

Rice Husk Ash Filled Natural Rubber. I. Overall Rate Constant Determination for the Vulcanization Process from Rheometric Data

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ABSTRACT: Black rice husk ash (BRHA) and white rice husk ash (WRHA) were incorporated into natural rubber (NR) using a laboratory-size two-roll mill. A conventional vulcanization system (CV) was chosen and cure studies were carried out on a TI-100 Curometer. The torque curves were obtained at 150, 160, 170, and 180°C. The overall rate and the apparent activation energy for the vulcanization process were calculated for each compound assuming that vulcanization follows first-order kinetics. For comparison

purposes, two commercial fillers, precipitated silica (Zeosil-175) and carbon black (N762), were also used. It was observed that addition of WRHA to NR compounds increased the cross-linking rate and lowered the apparent activation energy more markedly than the other fillers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1194–1203, 2003

Key words: rubber; kinetics; vulcanization

INTRODUCTION

Rice husk ash (RHA) is an agricultural waste, available in very large quantities throughout the world. Rice husk, which essentially functions as a protection to the rice grain, contains ~50–60% fixed carbon, the rest of it being silica and a variety of oxides in minor quantities. The ash obtained by burning the organic matter contained in the husk has a high melting point and porosity. Chemical analyses show that the ash may primarily be highly pure silica and that no metal constituents are present in sufficient quantities to cause deleterious effects on aging of the rubber vulcanizates.¹

In recent years, considerable efforts have been made to utilize the silicon-rich RHA for making cement and also as a source for metallurgical- and semiconductor-grade silicon.^{2–4} RHA applications in rubbers and plastics have also been mentioned by Haxo and Mehta¹ and, more recently, by Costa et al.^{5,6} Investigation on the fatigue behavior of epoxidized natural rubber (ENR) vulcanizates⁷ and the effect of partial replacement of silica by RHA in natural rubber composites⁸ were also recently proposed. It was observed that RHA reduced the fatigue life of ENR vulcanizates more drastically than carbon black (grade N330) and that the optimum RHA/silica weight ratio to assure

maximum enhancement of tensile and tear strengths was 20/30 (phr/phr). Nevertheless, a study on the kinetics of sulfur vulcanization of RHA-filled rubber compounds has to date never been considered.

Common techniques used to study rubber vulcanization include differential scanning calorimetry (DSC), chemical analysis, and oscillating disk rheometry (cure meter). The DSC technique is based on the assumption that the heat of reaction is related uniquely to the cross-linking reaction and is proportional to the extent of reaction. This assumption is questionable for a complex system. A chemical analysis involves a number of chemical reactions and, thus, is very time consuming. The cure meter is based on the fact that cross-linking density is proportional to the rubber stiffness.

In this paper we discuss the cure behavior of RHA-filled NR vulcanizates. Assuming that vulcanization follows first-order kinetics and using the Arrhenius equation, the overall rate and the apparent energy of the vulcanization were calculated using rheometer isotherms at different temperatures. For comparison purposes, two commercial fillers, silica and carbon black, were also used.

EXPERIMENTAL

Materials and compounding

All materials were used as received. Natural rubber (NR) was supplied by Irwin Indústria e Comercial Ltda and raw rice husk ash (RHA) by EMBRAPA

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TABLE I
Typical Formulation

Material	phr
Natural rubber	100
Zinc oxide	3.5
Filler	0–50
Stearic acid	2.5
CBS ^a	0.8
Aminox ^b	2.0
Sulfur	2.5

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

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

(Empresa Brasileira de Pesquisa Agropecuária). Carbon black (N762) was supplied by Columbian Chemicals Brasil S.A., and precipitated silica (Zeosil-175) by Rhodia Brasil Ltda. The antioxidant, Aminox, was supplied by Uniroyal Química S.A. Other compounding ingredients, such as zinc oxide, stearic acid, sulfur, and accelerator, were of reagent grade.

RHA was milled for 5 h and sieved on a 325-mesh sieve and will be referred to as either BRHA (black rice husk ash) or WRHA (white rice husk ash). These two ashes owe their differences to the burning conditions under which they are obtained. As, usual, the husks are burned in the open air, outside the rice mills; two types of fillers are formed. The upper layer of the husk mound is subjected to open burning and lower temperatures and yields BRHA in the form of a carbonized layer. The inner layer of the mound, being subjected to higher temperatures, yields WRHA.⁶

The formulation shown in Table I was employed to prepare the different compositions for evaluation of curing at different temperatures. Chemical composition was obtained by inductively coupled plasma emission spectroscopy. Particle size distribution was determined by using a GLOBAL LAB Image (SP0550) software package. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method, on an ASAP 2010 accelerated surface area and porosimetry system. Fillers densities were measured in a glass pycnometer, and pH was determined by the ASTM D 1512 method. The chemical and physical properties of BRHA, WRHA, silica, and carbon black are presented in Tables II and III.

Preparation of mixes and rheometry

Mixing was carried out on a two-roll mill at speed ratio of 1:1.25 at 70°C, according to ASTM D 3182. RHA was dried at 120°C, for 24 h, immediately before use. All fillers were incorporated into NR in loadings up to 50 phr, and a TI-100 Curometer, from Tecnología Industrial, was used at ±3°arc. Torque–time curves were registered at vulcanization temperatures of 150, 160, 170, and 180°C. For each temperature, three sam-

ples of each mix were analyzed, and the rheometric data were used to calculate the apparent activation energy.

RESULTS AND DISCUSSION

Sulfur vulcanization

Vulcanization consists of the formation of a molecular network by a chemical tying together of independent chain molecules. The resulting rubber chains retract forcibly to approximately their original shape after large mechanically imposed deformations. Vulcanization is thus an intermolecular reaction that causes an increase in the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force; that is, it increases elasticity while decreasing plasticity.⁹

The general course of vulcanization is described as follows (see Figure 1). First, an active accelerator complex is formed by some prior interaction between the accelerator and the activator in the presence of soluble zinc. This complex can react with molecular sulfur to form a sulfurating agent by the opening of the S₈ ring and its introduction into the complex structure.¹⁰ The existence of these complexes was detected chemically^{11,12} and also by combined nuclear magnetic resonance (NMR) and high-performance liquid chromatography (HPLC) analysis.¹³

Second, a sulfurating agent can react with rubber chains to form a cross-linking precursor. The precursor was identified by experimental evidence^{14,15} as an accelerator-terminated polysulfidic pendant group attached to the rubber chain.

Precursors subsequently undergo the formation of polysulfidic cross-links. In the mean time, loss of cross-linking efficiency may also take place due to decomposition and desulfuration of precursors.^{14,16} Because of the side reactions, formation of cyclic sulfide, conjugated dienes, trienes, ZnS, and a monosulfidic pendant group were observed. These resulting species are not able to contribute to cross-links. The

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 (silica)	74.85	97.00
Loss on ignition (LOI)	21.00	0.20

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

Property	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
Average pore diameter (\AA)	33.0	147.4	93.5	96.4
Micropore area (m^2/g)	88.2	1.8	48.3	3.7
% Micropore area	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

activity, concentration of zinc–accelerator complexes,^{15,17} and temperature play the central role in the competition among the above possible reactions routes.

Finally, the initially formed network matures and, during this process, similar desulfuration (cross-link shortening, eventually leading to monosulfidic cross-links) and decomposition of polysulfidic cross-links take place. In addition, a sulfur exchange reaction mechanism was proposed^{18,19} for the desulfuration process.

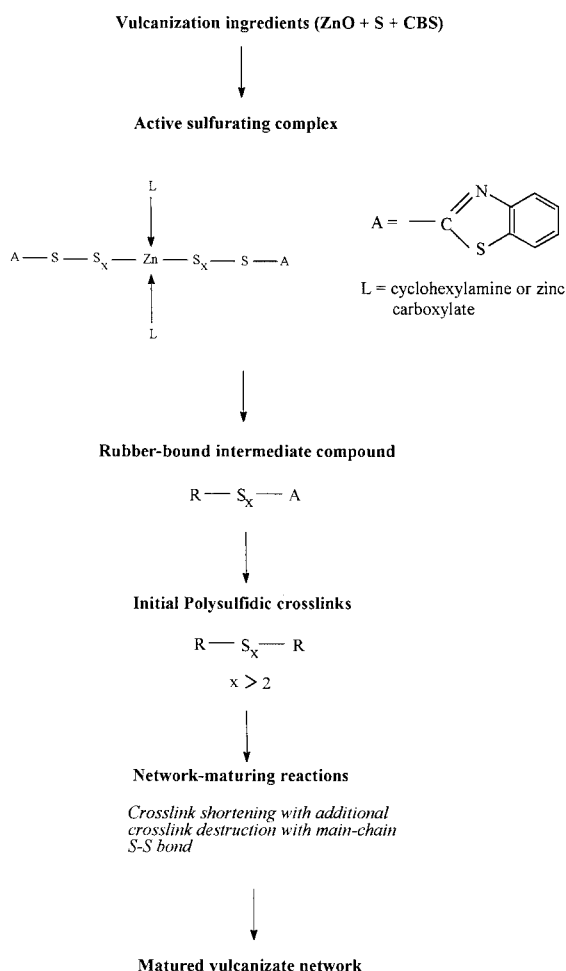


Figure 1 General reaction scheme for accelerated sulfur vulcanization.²⁰

Vulcanization rate from rheometer data

It was shown that increases in the rheometer torque values are directly related to cross-link density.²¹ Assuming first-order kinetics, the expression for vulcanization can be written in terms of torque as follows:

$$\ln \left(\frac{M_h - M_t}{M_h - M_l} \right) = kt \quad (1)$$

where M_t is the torque at a time t ; M_l and M_h represent minimum and maximum torques, respectively; and k is the rate constant for the vulcanization. Because the rate in the early stages reflects the character of the main forward reaction, M_t values at 25 and 45% torque changes were chosen to estimate the rate constants in this work.²¹ A combination of the Arrhenius equation and eq. 1 gives the convenient eq. 2 for determination of the apparent activation energy using rheometer data from isothermal runs, at different temperatures:

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

where $(t_{45\%} - t_{25\%})_\alpha$ and $(t_{45\%} - t_{25\%})_\beta$ are the time lags related to the torque changes from 25 to 45%, at temperatures T_α and T_β , respectively.

The variations of optimum cure time (t_{90}), minimum torque (M_l), and maximum torque (M_h) of BRHA-, WRHA-, silica-, and carbon black-NR vulcanizates at different temperatures are shown in Tables IV–VII.

The marked increment in minimum and maximum torques with increasing filler loadings indicates that the presence of fillers in the rubber matrix reduces the mobility of the macromolecular chains. The high values of maximum torque for carbon black and silica composites are the result of high restrictions to molecular motion imposed to the macromolecules because, probably, of the greater interaction between these commercial fillers and the rubber matrix. It is believed that smaller filler particle size, hence larger surface area, leads to a greater interaction, thus imposing an extra resistance to the flow of the resulting material.

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

Vulcanizate	Filler loading	Minimum torque (dN · m)	Maximum torque (dN · m)	Optimum Cure Time, t_{90} (min)
NR	0	4.9	41.6	11.86
NR-WRHA	10	1.6	45.0	10.06
	20	1.8	46.8	8.92
	30	2.6	48.2	8.76
	40	3.2	51.5	8.72
	50	4.6	55.2	8.32
NR-BRHA	10	2.2	47.2	11.86
	20	3.1	47.6	12.20
	30	3.6	48.6	12.60
	40	3.9	48.8	13.56
	50	4.3	49.2	13.80
NR-Carbon black	10	6.2	54.4	10.52
	20	8.1	56.9	10.56
	30	9.5	58.3	10.60
	40	10.1	64.4	10.78
	50	11.4	64.9	10.79
NR-Silica	10	8.8	43.5	13.20
	20	10.6	45.0	18.20
	30	13.8	47.5	21.88
	40	17.8	49.9	35.00
	50	23.0	52.8	58.30

As shown in Tables IV–VII, maximum torque of NR compounds, M_{tr} , decreases with increasing temperature. This result is because there is a decrease in the number of effective cross-links because, at higher temperatures, sulfur cross-links are more susceptible to breakage, which gives rise to intramolecular sulfur cyclization, and are no longer contributing to the net-

work formation. The network structure of an accelerated sulfur vulcanizate has been shown to depend significantly on the maturing reactions of the polysulfidic cross-links formed in the early part of vulcanization. These cross-links, initially formed during the accelerated sulfur vulcanization of NR, can undergo any of a number of competing reactions under the

TABLE V
Cure Time (t_{90}), and Minimum and Maximum Torque for BRHA-, WRHA-, Silica-, and Carbon Black-Filled NR Vulcanizates at 160°C

Vulcanizate	Filler loading	Minimum torque (dN · m)	Maximum torque (dN · m)	Optimum cure time, t_{90} (min)
NR	0	4.5	40.9	6.75
NR-WRHA	10	1.4	44.2	5.96
	20	1.6	45.6	5.48
	30	2.4	47.3	5.22
	40	3.0	50.4	4.97
	50	4.4	54.4	4.94
NR-BRHA	10	2.1	43.4	6.50
	20	3.0	44.1	6.56
	30	3.6	44.6	6.60
	40	4.6	44.8	6.81
	50	4.7	45.0	7.28
NR-Carbon black	10	5.3	53.4	5.55
	20	8.0	56.6	5.59
	30	9.1	57.1	5.60
	40	9.8	61.2	5.72
	50	10.0	62.6	6.22
NR-Silica	10	8.0	41.5	7.94
	20	10.0	43.0	13.31
	30	12.8	45.5	19.80
	40	15.8	47.8	31.00
	50	21.0	51.8	37.00

TABLE VI
Cure Time (t_{90}), and Minimum and Maximum Torque for BRHA-, WRHA-, Silica-, and Carbon Black-Filled NR Vulcanizates at 170°C

Vulcanizate	Filler loading	Minimum torque (dN · m)	Maximum torque (dN · m)	Optimum cure time, t_{90} (min)
NR	0	4.4	40.5	4.19
NR-WRHA	10	1.1	40.1	3.83
	20	1.3	44.7	3.52
	30	1.9	46.8	3.40
	40	2.6	47.9	3.16
	50	3.9	48.8	3.12
NR-BRHA	10	1.8	40.4	3.94
	20	2.7	41.1	3.96
	30	3.4	41.4	4.07
	40	4.0	41.7	4.26
	50	4.2	41.9	4.68
NR-Carbon black	10	5.0	52.9	3.36
	20	7.8	53.7	3.39
	30	8.9	54.9	3.40
	40	9.6	59.6	3.58
	50	9.8	59.8	3.91
NR-Silica	10	7.8	40.5	5.13
	20	9.8	42.7	8.50
	30	11.8	43.6	10.93
	40	15.0	44.8	15.30
	50	20.2	47.8	17.96

action of heat. One of the reactions involves the shortening of the polysulfidic chains, a process catalyzed by accelerator complexes and that can occur repeatedly until the cross-links are reduced to monosulfidic, with the release of sulfur for further cross-linking. Alternatively, the initial polysulfidic cross-links may suffer elimination by thermal scission at the carbon—sulfur

bond, leading to modifications in the main chain; for examples, the formation of cyclic sulfides and changes in the olefinic structure of the polyisoprene molecules. A third possible reaction is the interchange between polysulfidic cross-links at their points of attachment to the network chain. This reaction can lead to stress relaxation but does not alter the cross-link composi-

TABLE VII
Cure Time (t_{90}), and Minimum and Maximum Torque for BRHA-, WRHA-, Silica-, and Carbon Black-Filled NR Vulcanizates at 180°C

Vulcanizate	Filler loading	Minimum torque (dN · m)	Maximum torque (dN · m)	Optimum cure time, t_{90} (min)
NR	0	4.2	45.0	2.66
NR-WRHA	10	1.0	40.0	3.53
	20	1.2	42.7	3.12
	30	1.5	44.8	2.80
	40	2.1	45.8	2.40
	50	3.8	47.8	2.36
NR-BRHA	10	1.6	40.0	2.68
	20	2.5	41.0	2.72
	30	3.2	41.2	2.81
	40	3.8	41.5	2.90
	50	4.0	41.6	3.04
NR-Carbon black	10	5.0	51.8	2.31
	20	7.5	52.0	2.34
	30	8.6	53.0	2.40
	40	9.4	57.9	2.58
	50	9.7	58.0	2.71
NR-Silica	10	7.5	40.0	3.15
	20	9.5	42.0	4.46
	30	11.2	42.8	6.89
	40	14.7	43.0	9.95
	50	19.7	45.8	12.60

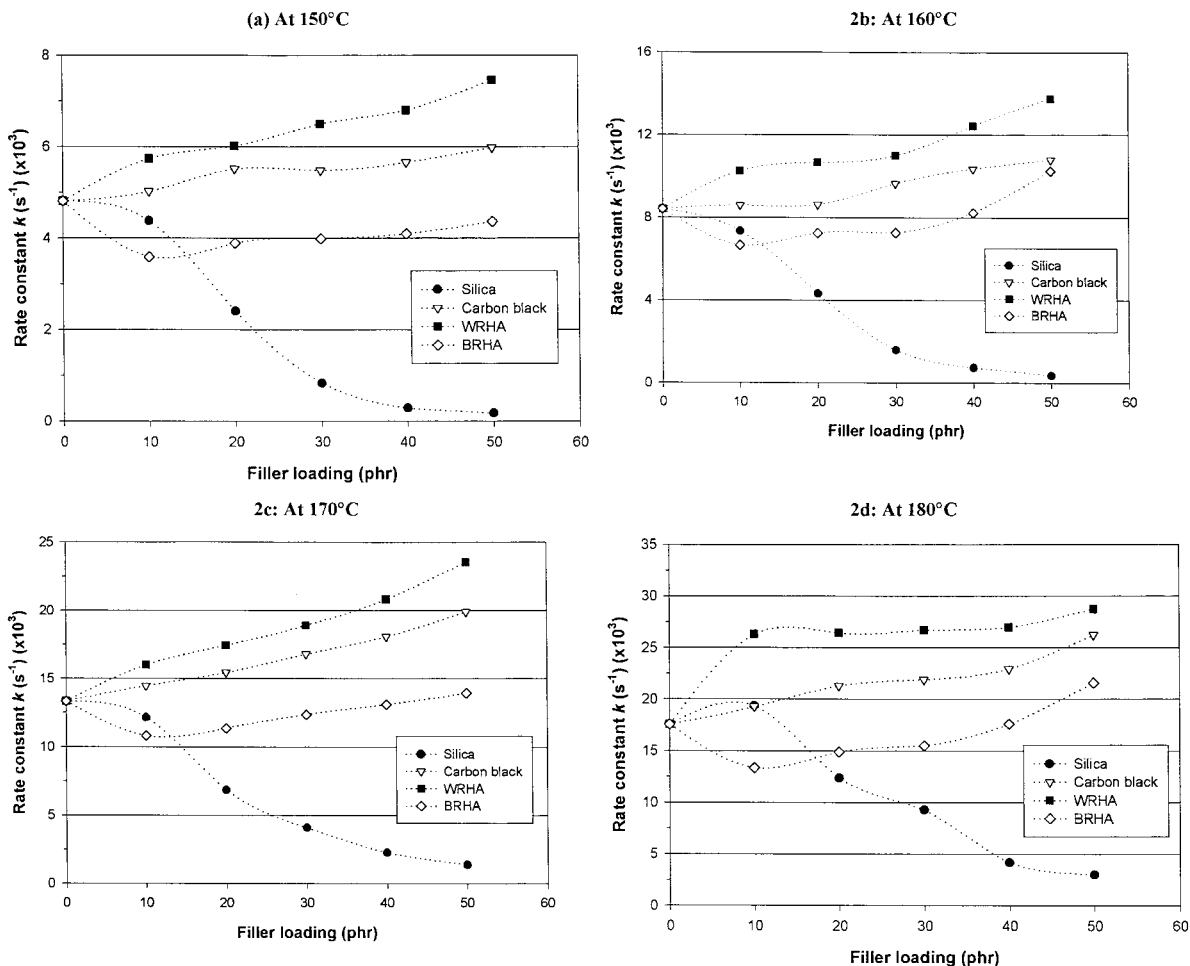


Figure 2 Rate constant as a function of filler loading for NR compounds at (a) 150°C, (b) 160°C, (c) 170°C, and (d) 180°C.

tion of the network. The relative rates of these maturing reactions, namely, desulfuration, decomposition, and interchange of sulfur bonds, are governed by: (a) the chemical structure of cross-links termini, (b) structure, concentration, and reactivity of the sulfurating complexes formed from accelerators and activators, and (c) the vulcanization temperature and time.^{20,21}

For the optimum cure time (t_{90}), it can be observed that compared with pure gum, WRHA accelerates the vulcanization process more than carbon black. On the other hand, BRHA does not interfere with this parameter. Silica imparts a somewhat different behavior; that is, t_{90} increases with increasing amounts of filler. These different trends in the cure characteristics may be attributed to differences in filler properties, such as surface area, surface reactivity, pH, particle size, moisture content, and metal content. Fillers are known to influence the cross-linking reaction during vulcanization. In most cases, the cause of this retardation can be traced to the greater or lesser acidity of the filler (indicated to some extent by the pH of its aqueous slurry, as shown in Table III), which does have influence on the kinetics of the cross-linking reaction.

According to Wagner,²² in systems with silica or silicates as filler, a faster cure rate is obtained with fillers having low surface area, high moisture content, and high metal oxide content. This relationship indeed seems to be the case because, among the fillers investigated in this work, carbon black and WRHA have the lowest surface areas and, thus, shorter t_{90} values. The retardation effect found in the silica vulcanizates can be attributed to a silica–accelerator system interaction. This filler reacts with zinc oxide and subsequently reduces the zinc available, thus slowing down its reaction with sulfur.²³ As shown in Tables IV–VII, with the increase in temperature, the optimum cure time (t_{90}) decreases for all NR compositions according to the “rule of thumb” that the rate of cure doubles for every 10°C increment.

Using the rheograph data in eqs. 1 and 2, the rate constants (Figures 2a–d) and the apparent activation energy (Figure 3) are estimated and presented in Table VIII.

Carbon black (N762) shows some catalytic effect on the vulcanization, with rate constant k increasing slightly with filler loading. Cotton²⁴ pointed out that

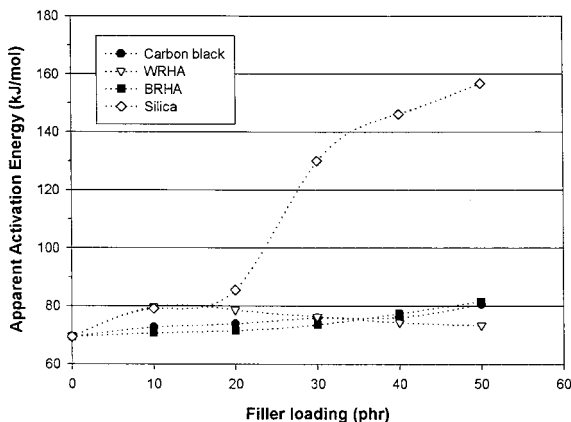


Figure 3 Effect of filler loading on apparent activation energy of NR compounds.

oxygen-containing groups at the carbon black surface exert a profound effect on the rate of cure reaction and maximum torque when present in NR formulations containing a CBS/sulfur curing system. Carbon blacks consist of 90–99% elemental carbon. The other constituents are (combined) hydrogen and oxygen. Hydrogen comes from the original hydrocarbon and is distributed throughout the carbon black particle. As the particles are formed in the reducing atmosphere of the flame, the oxygen appears subsequently and is, therefore, confined to the surface. The principal groups present are phenolic, ketonic, and carboxylic, together with lactones. Depending on the particular accelerator, phenolic and carboxylic groups can be considered those that most affect the cross-linking rate of a rub-

ber. The latter is the case for NR/CBS systems for which a significant dependence of the vulcanization rate on the carbon black surface total acidity was found.²⁴

Bhowmick and De,²⁵ in their study on cross-linking kinetics and network changes in unfilled and filled NR vulcanizates with a dithiodimorpholine-based accelerator system, show that the addition of carbon black enhances the polysulfidic cross-links as well as the total cross-links. It is likely that the filler surface prevents desulfuration and undesirable side reactions involving the cross-link precursors. Pal et al.²⁶ showed that both overall cross-link density and polysulfidic cross-links increase when carbon black is added in the range 0–5 phr in the conventional system. Further addition of carbon black does not significantly change the network structure. This observation shows that the reinforcing black filler at amounts up to 5 phr catalyzes the sulfuration processes, whereas higher loadings do not have any further effect on the sulfuration processes and, eventually, on the network structure in the conventional system.

For silica-NR compounds, the rate constant k decreases markedly with filler loading in the temperature range investigated. There is a reduction of 96.3% in the k value for silica-NR compound with 50 phr in relation to pure gum at 150°C. Compounds containing reinforcement fillers like silica must be processed and compounded differently from unfilled gums or even from carbon black-loaded rubbers. Silica is light, fluffy, and difficult to incorporate. Its acidity is responsible for cure retardation, and additional ingredi-

TABLE VIII
Rate Constants and Apparent Activation Energies for Rubber Compounds at Different Temperatures

Composition	Rate constant ($1000 \times k, s^{-1}$)				E_A (kJ/mol)
	150°C	160°C	170°C	180°C	
NR	4.811	8.412	13.345	17.568	69.48
NR-Carbon black 10	5.020	8.586	14.468	19.260	72.78
NR-Carbon black 20	5.127	8.620	15.455	21.288	73.96
NR-Carbon black 30	5.485	9.640	16.810	21.895	75.26
NR-Carbon black 40	5.661	10.358	18.100	22.959	76.10
NR-Carbon black 50	5.986	10.797	19.914	26.233	80.63
NR-WRHA 10	5.743	10.252	16.008	26.301	79.82
NR-WRHA 20	6.018	10.663	17.448	26.431	78.71
NR-WRHA 30	6.504	10.955	18.929	26.734	76.42
NR-WRHA 40	6.804	12.435	20.838	26.991	74.36
NR-WRHA 50	7.459	13.769	23.563	28.756	73.38
NR-BRHA 10	3.594	6.666	10.811	13.358	70.77
NR-BRHA 20	3.892	7.249	11.368	14.890	71.58
NR-BRHA 30	3.993	7.268	12.383	15.508	73.63
NR-BRHA 40	4.096	8.233	13.125	17.602	77.44
NR-BRHA 50	4.368	10.252	13.948	21.596	81.62
NR-Silica 10	4.379	7.343	12.151	19.370	79.15
NR-Silica 20	2.403	4.323	6.842	12.358	85.61
NR-Silica 30	0.833	1.596	4.087	9.277	130.07
NR-Silica 40	0.286	0.739	2.265	4.172	146.26
NR-Silica 50	0.178	0.360	1.374	2.997	156.87

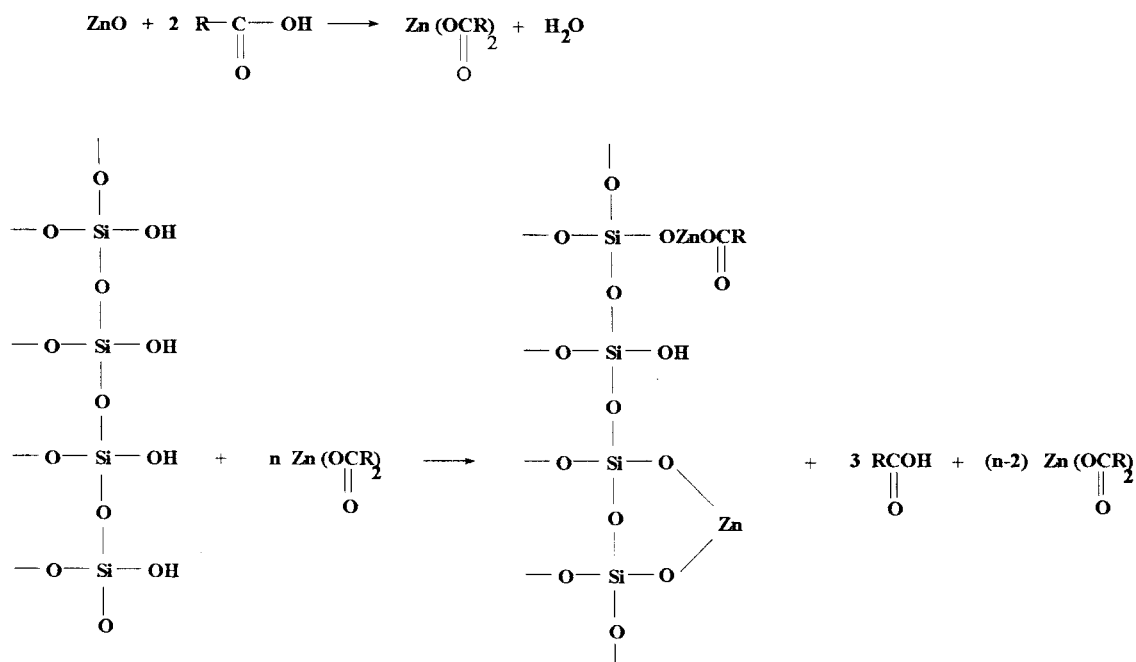


Figure 4 Ion exchange between silanol groups and zinc stearate on silica surface.²⁸

ents like amines or glycols usually have to be added to overcome this feature, which has not been done in this work. Manufacturers of certain types of silica suggest that better properties are obtained in accelerator-sulfur cured rubber-silica compounds if zinc oxide is omitted. Fetterman,²⁷ studying the influence of silica on the cure behavior of rubbers, concluded that its effect on cure retardation is directly proportional to the total surface area of the silica present and that sulfur functionality is dependent on both the particle size and the total silica content. Mukhopadhyay and De²⁸ suggest 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 silanol groups and zinc stearate. In such a reaction, stearic acid is liberated, which then solubilizes more zinc oxide and modifies the silica surface (Figure 4). Comparing silica and carbon black in Table III, it can be seen that the pH values for these two fillers are very close. Thus, this parameter alone cannot be responsible for the retardation effect of silica. However, because the vulcanization was carried out in the presence of ZnO, the system total acidity may have become of such a magnitude as to drastically interfere with the reaction rate.

For the BRHA-NR compounds, the influence of this filler on k values seems to be similar to that of carbon black, although to a lesser extent. The dual nature of BRHA, given by the presence of both silica and carbon components, with different physical and chemical properties, may have been the responsible for the reduced efficiency of this filler in rubber vulcanization. In addition, BRHA was found to be extremely

porous, according to the discrepancy between particle size and surface area. The BET nitrogen adsorption method, used to obtaining these parameters, measures all areas accessible to the nitrogen molecules, like pores, cracks, and cavities in the filler aggregates. Because the nitrogen molecule is much smaller than the hydrocarbon molecules, particularly segments of an elastomer chain molecule, the N_2 adsorption method then results in surface areas much larger than the real values for the rubber compound. In Table III, the surface area for BRHA is $109 \text{ m}^2/\text{g}$, but pores contribute 80.1% to this value. It is known that carbon black particles with pores and cracks have higher surface areas than carbon black particles of similar size with no such features. The presence of pores can result in cure retardation because of the increased adsorption and inactivation of rubber curatives entrapped in the cavities. In most cases the pores are too small for polymer chains to enter, although some smaller molecules in the compound may do so; large internal surface areas may be detrimental because a certain proportion of accelerator may become immobilized and inactivated.

For the WRHA-NR compounds, there is a remarkable increase in rate constants as filler loading is increased. The chemical composition of WRHA (Table II) shows that this filler is 97% silica, whereas the loss on ignition (LOI) is only 0.20% and the oxide content is 19.3% larger than in BRHA. In addition, WRHA exhibits a small surface area for interaction with rubber. All these factors might be responsible for the catalytic effect of WRHA on NR vulcanization.

The effectiveness of accelerated sulfur systems in cross-linking rubber is thought to be dependent on the solubility and reactivity of the "sulfurating reagents" formed from the vulcanizing ingredients. These are metal, usually zinc, salts derived from the accelerator and metal oxide and are rendered soluble by amine or carboxylate ligands (Figure 1). Zinc, although satisfying extremely well the electronic and steric requirements in the complexes, seems unlikely to be the only contender for this role because the electronic states and solubility of the metal complexes can be altered by varying the concentrations of ligand-forming amines and fatty acids and the vulcanization temperature.²⁹

Substitution of zinc by other metals may alter the efficiency of cross-linking. Evidence for this possibility is the observation of "stiffer vulcanizates" obtained by replacing zinc oxide by bismuth trioxide, cadmium oxide, mercuric oxide, litharge, and lead in an MBT-accelerated high-sulfur system, as shown in early investigation.²⁹

Russel et al.³⁰ used a number of different metal oxides in molar basis substitution for zinc oxide in a vulcanizing EV-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. Other oxides investigated, MgO, SnO₂, Pb₃O₄, Sb₂O₃, TeO₂, Fe₂O₃, Cr₂O₃, and Co₂O₃, used in admixture with zinc oxide in the same base mix, gave modulus values equal to or lower than those obtained with zinc oxide alone. Only the inclusion of cadmium oxide significantly retarded the onset of cure of the EV-system studied.

To understand why zinc oxide is selected over the other metal oxides, a comparative study was conducted with titanium dioxide and magnesium, calcium, lead, and zinc oxides.³¹ A plot of the electronegativity of these six metals versus rheometer torque ($M_h - M_i$) indicates that unless a given electronegativity is in the range of 1.6 to 1.8, optimum vulcanizate properties will not be obtained. Electronegativity is a measure of the affinity of the metal atom for electron attraction. For metals of electronegativity <1.55, a consequent shift to ionic bonding with sulfur induces a reduction in electrophilicity in the penultimate sulfur atoms of the sulfurating complexes (Figure 1). Conversely, with metals of electronegativity >1.85, such as iron, the greater covalent character of the $M^+ \dots S^-$ linkage with reduced charge separation would adversely affect generation of amine or carboxylate ligands to the metal ion (Figure 1), which in turn would reduce the solubility of the sulfurating reagent, with consequent drops in the sulfurating agent activity, and in vulcanizate properties.³¹

In Figure 3, the apparent activation energy calculated using rheometer isotherms at two different temperatures (eq. 2) is shown. BRHA and carbon black exhibit similar behavior for all compositions. WRHA

and silica are equivalent up to filler loading of 20 phr, and then silica shows a pronounced increase in E_a values (51.9%, going from 20 to 30 phr). For WRHA, filler loadings >20 phr seem to introduce a catalytic effect, resulting in decreasing E_a values. This positive effect might be due to characteristics like small surface area and loss on ignition, and oxide content.

CONCLUSIONS

Carbon black shows some catalytic effect in the vulcanization process, with rate constant k increasing slightly with filler loading at all temperatures. The influence of BRHA filler on k values follows the profile found for carbon black, but to a lesser extent. The dual nature of the BRHA filler, given by the presence of both silica and carbon components, with different physical and chemical properties, and its extremely porous character may have reduced the efficiency of this filler in the rubber vulcanization process. The E_a values for carbon black and BRHA compositions are similar within the entire filler loading range.

For silica-NR compounds, with the increase in filler content, k decreases at all temperatures investigated and E_a values increase markedly. This retardation in the vulcanization reaction may be attributed to the acidic character of silica. In this study, additional ingredients (amines or glycols) that are usually added to overcome this feature were not used, resulting in a more intense effect.

For the WRHA-NR compounds, there is a remarkable increase in rate constant with filler loading and, at loadings >20 phr, a catalytic effect with consequent decreases in E_a values seems to exist. This fact can be attributed to smaller surface area and loss ignition, and, mostly, to the oxide content present in WRHA, which may accelerate the vulcanization process in the presence of zinc oxide.

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