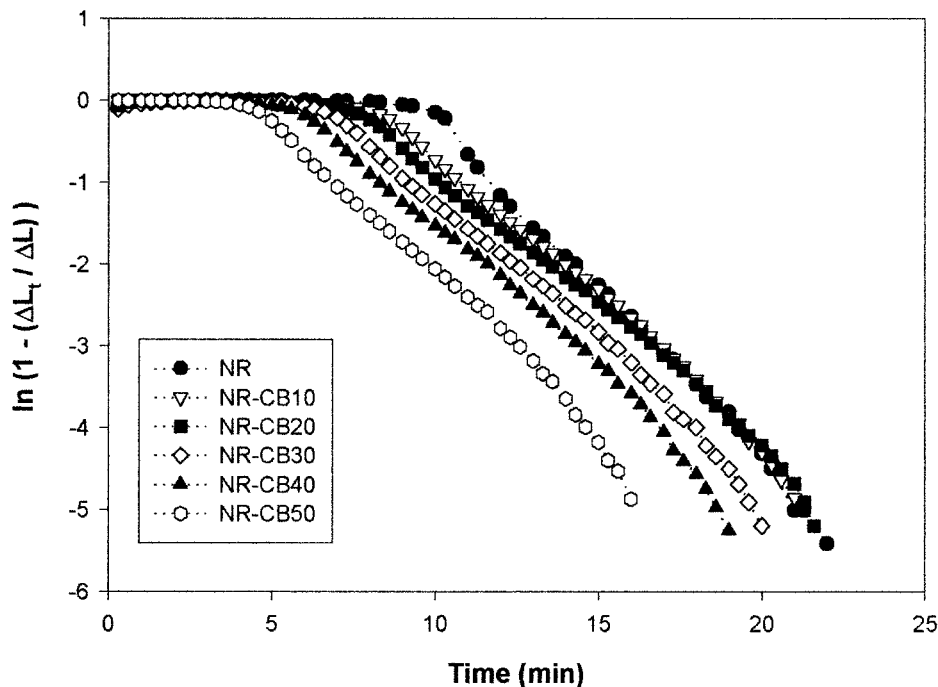


Figure 3 A plot for the estimation of k_2 for CB filled NR compounds at 150°C.

interaction with rubber might be responsible for the catalytic effect of this ash on NR vulcanization.

The presence of ZnO in formulations is recognized as being important for attaining vulcanizates with good physical properties. However, undoubtedly, the single most intriguing species in the vulcanization literature is the sulfur-rich zinc accelerator complex.

From as early as 1921, such complexes have been suggested to exist, being formed at higher temperatures when zinc accelerator complexes, notably zinc dithiocarbamates and mercaptobenzothiazolates, incorporate one or more sulfur atoms. Such complexes are solubilized and made reactive through the action of ligands derived from accelerators (amines from

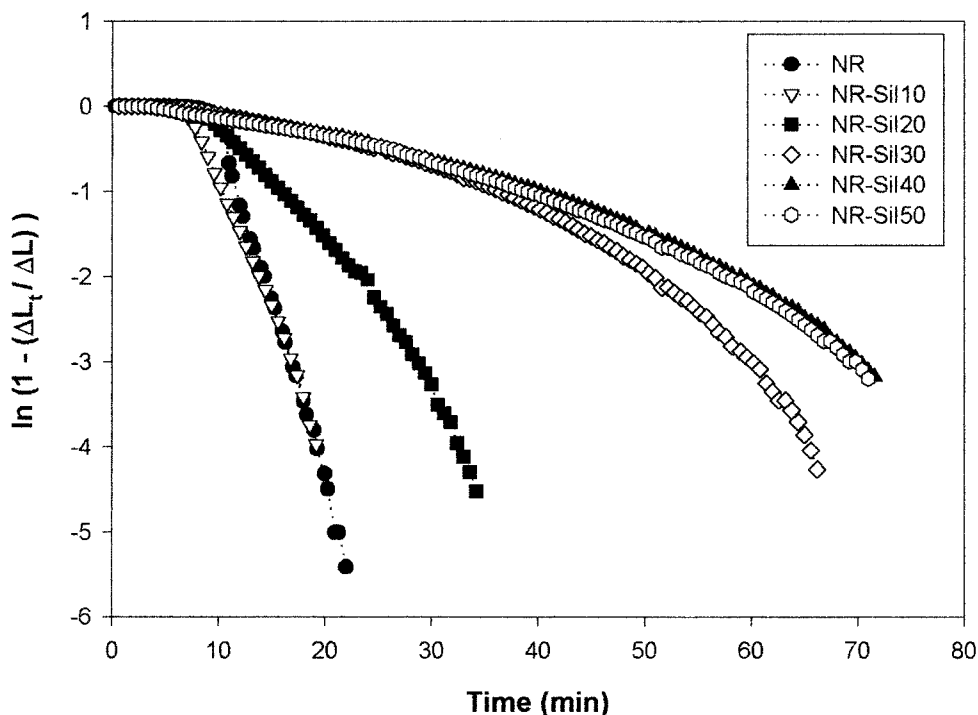


Figure 4 A plot for the estimation of k_2 for silica filled NR compounds at 150°C.

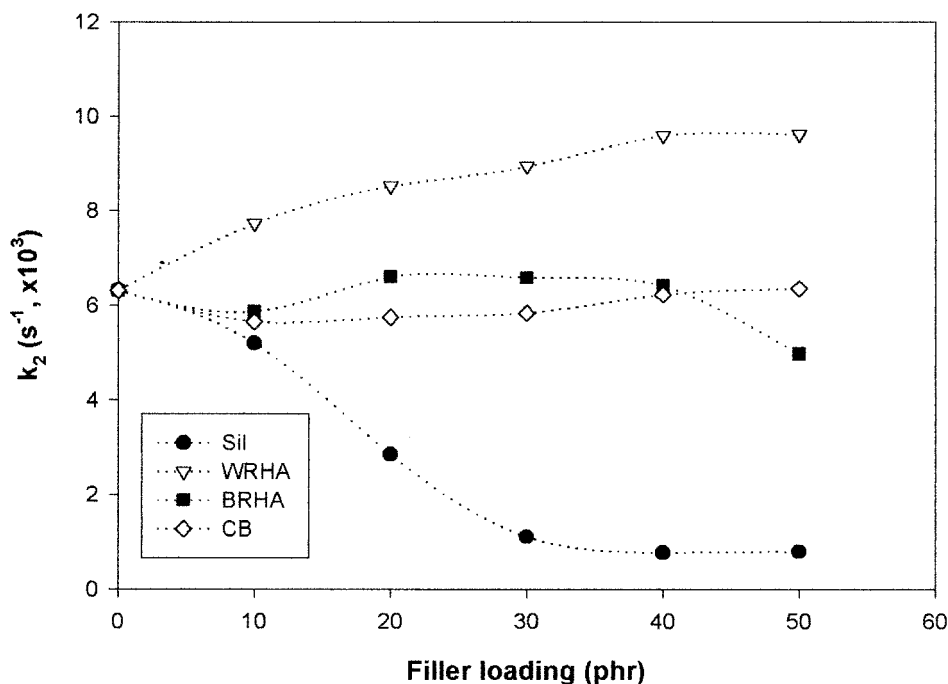


Figure 5 The evaluation of the k_2 constant for filler loading at 150°C.

sulfenamides), activators (stearic acid or zinc stearate), or secondary accelerators such as amines, amides, ureas, and guanidines. These species have remained intriguing because they have always defied detection; any evidence for their existence is indirect and challengeable. Nevertheless, sulfur-rich zinc accelerator complexes are attributed a central role in any vulcanization scheme. They are claimed to activate elemental sulfur, assist in the exchange and transport of sulfur atoms throughout the vulcanizing rubber, and affect the formation of sulfur crosslinks.^{19–21}

Substitution of zinc by other metals may alter the efficiency of crosslinking. Versloot et al.²¹ studied the mechanism of the sulfur vulcanization of rubber using 2,3-dimethyl-2-butene as a simple, low-molecular model alkene, with a mixture of various metal oxides instead of zinc oxide. They concluded that, in the presence of organic accelerators based on tetraalkylthiuram disulfides, zinc oxide is still the best activator.

Metallic complexes of dimethyldithiocarbamate [$M(\text{dmtc})_2$ complexes], in which M stands for Cd, Cu, Pb, or Ni, are not good substitutes for zinc complexes. The ethyl analogs, however, can certainly be applied in the vulcanization process as an alternative for the zinc complexes, because they show comparable or better reactivity. However, it is unlikely that cadmium complexes will be used as a replacement for zinc, because of their high toxicity. Copper and lead complexes can be useful replacements if a given vulcanization process is too fast and one wants to lower the reaction rate (alternative vulcanization retarders).

Russel et al.²² used a number of different metal oxides in molar basis substitution for zinc oxide in an efficient vulcanization system. It was observed that no single oxide was more efficient than zinc oxide, but some oxides did show a small improvement when used in conjunction with zinc oxide. Thus, in the present case, the presence of impurities such as metallic oxides or silicates in the WRHA chemical composition, together with ZnO, may account for the synergic effect resulting in an increase in k_2 with filler loading (e.g., in 50 phr of WRHA, the content in metallic oxides or silicates is 2.16 phr).

In Figures 2 and 5 it can be noted that, for the BRHA-NR compounds, the k_2 value changes very little between 10 and 40 phr and then suddenly decreases. Attention must be paid to the dual nature of BRHA, which is attributable to the presence of both silica and carbon components with different physical and chemical properties. In our previous studies,^{10,11} we noted that the influence of this filler on the overall rate values was similar to that of CB. BRHA is an extremely porous material, and this can be noticed from the discrepancy between the particle size and surface area as given in Table III. The surface area for BRHA is 109 m²/g but the pores collaborate with 80.1% of this value. The presence of pores can result in cure retardation because of higher levels of adsorption and inactivation of rubber curatives becoming entrapped in the cavities. Thus, the small catalytic effect given by BRHA is counterbalanced by the inactivation of the curatives when this filler is present in large amounts.

For CB it can be observed (Figs. 3, 5) that the k_2 constant decreases with small loadings but then starts to increase gradually with additional loadings. Cotten⁹ observed that oxygen-containing groups at the CB surface exert a profound effect on the rate of cure (k_2) and on the maximum increase in torque (ΔL) when tested in NR formulations containing a CBS/sulfur curing system. However, this is not a general pattern because no effect of surface groups on sulfurless TMTD cure was observed, and the rate constant k_2 was the same for all blacks. In the study of Bhowmick and De,²³ it was observed that the addition of HAF black remarkably increases the proportion of polysulfidic crosslinks from about 20 to over 50% in an efficient vulcanization system for curing temperatures of 150 and 180°C. Although the increase in the crosslink density in the filled system can be attributed to increased polymer–filler attachment, which gives rise to restricted swelling in solvents, Bhowmick and De²³ point out that the CB surface may catalyze the sulfuration processes and the observed increase in crosslink density may be due to the increase in covalent crosslinks, not merely to polymer–filler attachment.

Pal et al.²⁴ observed that in the case of the HAF black filled conventional system accelerated by CBS, both the crosslink density and polysulfidic crosslinks pass through a maximum with the increase in cure time. Apart from this, it was very worthwhile to note that the overall crosslink density and proportion of polysulfidic crosslinks increased 0–5 phr in the presence of HAF black in the conventional system. Further addition of HAF black did not significantly change the network structure. This observation showed that reinforcing black filler at 5 phr loading catalyzes the sulfuration process and that higher loadings do not have any further effect on the sulfuration process and, eventually, on the network structure in the conventional system.

For silica (Sil) it is observed through Figures 4 and 5 that there is a lowering of the k_2 values with increasing filler loading. In addition, for loadings higher than 20 phr the curve in Figure 5 exhibits deviations from the proposed linear mathematical model, which are more pronounced than those found with RHAs and CB. Lowering of the k_2 values was also obtained by Pal et al.²⁴ and Coran²⁵ with low sulfur vulcanization systems, which was attributed to the shortening of the sulfur chain in the crosslink precursor. This would induce stability against the homolytic cleavage of S—S bonds (initiation) or a thiyl radical exchange reaction (propagation). In Parts I and II^{10,11} of this study we applied the reasoning of Mukhopadhyay and De,²⁶ who suggested that the most plausible explanation for the specific action of silica would be the occurrence of an ion exchange reaction on the silica surface between the silanol groups and zinc stearate. In such a reaction,

stearic acid is liberated, which then solubilizes more zinc oxide and modifies the silica surface.

McGill and Shelver²⁷ observed that, in the absence of rubber, benzoic and stearic acids react with MBTS and its polysulfides (MBTP) at vulcanization temperatures to form the acid-accelerator complexes 2-benzoylthiobenzothiazole (BzM) and stearicthiobenzothiazole (StM), respectively. The destruction of MBTP by carboxylic acids will reduce the concentration of accelerator polysulfides (formation of A, Scheme 2) available in the compounds and should impact negatively on vulcanization. In another investigation, McGill and Shelver²⁸ show that, when polyisoprene is vulcanized with MBTS/sulfur in the absence of ZnO and in the presence or absence of benzoic and stearic acids, the crosslink density of MBTS vulcanizates is halved by the addition of carboxylic acids. This can be explained in terms of the attack of the acids on the accelerator polysulfides.

Otherwise, when benzoic and stearic acids were heated with MBTS/sulfur/ZnO isothermally at 150°C in the absence of rubber, the acids readily reacted with ZnO and, at vulcanization temperatures, little or no free acid remained. The zinc salts are less reactive toward the accelerators and accelerator polysulfides than are the acids; thus, in the presence of ZnO, carboxylic acids should not have a detrimental effect on the vulcanization reaction.²⁹ McGill and Shelver³⁰ also investigated the effect of benzoic and stearic acids on MBTS and TMTD-accelerated sulfur vulcanization of polyisoprene compounds containing ZnO at 150°C. In the presence of ZnO, the acids are rapidly converted to their zinc salts that, unlike the acids, do not attack the accelerator polysulfides but instead promote vulcanization. Zinc salts do not affect the addition of accelerator polysulfides to the chain, but the rate of crosslinking through the pendent groups is facilitated.

Because compounds containing reinforcing fillers like silica must be processed and compounded in a different manner than unfilled gums or even CB loaded rubbers, which is with the aid of additional ingredients like amines or glycols to neutralize the silica acidity responsible for cure retardation [e.g., poly(ethylene glycol) is used to prevent the adsorption of curatives on the silica surface], a little increase in silica loading is sufficient to cause a negative effect on NR vulcanization, leading to low values for the specific rate of crosslink formation (k_2). Although a current practice, this acidity correction was not done in this work.

The t_{display} required for the depletion of A (Scheme 1) and k_1 results for the different fillers are shown in Figures 6 and 7, respectively. The t_{display} is the time at which the vulcanization process becomes an unperurbed first-order process, and an increase in k_1 shortens the delay period with no other major change in the vulcanization. It can be observed in Figure 7 that the k_1 value for the unfilled compound is lower than that for

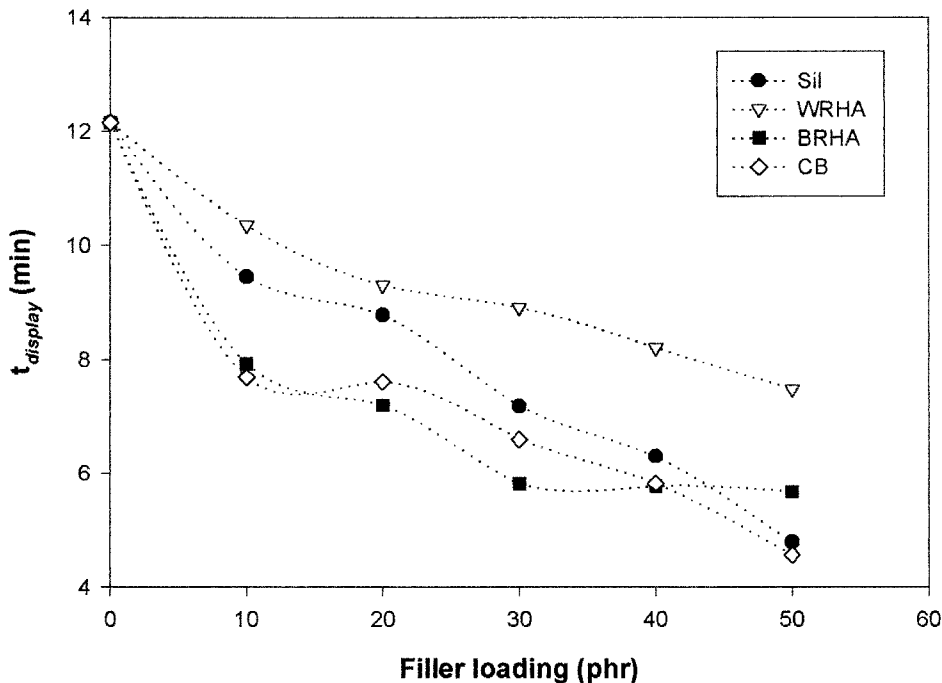


Figure 6 The evaluation of the $t_{display}$ for filler loading at 150°C.

the filled ones. This results in a faster formation of crosslink precursors in the filled than in the gum compound.

BRHA and CB filled NR compounds have similar behavior with regard to either $t_{display}$ or k_1 values as the filler loading is increased, but now we must consider a different reasoning. BRHA is extremely porous

and k_1 values increase despite the filler porosity (adsorption and inactivation of rubber curatives entrapped in the cavities of the filler). However, this does not represent a positive effect upon crosslink formation as verified in previous investigations.^{10,11} According to Bhowmick and De,²³ CB filled NR compounds show an increase in the specific rate of

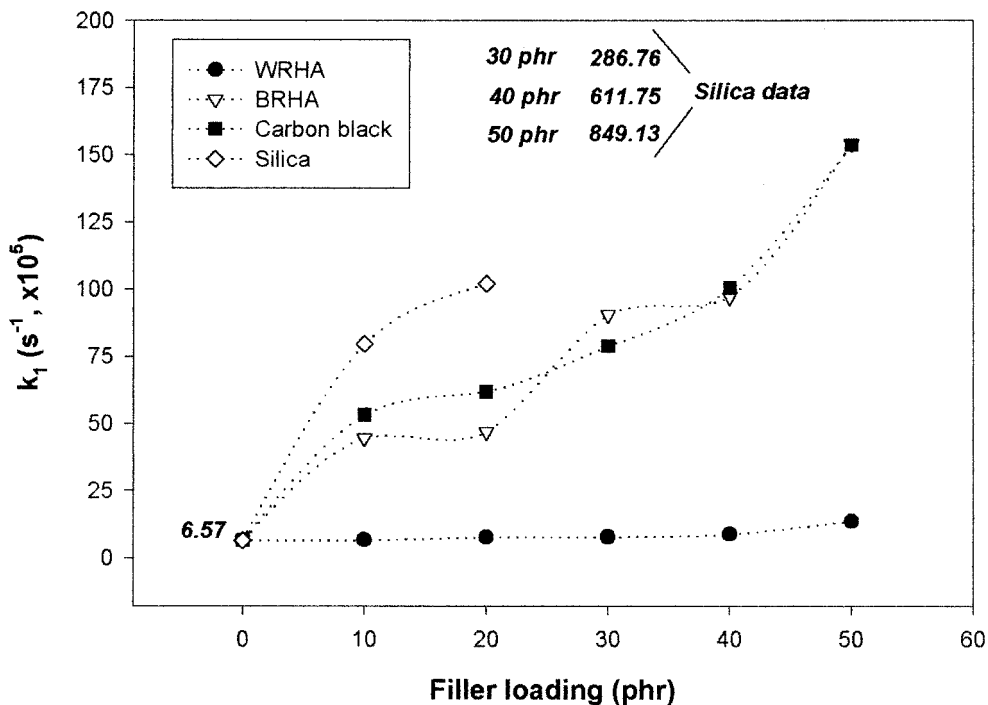


Figure 7 The evaluation of the k_1 constant for filler loading at 150°C.

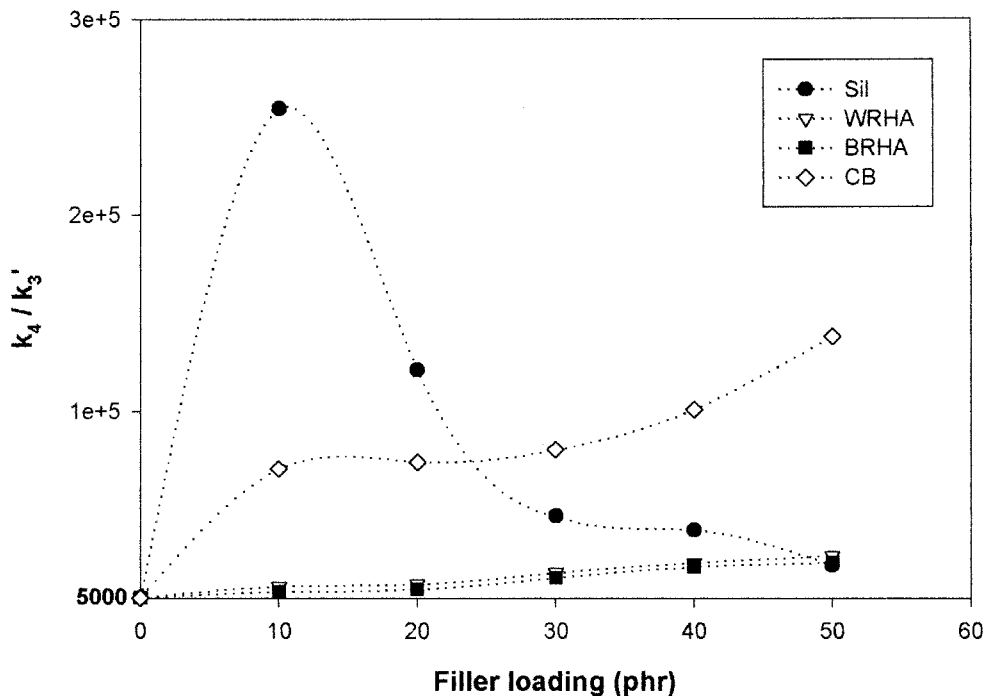


Figure 8 The evaluation of the k_4/k_3' ratio for filler loading at 150°C.

crosslink formation and a decrease in the delay period, but this does not in any way change the mechanism of the reaction. In other words, the effect that CB has on the accelerated sulfur vulcanization is purely catalytic. The increase of k_1 with the addition of filler indicates faster formation of the crosslink precursor (Scheme 2).

For silica filled NR compounds, there is a smooth decrease in t_{display} (Fig. 6) similar to WRHA compounds up to 20 phr; but then the values decrease abruptly, which shows that this reaction step is much faster for higher silica loading, as seen from the k_1 plot in Figure 7. As suggested by Mukhopadhyay and De,²⁶ there is an ion exchange reaction on the silica surface between silanol groups and zinc stearate, in which stearic acid is liberated. Coran²⁵ conducted kinetic studies with MBTS and CBS acceleration and shows that the initial rate-controlling step, characterized by k_1 , becomes faster with increasing stearic acid concentration, but the rate of crosslink formation (controlled by the reaction step characterized by k_2) decreases. As already explained, large k_1 values but small k_2 values for silica filled NR compounds are consistent with the negative effect upon vulcanization as shown by rheometric dates (increase in t_{90}).

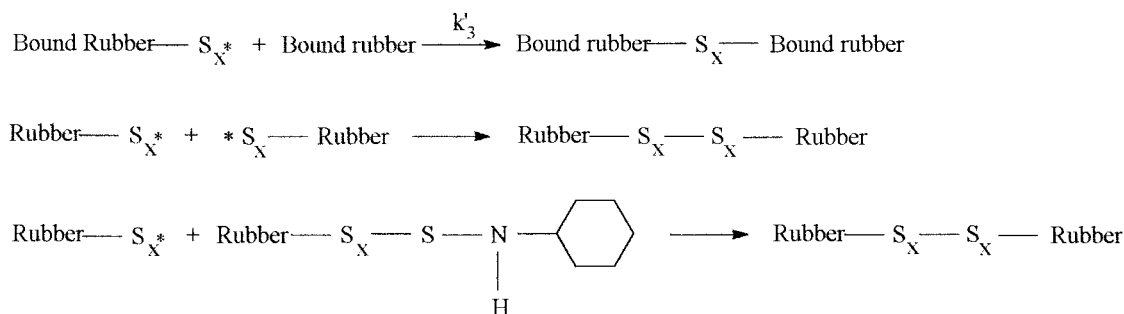
The delayed action in a vulcanization process is a "clock reaction" where starting materials or early formed intermediates (monomeric polysulfides) inhibit the reactions of later formed intermediates (polymeric polythiyl radicals) to form product (crosslinks). Crosslink formation is inhibited by the presence of monomeric polysulfide reaction products from the accelerator and sulfur (Scheme 2).

The k_4/k_3' results for the different fillers are shown in Figure 8. This ratio is a measure of the abruptness of the start of crosslink formation. If the changes are restricted to the k_4/k_3' ratio, compounded stocks exhibiting larger ratio values would be expected to exhibit longer scorch delay periods because of the increased ability of the accelerator and/or its initial reaction products with sulfur to quench the immediate precursor to crosslink formation¹⁴ (Scheme 2).

From Figure 8 it can be observed that k_4/k_3' ratios for WRHA and BRHA filled NR compositions are very close and do not change significantly with filler loading. For silica compositions there is a rapid increase up to 10 phr and a posterior decrease. The adsorption of curatives by silica results in long scorch times and reduced ΔL . The deleterious effect of silica upon the vulcanization can explain the anomalies found for the k_4/k_3' ratio.

There is a gradual increase in the ratio with filler loading for CB compositions. Pal et al.²⁴ verified that the k_4/k_3' ratio, which may be considered as a measure of the preference of the radical (rubber- S_x) either to be quenched by monomeric polysulfide or to form a crosslink with another rubber molecule, is greater in the conventional cure system. The high values of k_4/k_3' found in the present investigation, especially for higher loadings of CB, indicate that the reaction involving k_4 is preferred to a greater extent and that very little crosslink formation will occur until A is essentially depleted (Schemes 2, 3).

Addition of CB increases the bound rubber content and thus slows down k_3' ; but at a higher concentration



Scheme 3 The effect of carbon black on bound rubber.²⁴

of rubber- S_x , the polymeric thiyl radical may react as shown in Scheme 3. This would increase the polysulfidic concentration. The enhancement of polysulfidic crosslinks with the addition of black could thus be explained. At higher loadings of filler, rubber-filler attachment overshadows the network structure and the properties become independent of the vulcanization system and are governed by the filler concentration.²⁴

CONCLUSIONS

A specific model for the vulcanization process accelerated by CBS was used in order to investigate the real role of WRHA in crosslink formation using the data from an oscillating disk rheometer. The different kinetic constants were calculated and the effect of RHA was interpreted in accordance with a simple sequential reaction scheme proposed by Coran.¹⁴

For WHRA filled NR compounds there is a remarkable increase in the k_2 rate constant as filler loading is increased. The presence of impurities, which occur in the form of metallic oxides or silicates, and a small surface area for interaction with rubber might be responsible for the catalytic effect of this filler on NR vulcanization. For the k_1 rate constant and the k_4/k_3' ratio, no significant change was found with filler loading. Thus, as verified in previous studies,^{10,11} WRHA may accelerate the vulcanization process in NR compounds in the presence of zinc oxide whereas BRHA filler does not have any catalytic effect or has only a minor extension. As for the commercial fillers, CB and silica show the expected behaviors, in accordance with the literature.

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