Rice-Husk-Ash-Filled Natural Rubber. II. Partial Replacement of Commercial Fillers and the Effect on the Vulcanization Process

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ABSTRACT: In a previous investigation, we observed that in the presence of a conventional vulcanization system, the addition of white rice husk ash (WRHA) to natural rubber (NR) compounds increased the rate of crosslinking and lowered the apparent activation energy (E_a) of the vulcanization reaction more strongly than the other fillers used. In this work, commercial fillers, such as precipitated silica (Zeosil-175) and carbon black (N762), were partially replaced by black rice husk ash and WRHA. Cure studies were carried out on a TI-100 curometer at 150, 160, 170, and 180°C, and the overall rates and the E_a's for the vulcanization process were calculated for each compound, with the assumption that vulcanization followed first-order kinetics. Again, WRHA showed some catalytic effect on the NR vulcanization. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1405–1413, 2003

Key words: natural rubber; rice husk ash; vulcanization

INTRODUCTION

Rice husks mainly contain lignin, cellulose, and hydrated silica (Sil). Through burning, rice husk yields two grades of fillers, namely, white rice husk ash (WRHA), with a high Sil content, and black rice husk ash (BRHA), with a low Sil content. The combustion conditions are the key to this difference. The carbon-containing materials must be burned away, but too high a temperature or too long a residence time will lead to a fused crystallized mass with no useful properties at all.[1]

WRHA has been used as a filler in natural rubber (NR), styrene butadiene rubber, nitrile rubber, butadiene rubber, and ethylene–propylene–diene rubber.[1] When incorporated into epoxidized NR, WRHA can increase tensile strength, tear strength, and hardness.[2–4] In general, WRHA is not as good as fumed Sil or carbon black (CB) as far as mechanical properties are concerned,[2–4] but it can totally or partially replace these commercial fillers, depending on the particular characteristics in which one is interested.[5] BRHA has a lower Sil content, typically around 54%, and a substantial carbon content, around 44%. It can also be used as a filler for rubbers, but the effect is not as good as with WRHA.[6,7]

In an earlier work,[8] we observed that when incorporated in NR compounds, WRHA increases the overall rate and lowers the apparent activation energy (E_a) for the vulcanization process. This fact was attributed, mainly, to the oxides content present in WRHA. In this study, precipitated Sil (Zeosil-175) and CB (N762) were partially replaced by BRHA and WRHA, and the influence of this replacement on the cure behavior of NR vulcanizates was estimated. Once again, the study was conducted on an oscillating disk rheometer (cure meter) (Tecnología Industrial, São Paulo, Brazil), and it was assumed that vulcanization followed first-order kinetics.

EXPERIMENTAL

Materials and methods

NR was supplied by Irwin Indústria e Comércio Ltd. (Rio de Janeiro, Brazil). The fillers were CB (N762) from Columbian Chemicals Brasil S.A (Rio de Janeiro, Brazil), Sil (Zeosil-175) from Rhodia Brasil Ltd. (Rio de Janeiro, Brazil), and rice husk ashes (RHAs) supplied by EMBRAPA (Empresa Brasileira de Pesquisa Agropecuária (Rio de Janeiro, Brazil)), which were milled for 5 h and sieved on a 325-mesh sieve before use. The

Material	phr
NR	100
Zno	3.5
Filler	Variable
Stearic acid	2.5
CBS	0.8
Aminox[a]	2.0
Sulfur	2.5

[a] Antioxidant–low-temperature reaction product of diphenylamine and acetone.

other compounding ingredients were of reagent grade and were used as received. Table I shows the formulation used to prepare the different compositions.

The ashes were analyzed for chemical composition on an inductively coupled plasma emission spectrometer, and the results are shown in Table II. Particle size distribution, surface area, and density for each of the four fillers are presented in Table III and were determined with the Global Lab Image (SP0550) software package (Tecnología Industrial, São Paolo, Brazil), an ASAP 2010 accelerated surface area and porosimetry system (through the Brunauer-Emett-Teller (BET) method), and a glass pyknometer (Tecnología Industrial, São Paolo, Brazil), respectively. Method ASTM D 1512 was followed to measure pH.

Preparation of mixes and rheometry

RHA was dried at 120°C for 24 h immediately before use. Commercial fillers were partially replaced by RHA in a stepwise fashion, the total load kept at 50 phr. Mixing was carried out on a two-roll mill at speed ratio of 1:1.25 at 70°C, according to ASTM D 3182. A TI-100 curometer from Tecnología Industrial was used at a ±3° arc, and torque–time curves were registered at vulcanization temperatures of 150, 160, 170, and 180°C. For each temperature, triplicates of each composition were considered, and the rheometric data were used to calculate E_a.

RESULTS AND DISCUSSION

The general course of the vulcanization process is shown in Scheme 1. At first, the vulcanization ingredients, also called *curatives*, are mixed with a polymer that contains unsaturations in the backbone, such as polyisoprene. The presence of unsaturations allows the substitution of an allylic hydrogen atom with a sulfur bridge. The onset of the vulcanization process is usually effected by the heating of the mixture and involves a sequence of discrete reactions.[9]

The curatives react with sulfur to form active sulfurating agents, their identity depending on the particular vulcanization system present. The active sulfurating agent reacts with the rubber chain to yield a crosslink precursor, which subsequently forms initial crosslinks containing a relatively large number of sulfur atoms in the bridge. Crosslink shortening due to desulfuration may be accompanied by crosslink degradation and modification (e.g., oxidation) of the rubber molecules and result in the final rubber network.[9]

Assuming first-order kinetics, the expression for the vulcanization rate constant (k) can be written in terms of torque as[10]

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

where M_t is the torque at a given time t and M_l and M_h are the minimum and maximum torques, respectively. Because the rate in the early stages reflects the character of the main forward reaction, M_t values at 25 and 45% of the total torque change can be used to estimate the rate constants.[10] By a combination of the Arrhenius equation and eq. (1), the convenient eq. (2) for the E_a with rheometer data from isothermal runs, at different temperatures, is derived:

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

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 (R is a gas constant, in adequate unit [8.314 J/(K.mol)]).

Tables IV–VII show rheometric parameters, as optimum cure time (t_{90}), M_l, and M_h, at different temperatures for NR compositions, in which Sil and CB were partially replaced by BRHA and WRHA.

TABLE II
Chemical Composition of RHA

Chemical composition (%)	BRHA	WRHA
CaO	0.40	0.77
MgO	0.38	0.53
Fe_2O_3	0.13	0.25
K_2O	1.22	1.05
Na_2O	0.13	0.30
Al_2O_3	0.23	0.27
MnO	0.16	0.14
TiO_2	0.01	0.01
P_2O_5	0.96	1.00
SiO_2 (Sil)	74.85	97.00
LOI	21.00	0.20

TABLE III
Physical Properties of RHA, Sil, and CB

Property	BRHA	WRHA	Sil	CB
Mean particle size (μm)	2.5	2.2	0.018	0.054
Surface area (m^2/g)	109	17	185	30
Average pore diameter (Å)	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

With an increase in the participation of reinforcing filler, CB or Sil, in the filler load, M_l markedly increased. This held for both ashes and indicated that a higher contribution of these commercial fillers reduced the mobility of the macromolecular chains due, probably, to the greater interaction between the small reinforcing filler particles and the rubber. For Sil/WRHA-filled and Sil/BRHA-filled NR compounds, this was expected. Sil has the unique characteristic of having many hydroxyl groups on the particle surface.[11,12] Because intermolecular hydrogen bonds between hydroxyl groups on the surfaces of adjacent Sil particles are very strong, tightly held aggregates can easily form.[13] This characteristic can cause the poor dispersion of Sil in the rubber matrix and contributes to build viscosity more rapidly than most fillers; this is

Final network
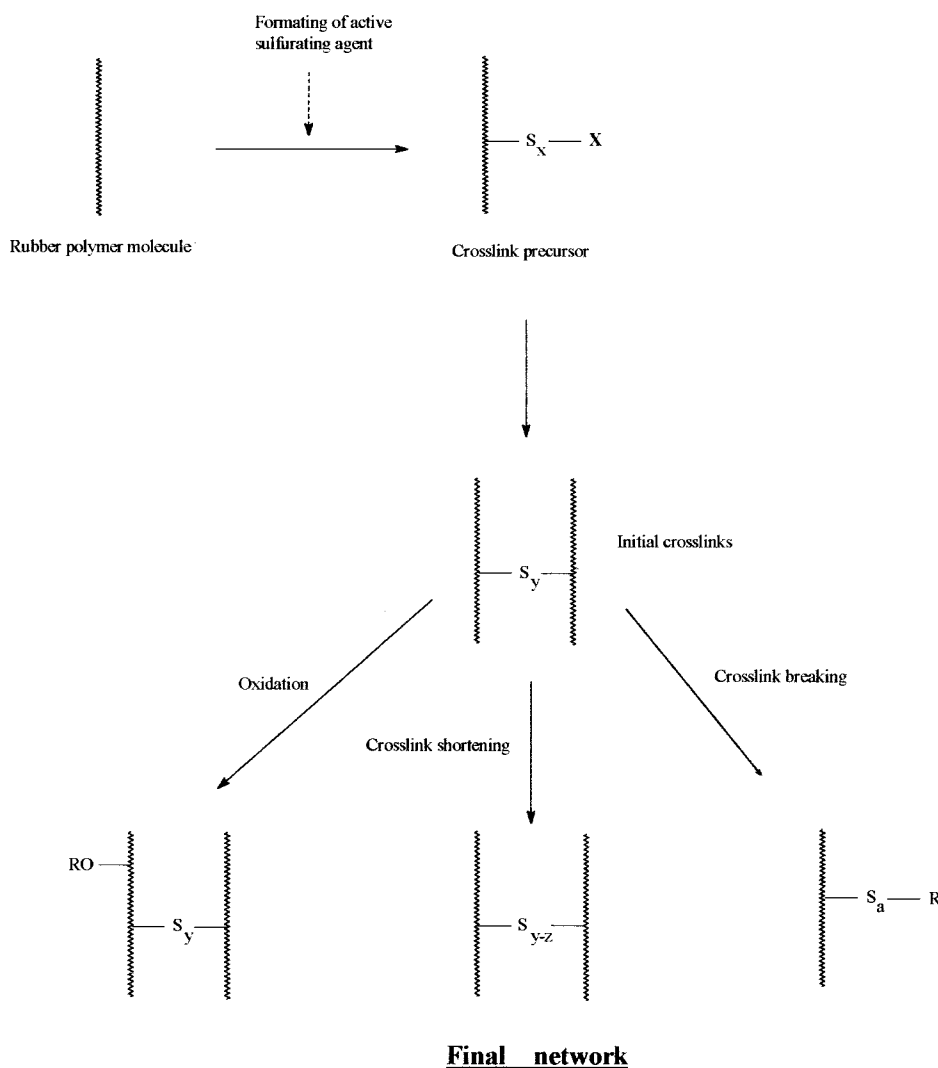
Scheme 1 Generalized course of accelerated sulfur vulcanization (X = accelerator residue).[22]

TABLE IV
t_{90}, M_l, and M_h for NR Vulcanizates with Commercial
Fillers Partially Replaced by WRHA or BRHA at 150°C

Filler loading (phr/phr)	M_l (dNm)	M_h (dNm)	t_{90} (min)
CB/WRHA			
50/0	11.4	64.9	10.8
40/10	6.7	59.3	11.3
30/20	6.5	58.2	10.0
20/30	5.9	57.4	9.5
10/40	5.5	56.6	9.1
0/50	4.6	55.2	8.3
CB/BRHA			
50/0	11.4	64.9	10.8
40/10	10.4	56.1	12.6
30/20	9.0	52.8	13.8
20/30	8.7	51.5	14.4
10/40	7.5	50.1	15.8
0/50	4.3	49.2	13.8
Sil/WRHA			
50/0	23.0	52.8	58.3
40/10	22.6	51.9	47.8
30/20	17.0	51.3	43.4
20/30	15.0	50.7	32.8
10/40	9.8	50.0	25.8
0/50	4.6	55.2	8.3
Sil/BRHA			
50/0	23.0	52.8	58.3
40/10	17.5	51.8	54.8
30/20	11.4	51.0	53.0
20/30	7.9	50.6	36.6
10/40	4.7	50.1	27.2
0/50	4.3	49.2	13.8

especially true in the case of Sil with high surface areas. Viscosity is also dependent on the adsorbed moisture present on the Sil during compounding. This moisture behaves as a pseudoplasticizer, but its effect will vary with the ambient humidity and the rubber processing conditions.

As shown in Tables IV–VII, M_h decreased with increasing temperature. This may have been caused by the maturing reactions involving the polysulfidic crosslinks formed in the early stages of vulcanization, as discussed in our previous article.[8] For t_{90}, when CB or Sil were replaced totally or partially by WRHA, the vulcanization process was accelerated. However, BRHA showed this effect only when replacing Sil. For Sil-filled rubber compounds with an accelerated sulfur cure system, the curatives were adsorbed on the Sil surface so that they had longer t_{90}'s, and the state of cure was substantially reduced when compared to that of CB-filled compounds. The magnitude of these effects widened with the total available surface (i.e., a combination of loading and specific surface area) of the Sil.[13] Therefore, when Sil was replaced by BHRA, vulcanization was accelerated because the amount of Sil became lower so that most curatives would be

available for vulcanization. This was not observed when BRHA was mixed with CB, which precluded the possibility of BRHA having a synergistic effect on vulcanization, as was the case with WRHA. These different trends in the cure characteristics of BRHA and WRHA may have been caused by differences in surface area, surface reactivity, and metal content. The effect of temperature on t_{90}, shown in Tables IV–VII, for all compositions, agreed with the rule of thumb, which holds for vulcanization and for many other chemical reactions and states that the rate doubles for every 10°C increase in temperature.

By applying eqs. (1) and (2) to the rheographs data, the rate constants shown in Tables VIII and IX and the E_a's seen in Figure 1, were estimated.

In part I of this series of articles,[8] we observed that CB showed some catalytic effect on vulcanization and that k increased slightly with filler loading, whereas for WRHA, this catalytic effect only appeared above a filler loading of 20 phr. For BRHA, its influence on k values seemed to be similar to that of CB, although to a lesser extent, whereas for Sil–NR compounds, the rate constant decreased markedly with filler loading.

Through the replacement of CB with a low content of WRHA, a slight deceleration occurred, as shown by

TABLE V
t_{90}, M_l, and M_h for NR Vulcanizates with Commercial
Fillers Partially Replaced by WRHA or BRHA at 160°C

Filler loading (phr/phr)	M_l (dNm)	M_h (dNm)	t_{90} (min)
CB/WRHA			
50/0	10.0	62.6	6.2
40/10	6.3	58.7	6.3
30/20	6.2	57.3	5.7
20/30	5.8	56.9	5.4
10/40	4.7	54.5	5.2
0/50	4.4	54.4	4.9
CB/BRHA			
50/0	10.0	62.6	6.2
40/10	8.5	54.3	6.4
30/20	8.0	51.8	6.9
20/30	7.5	49.2	8.0
10/40	6.6	48.4	8.6
0/50	4.7	45.0	7.3
Sil/WRHA			
50/0	21.0	51.8	37.0
40/10	20.1	51.4	22.4
30/20	13.2	50.9	19.5
20/30	11.0	50.6	18.8
10/40	9.2	49.9	7.1
0/50	4.4	54.4	4.9
Sil/BRHA			
50/0	21.0	51.8	37.0
40/10	18.8	51.0	27.1
30/20	12.0	50.6	25.8
20/30	7.8	50.0	15.6
10/40	5.2	49.3	8.0
0/50	4.7	45.0	7.3

TABLE VI
t_{90}, M_l, and M_h for NR Vulcanizates with Commercial Fillers Partially Replaced by WRHA or BRHA at 170°C

Filler loading (phr/phr)	M_l (dNm)	M_h (dNm)	t_{90} (min)
CB/WRHA			
50/0	9.8	59.8	3.9
40/10	7.8	57.7	3.7
30/20	6.1	56.7	3.5
20/30	4.9	56.3	3.4
10/40	4.2	54.0	3.3
0/50	3.9	48.8	3.1
CB/BRHA			
50/0	9.8	59.8	3.9
40/10	9.4	52.7	4.0
30/20	8.4	49.7	4.1
20/30	7.4	46.8	4.2
10/40	6.3	46.1	4.4
0/50	4.2	41.9	4.7
Sil/WRHA			
50/0	20.2	47.8	18.0
40/10	15.3	47.5	10.6
30/20	12.5	46.3	10.0
20/30	10.4	45.9	9.3
10/40	9.0	45.4	4.4
0/50	3.9	48.8	3.1
Sil/BRHA			
50/0	20.2	47.8	18.0
40/10	16.4	45.7	15.5
30/20	10.9	44.5	13.4
20/30	7.5	43.0	12.5
10/40	4.4	42.5	5.4
0/50	4.2	41.9	4.7

a decrease in the k value. However, as the proportion of the ash increased, k also increased, and at 50 phr ash content (and no CB), k had the highest value. This held for all temperatures. The addition of WRHA slightly lowered the E_a.

It is well known that CB reduces the scorch time and increases the rate of crosslinking in the accelerated sulfur vulcanization of rubbers.[14,15] CB increases the apparent crosslink density, as evidenced by the restriction it imparts to the swelling of the vulcanizates in a given solvent. However, straight-line plots of the Kraus equation[16] obtained with filled compounds have shown that in many vulcanizates, the true crosslink densities are unaffected by the addition of CB to the compound. This does not apply in all cases. Porter[17] showed that in a 2-mercaptobenzothiazole-accelerated NR vulcanization, CB increased the maximum true crosslink density by 25%, whereas Pal and De[18] reported a 20% increase in an NR–N-cyclohexyl-2-benzothiazole-2-sulfenamide (CBS) system. In addition to having a large surface area with which the rubber and curatives may interact, CBs have a high surface reactivity, thanks to a variety of reactive oxygen-containing groups.[16–19] In this study, the small

surface area of WRHA and, mostly, the presence of impurities such as potassium, sodium, calcium, magnesium, iron, phosphorous, and aluminum, which occurred in the form of oxides or silicates, may have been favoring the vulcanization process.

In accelerated sulfur vulcanization, the addition of ZnO to the formulation is recognized as an important factor for the attainment of good physical properties. Stearic acid is commonly added as a coactivator and reacts very rapidly with ZnO above its melting point and during compounding; because the shearing forces prevent the formation of a zinc stearate layer around ZnO particles, the reaction readily goes to completion. The ion Zn^{2+} in its soluble form as zinc stearate can form a chelate with the accelerator molecule, as shown in Scheme 2, which undergoes scission at the S—S bond, giving rise to a crosslink and a new crosslink precursor. Although it has a lower reaction rate, this route leads to a higher degree of vulcanization.[20] This mechanism, suggested by Coran,[21] also shows that in the absence of zinc oxide, no chelate can be formed, and the crosslink formation proceeds at a higher rate. However, because no crosslink precursor is regenerated as a result of the S—S bond scission, the compound is less vulcanized.

TABLE VII
t_{90}, M_l, and M_h for NR Vulcanizates with Commercial Fillers Partially Replaced by WRHA or BRHA at 180°C

Filler loading (phr/phr)	M_l (dNm)	M_h (dNm)	t_{90} (min)
CB/WRHA			
50/0	9.7	58.0	2.7
40/10	7.4	56.8	2.6
30/20	6.2	55.8	2.5
20/30	5.1	54.2	2.4
10/40	4.8	52.9	2.4
0/50	3.8	47.8	2.4
CB/BRHA			
50/0	9.7	58.0	2.7
40/10	9.0	52.6	2.8
30/20	8.4	49.3	2.9
20/30	7.0	44.3	3.0
10/40	6.3	42.9	3.0
0/50	4.0	41.6	3.0
Sil/WRHA			
50/0	19.7	45.8	12.6
40/10	15.8	45.0	5.5
30/20	10.3	44.6	5.7
20/30	7.4	44.0	5.9
10/40	4.4	43.4	2.7
0/50	3.8	47.8	2.4
Sil/BRHA			
50/0	19.7	45.8	12.6
40/10	19.2	44.8	7.9
30/20	13.7	44.0	7.5
20/30	9.6	42.9	7.3
10/40	8.1	42.0	3.4
0/50	4.0	41.6	3.0

TABLE VIII
Rate Constants and E_a's for NR Compounds with CB Partially Replaced by WRHA
or BRHA at Different Temperatures

Composition	Rate constant (1000 × k [s^{-1}])				E_a (kJ/mol)
	150°C	160°C	170°C	180°C	
CB/WRHA (phr/phr)					
50/0	5.986	10.797	19.914	26.233	80.63
40/10	4.842	8.911	12.975	23.221	80.97
30/20	5.372	10.100	15.909	23.630	78.24
20/30	5.671	10.250	16.070	24.354	76.97
10/40	5.926	10.474	16.285	24.419	74.64
0/50	7.459	13.769	23.563	28.756	73.38
CB/BRHA (phr/phr)					
50/0	5.986	10.797	19.914	26.233	80.63
40/10	3.814	7.535	13.857	22.107	93.87
30/20	3.563	7.200	11.974	21.637	94.43
20/30	3.133	6.378	11.259	18.593	94.34
10/40	3.006	6.101	10.487	16.222	89.43
0/50	4.368	10.252	13.948	21.596	81.62

Doubtless, the single most intriguing species in the vulcanization literature is the sulfur-rich zinc accelerator complex. This species has remained intriguing because it has always defied detection, any evidence for its existence being indirect and challengeable. Nevertheless, sulfur-rich zinc accelerator complexes are attributed a central role in any vulcanization scheme. Through the application of a combination of quantum chemical and model investigations, zinc dithiocarbamates and mercaptobenzothiazolates have been found to homogeneously catalyze a number of essential vulcanization reactions. First, there is their ability to incorporate sulfur atoms in the zinc–ligand bond. Not only does this render the incorporated sulfur atoms more reactive, but also, the complex can act as a sulfur-atom carrier, transporting them from sulfur-rich to sulfur-poor areas in the rubber. The second important feature of zinc complexes is their Lewis acidity, through which various substrates, such as crosslinks and crosslink precursors, are activated.[21,22]

When CB was partially replaced by BRHA, the k values decreased with the ash loading (see Table VIII). E_a was higher in the presence of BRHA but was practically independent of its proportion in the filler mixture. Although BRHA can be considered more alike to CB than WRHA, its dual chemical composition (Sil and carbon components) and the extremely porous character that might immobilize and inactivate the accelerator molecules to a certain degree may be the features accounting for the negative effect of this filler on the vulcanization process.

The use of Sil in rubbers requires special consideration not demanded to the same degree by other fillers. The most frequently used accelerator systems are

TABLE IX
Rate Constants and E_a's for NR Compounds with Sil Partially Replaced by WRHA
or BRHA at Different Temperatures

| Composition	Rate constant (1000 × k [s^{-1}])				E_a (kJ/mol)
	150°C	160°C	170°C	180°C	
Sil/WRHA (phr/phr)					
50/0	0.178	0.360	1.374	2.997	156.87
40/10	0.592	1.296	3.033	5.208	117.69
30/20	0.646	1.383	3.054	5.323	113.62
20/30	0.724	1.546	3.698	5.354	109.80
10/40	4.786	8.250	13.101	22.289	80.93
0/50	7.459	13.769	23.563	28.756	73.38
Sil/BRHA (phr/phr)					
50/0	0.178	0.360	1.374	2.997	156.87
40/10	0.354	1.090	1.800	5.042	135.08
30/20	0.382	1.265	2.153	5.354	134.86
20/30	0.615	1.743	4.101	8.470	105.54
10/40	2.577	5.436	11.377	18.240	93.87
0/50	4.368	10.252	13.948	21.596	81.62
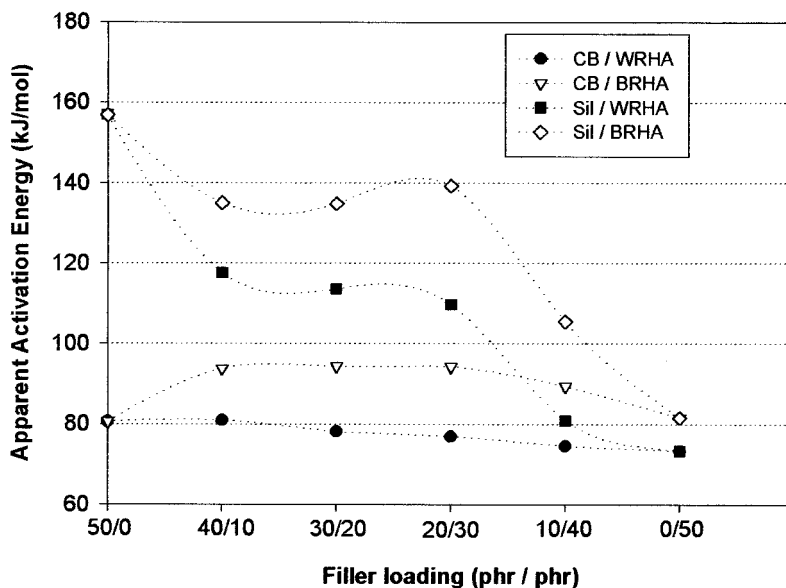
Figure 1 Effect of the partial substitution of commercial fillers with RHA on the E_a of NR compounds.

severely deactivated in the presence of Sil, and thus, sulfur-cured rubbers containing Sil must somehow be modified so that optimum performance are obtained. Some general guidelines include the desirability of (1) combinations of two or more accelerators, (2) the addition of glycol activators to lessen accelerator demand and buffer moisture variations, and (3) sulfur donor (or EV) cure systems that provide efficient crosslinking and benefits in property optimization and

heat aging. Thus, when Sil was replaced by WRHA or BRHA, small changes in the rate constant k were observed for ash contents up to 30 phr. As higher amounts of ash were present, vulcanization underwent an acceleration, which was more pronounced for WRHA, causing a significant reduction in E_a.

The catalytic effect of the ashes on vulcanization could be attributed to the presence of a small, but nevertheless significant, quantity of metal oxides,
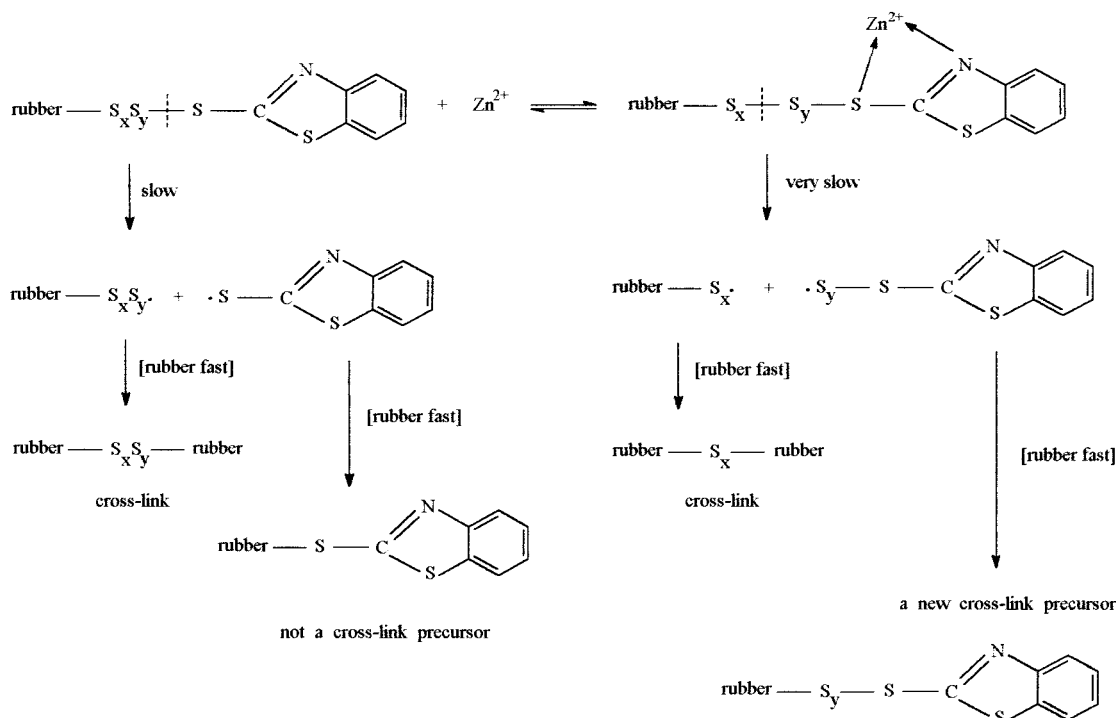
Scheme 2 Chelated form of the accelerator and Zn^{2+} proposed by Coran.[9]

$$ZnO + 2\ R-\underset{\underset{O}{\|}}{C}-OH \longrightarrow Zn\underset{\underset{O}{\|}}{(OCR)_2} + H_2O$$
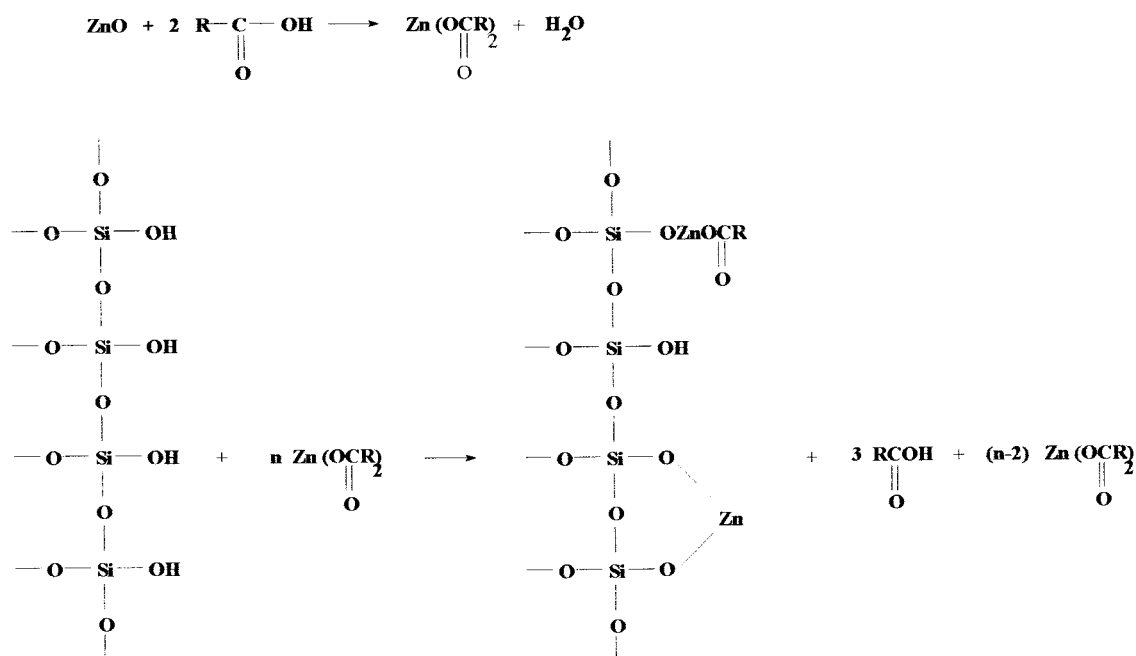

Figure 2 Ion-exchange reaction between silanol groups and zinc stearate on the Sil surface.[23]

which in combination with the zinc oxide added, may have played an important role as neutralizing agents for the stearic acid eventually evolved. Mukhopadhyay and De[23] suggested that the most plausible explanation for the specific deceleration effect of Sil would be the occurrence of an ion exchange reaction on the Sil surface between silanol groups and zinc stearate, with the liberation of stearic acid (see Fig. 2). Aliphatic acids, notably stearic acid, are commonly used in accelerated sulfur vulcanization formulations. However, the amount of a given acid in a formulation must be rigorously balanced due to the opposite effects it can impose. The retarding effect on vulcanization and the activating effect of acids on certain accelerators is well recognized.[24] Stearic acid melts below compounding temperatures, and very soon at this stage, it will readily react with ZnO. Because ZnO is normally present in excess, there will be no free acid in the compound, only ZnO and zinc stearate. As stearic acid is liberated as a result of its interaction with Sil, it can interact with the accelerator polysulfides at vulcanization temperatures leading to the partial decomposition of these polysulfides, thus, reducing the amount available for vulcanization when ZnO is not present.[25]

CONCLUSIONS

In the first part of this investigation,[8] we reported that the vulcanization process had been accelerated in the presence of WRHA and zinc oxide, whereas BRHA filler did not present any significant catalytic effect.

In this study, CB (N762) and Sil (Zeosil-175) were partially replaced by WRHA and BRHA, and the results obtained allowed the following conclusions:

1. When WRHA partially replaced CB or Sil, there was a catalytic effect on the vulcanization process, although to a lesser extent than that occasioned by the presence of WRHA alone. This could be attributed to the smaller surface area and loss on ignition (LOI) of this filler and, mostly, to the presence of impurities, which occurred in the form of metallic oxides or silicates and caused a reduction in E_a for both systems, CB/WRHA and Sil/WRHA.

2. When BRHA partially replaced Sil, there was also a reduction in E_a, although one less pronounced than for WRHA. This fact that at first glance, would be considered as due to a direct influence of the ash on the vulcanization mechanism, turned out to be a matter of prosaic interest, as the same trend was not found when BRHA replaced CB. In this case, the vulcanization was negatively influenced, leading to lower rate constant values.

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