Effect of Clay on Vulcanization, Network Structure, and Technical Properties of Natural Rubber in the Presence of Silane Coupling Agents

PRANAB K. PAL, S. N. CHAKRAVARTY,* and S. K. DE, *Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India*

Synopsis

The presence of silane coupling agents do not cause a change in network structure in clay-filled natural rubber vulcanizates, both in sulfur vulcanization and peroxide vulcanization systems. However, the improvement in technical properties in the presence of silane coupling agents is more in the peroxide vulcanization system and is accompanied by enhanced polymer–filler interactions. Scanning electron microscopy (SEM) studies have been made in order to understand the failure behavior.

INTRODUCTION

Recently, Pal and De[1,2] have studied the effect of reinforcing black and silica on the sulfuration processes during vulcanization. It was found that in the case of reinforcing HAF black (N 330), the addition of 5 phr filler catalyzes the sulfuration processes of natural rubber (NR) resulting in increases in the total crosslink density and polysulfidic crosslinks in conventional system (*N*-cyclohexyl benzothiazyl sulfenamide 0.6 phr, sulfur 2.5 phr). Beyond 5 phr, the network structure does not change. In the case of an efficient vulcanization (EV) system (*N*-cyclohexyl benzothiazyl sulfenamide 3.5 phr, sulfur 0.5 phr), there was no such augmentation in total crosslink density and polysulfidic crosslinks due to the addition of HAF black. In the case of reinforcing silica, it was found that silica in the presence of additives did not have any effect on the sulfuration processes during vulcanization as well as on the network structure of NR vulcanizates. Additives included activators [triethanolamine (TEA) and ethyleneglycol (EG)] and a coupling agent [bis(triethoxysilylpropyl)tetrasulfide (Si-69)].

Recently more attention is being paid to the mineral fillers like silica and clay, due to the high prices of carbon black.[3–11] Precipitated silica, although not petrochemical-based like carbon blacks, are energy-sensitive because of the power requirements necessary for reacting, precipitating, and drying. However, clays are much less energy-dependent and not as susceptible to sharp price increases. It is expected that clays will play a much larger role in future rubber technology. Much effort has been expended in upgrading low cost mineral fillers, viz., clays by treating them with reactive silanes in order to obtain a cost-effective re-

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* Modi Rubber Ltd., Modipuram 250110, India.

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TABLE I
Formulations of Mixes

Mix	A	B	C	D	E	F	G	H	I	J	K	L	M
Natural rubber[a]	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2
China clay[b]	—	5	20	40	60	5	20	40	60	5	20	40	60
A-172[c]	—	—	—	—	—	0.37	1.50	3.00	4.50	—	—	—	—
Si-69[d]	—	—	—	—	—	—	—	—	—	0.37	1.50	3.00	4.50
CBS[e]	1	1	1	1	1	1	1	1	1	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

[a] Natural rubber, crumb grade, obtained from the Rubber Research Institute of India, Kottayam.

[b] Semireinforcing type obtained from Dunlop India Ltd., Sahaganj.

[c] Vinyltris(2-methoxyethoxy)silane, obtained from Indian Cable Co., Ltd., Jamshedpur.

[d] Bis(triethoxysilylpropyl)tetrasulfide, obtained from Dunlop India Ltd., Sahaganj.

[e] *N*-cyclohexyl benzothiazyl sulfenamide, obtained from Alkali Chemical Corp. of India Ltd., Rishra.

placement for carbon black. Some studies have been made on silane-treated clays.[11-14]

In the present work we have studied how the clay affects the vulcanization, network structure, and technical properties of natural rubber in the presence of silane-coupling agents [vinyltris(2-methoxyethoxy)silane (that is, A-172) and bis(triethoxysilylpropyl)tetrasulfide (that is, Si-69)]. We have included sulfur as well as dicumyl peroxide (DCP) vulcanization systems in order to study variation of network structure and polymer–filler interaction with coupling agents in different vulcanization systems.

In the last part of the present work, we have carried out SEM studies of failure surfaces in order to explain the mechanism of failure of clay-filled vulcanizates in the presence and absence of silane coupling agents. Of late, SEM studies have been used to study failure surfaces of rubber products.[15-19]

EXPERIMENTAL

The formulations of the mixes are shown in Tables I and II. Their curing parameters as obtained from Monsanto rheometer (R-100) are shown in Tables

TABLE II
Formulations of Mixes

Mix	N	O	P	Q	R	S	T	U	V
Natural rubber[a]	100	100	100	100	100	100	100	100	100
Dicumyl peroxide[b]	2	2	2	2	2	2	2	2	2
China clay[c]	—	5	20	40	60	5	20	40	60
A-172[d]	—	—	—	—	—	0.37	1.50	3.00	4.50

[a] Natural rubber, crumb grade, obtained from the Rubber Research Institute of India, Kottayam.

[b] Di($\alpha\alpha$-dimethylbenzyl)-peroxide, obtained from BDH Chemicals Ltd., Poole, England.

[c] Semireinforcing type obtained from Dunlop India Ltd., Sahaganj.

[d] Vinyltris(2-methoxyethoxy)silane, obtained from Indian Cable Co., Ltd., Jamshedpur.

TABLE III
Curing Characteristics of the Mixes (Sulfur Vulcanizing Systems) at 150°C

	No additive				A-172				Si-69			
Clay(phr):	5	20	40	60	5	20	40	60	5	20	40	60
Mix	A	B	C	D	E	F	G	H	I	J	K	L	M

Mix	A	B	C	D	E	F	G	H	I	J	K	L	M
Clay(phr)	5	20	40	60	5	20	40	60	5	20	40	60	
Rheometric scorch time t_2 (min)	5	4	4	4.5	4	4	4.5	4.5	3	3	3	3	3
Optimum cure time (min)	10.5	9.5	10	10.5	11	10	10.5	12	12.5	10.5	11	12	13.5
Reversion time (min)	32	26	24	24	22	24	22	22	21.5	46	46	44	38
Maximum rheometric torque (N·m)	7.9	7.9	8.0	8.3	8.7	7.8	7.6	7.5	7.5	8.3	8.3	8.2	7.9

III and IV. The mixes were prepared on a (32.5 cm × 15 cm) laboratory mill. Vulcanization was carried out at 150°C in an electrically heated press. Moldings were cooled immediately in water after the end of the curing cycle.[20]

Determination of Degree of Reinforcement

The extent of reinforcement was determined using the equation of Cunneen and Russell[21] [eq. (3)], which is a modification of the original equation given by Lorenz and Parks[22] [eq. (1)]:

$$\frac{Q_f}{Q_g} = ae^{-Z} + b \tag{1}$$

Also

$$\frac{Q_f}{Q_g} = \frac{V_{r0}(1 - V_{rf})}{V_{rf}(1 - V_{r0})} \simeq \frac{V_{r0}}{V_{rf}} \tag{2}$$

So,

$$\frac{V_{r0}}{V_{rf}} = ae^{-Z} + b \tag{3}$$

where Q is the amount of solvent imbibed per unit weight of the rubber, f and g refer to filled and gum mixes, and V_{r0} and V_{rf} are the volume fractions of rubber in unfilled and filled volcanizates, respectively, swollen in a solvent, Z is the weight fraction of filler in the vulcanizate, and a and b are constants characteristic of the system. By plotting V_{r0}/V_{rf} against e^{-Z}, values of a (slope) and b (intercept) were determined. The higher the value of a, the higher the swelling restriction and reinforcement.[23]

A method of determining "true" chemical crosslink density of the vulcanizates after due correction for polymer–filler interaction as suggested by Cunneen and Russell[21] has been used in the present study as well as in our previous studies.[1,2]

TABLE IV
Curing Characteristics of the Mixes (Peroxide Vulcanizing Systems) at 150°C

	No additive				A-172			
Clay(phr):	5	20	40	60	5	20	40	60
Mix	N	O	P	Q	R	S	T	U	V

Mix	N	O	P	Q	R	S	T	U	V
Rheometric scorch time t_2 (min)	2.5	2.0	2.0	2.0	2.5	2.0	2.5	2.5	2.5
Optimum cure time (min)	21.5	23.5	24.0	24.5	25.0	22.0	22.5	23.0	24.0

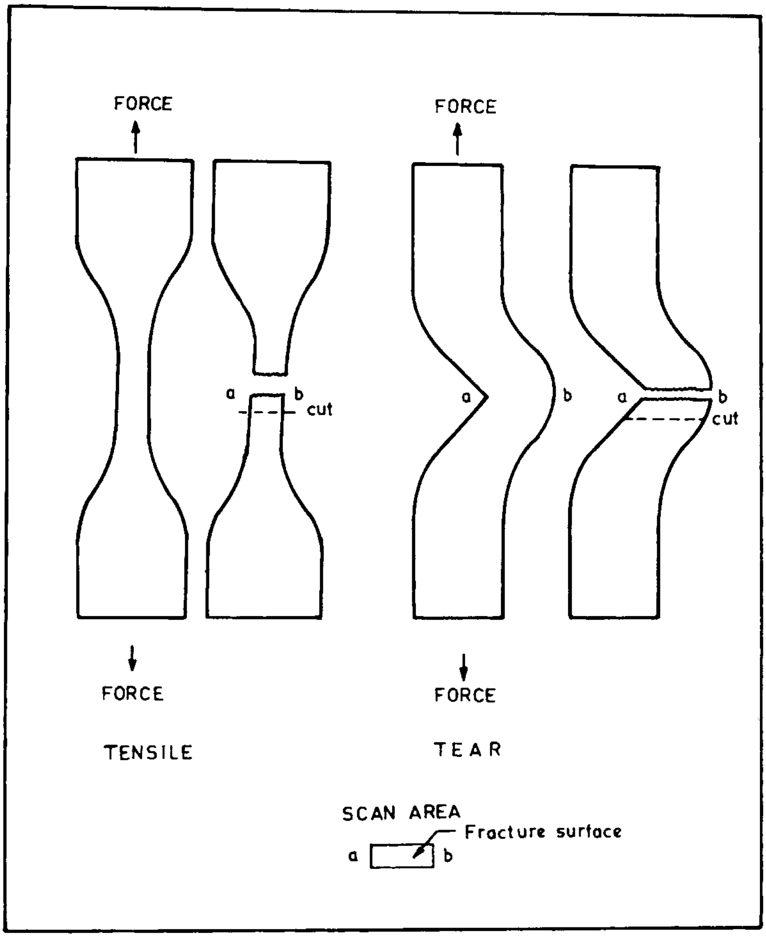


Fig. 1. Mode of failure after tension and tear, and the scan area of fractured sample.

Polymer–filler attachment, defined as the coupling bond, was determined from the difference of "apparent" chemical crosslink density (derived without correction for polymer–filler interaction[23,24]) and "true" crosslink density as determined above.

The degree of reinforcement was also studied by using Kraus equation[25]

$$V_{ro}/V_{rf} = 1 - m\phi/(1 - \phi) \tag{4}$$

here

$$m = 3c(1 - V_{r0}^{1/3}) + V_{r0} - 1 \tag{5}$$

Here ϕ is the volume fraction of filler in the filled vulcanizate and c is a constant characteristic of the filler, but independent of the polymer, the solvent or the degree of vulcanization. The slope of the curve obtained by plotting V_{r0}/V_{rf} vs. $\phi/(1 - \phi)$ provides an idea about the degree of reinforcement. The higher the slope, the higher the reinforcement.

Determination of Network Structure and Technical Properties

Chemical crosslinks, the proportion of polysulfidic crosslinks, sulfur combined $[S_c]$ in the network, free sulfur, sulfide sulfur $[S^{-2}]$ concentrations, and technical properties of the vulcanizates were determined by the methods as reported in our earlier studies.[1,20]

Ammonia-Modified Swelling

For measuring the polymer–filler attachment (or coupling bond) experimentally, polymer–filler bonds were cleavaged chemically by swelling the vulcanizate samples for 48 h in flat dishes containing benzene in ammonia atmosphere,[26] prepared by placing concentrated NH_4OH in the bottom of a closed desiccator. After swelling in ammonia atmosphere, the samples were thoroughly washed with benzene and dried in a vacuum desiccator at room temperature (28°C) and tested for stress–strain properties and polymer–filler attachment by swelling of the dried specimen in benzene. The difference in chemical crosslink density as obtained by swelling studies in benzene, of the original vulcanizates and the same after ammonia treatment gives a measure of the polymer–filler attachment or coupling bond.

Scanning Electron Microscopy Studies

Figure 1 indicates the direction in which force was applied in tensile and tear tests. After tensile and tear tests, the respective fracture surfaces were carefully

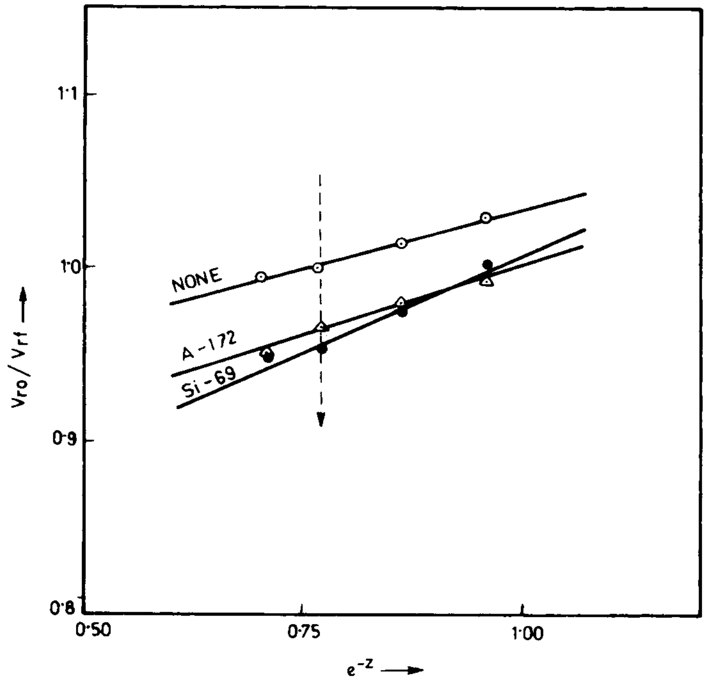


Fig. 2. Plot of V_{r0}/V_{rf} vs. e^{-Z} for the sulfur system.

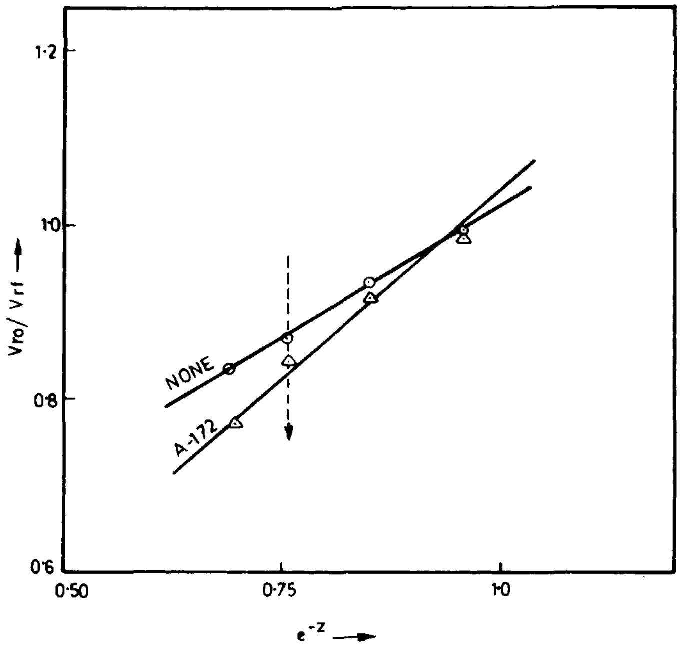


Fig. 3. Plot of V_{r0}/V_{rf} vs. e^{-Z} for the peroxide system.

cut out from one of the two pieces of the failed test specimens without touching the surface. These test specimens were stored in a desiccator in order to avoid contamination and then sputter-coated with gold within 24 h of testing. SEM photographs of the tested specimens were taken using a Phillips 500 Model scanning electron microscope. The respective scan areas of the specimens are also shown in Figure 1.

RESULTS AND DISCUSSION

Reinforcement Characteristics

In order to evaluate polymer–filler interaction, we have plotted the values of V_{r0}/V_{rf} vs. e^{-Z} for the sulfur system in Figure 2 and for the DCP system in Figure 3.

In Figure 2, it is found that a few V_{r0}/V_{rf} points for the mix with no coupling agent were above 1.0, indicating lack of reinforcement due to dewetting and vacuole formation[23] in the swollen rubber matrix in the absence of coupling agent. The mix containing Si-69 provides a higher slope than that of mix containing A-172, which in turn provides a higher slope than that of mix with no additive. In Figure 2, the dotted line drawn at a particular e^{-Z} shows the relative reinforcing power of coupling agents in sulfur vulcanization system as follows,

no additive < A-172 < Si-69

In Figure 3, it is found that all the V_{r0}/V_{rf} points for the mix without coupling agent are below 1.0, indicating an absence of dewetting and vacuole formation in the swollen rubber matrix. However, the mix containing A-172 shows a steeper

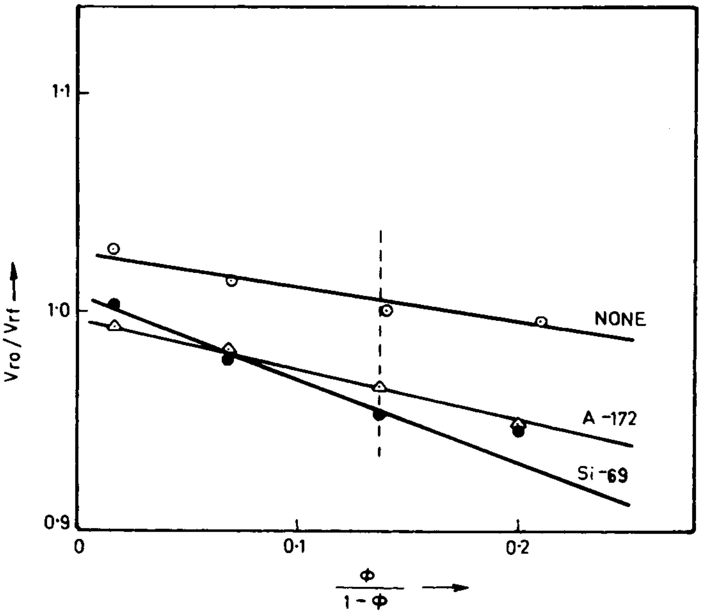


Fig. 4. Plot of V_{r0}/V_{rf} vs. $\phi/(1-\phi)$ for the sulfur system.

slope than that of mix having no coupling agent. Hence in the DCP vulcanization system, the relative reinforcing power is as follows:

no additive < A-172

The above statements regarding reinforcing activity of coupling agents were also verified by the Kraus plots as shown in Figures 4 and 5, respectively. The

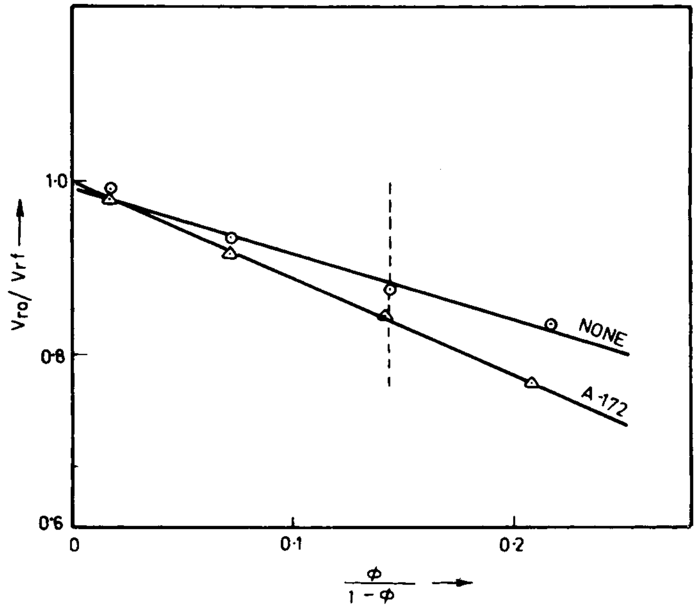


Fig. 5. Plot of V_{r0}/V_{rf} vs. $\phi/(1-\phi)$ for the peroxide system.

order of steepness of the slopes obtained by plotting V_{r0}/V_{rf} vs. $\phi/(1-\phi)$ is given by

in the sulfur system: no additive < A-172 < Si-69

in the DCP system: no additive < A-172

Figures 2 and 3 provide the following equations, which have been used in calculating V_{r0} required for calculating the chemical crosslink density after correction for restriction of swelling due to polymer–filler attachment[21,24]:

for the sulfur vulcanization system:

$$\text{with no additive:}\quad V_{r0}/V_{rf} = 0.09e^{-Z} + 0.91 \tag{6}$$

$$\text{with A-172:}\quad V_{r0}/V_{rf} = 0.17e^{-Z} + 0.83 \tag{7}$$

$$\text{with Si-69:}\quad V_{r0}/V_{rf} = 0.25e^{-Z} + 0.75 \tag{8}$$

for the DCP vulcanization system:

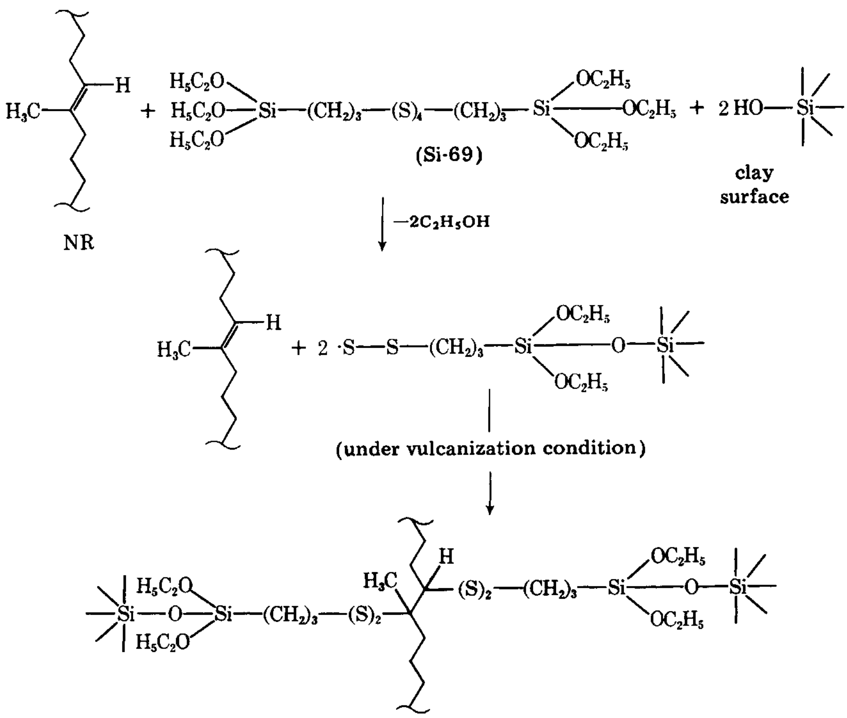
$$\text{with no additive:}\quad V_{r0}/V_{rf} = 0.58e^{-Z} + 0.42 \tag{9}$$

$$\text{with A-172:}\quad V_{r0}/V_{rf} = 0.70e^{-Z} + 0.30 \tag{10}$$

Hence, from analyses of these equations, it is revealed that polymer–filler interaction or polymer–filler attachment in both cases (with and without A-172) are higher in the DCP vulcanization system than that of the sulfur vulcanization system.

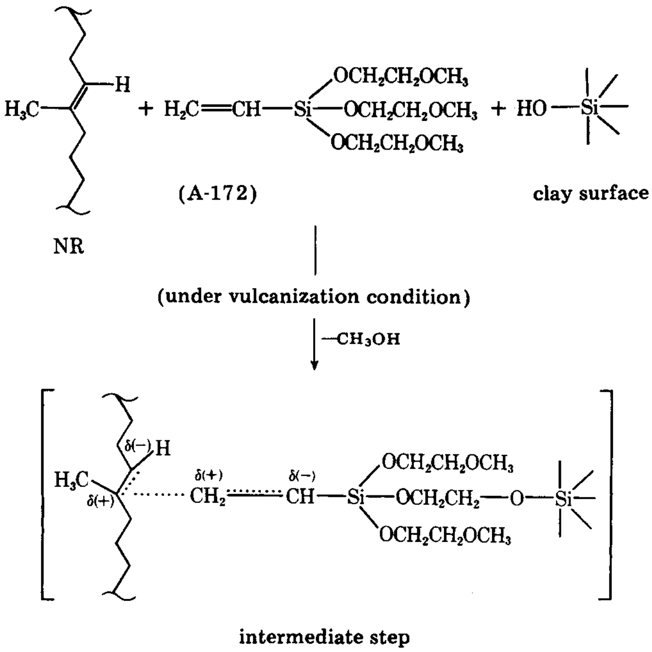
A mechanism of reinforcement due to the incorporation of (a) Si-69 and (b) A-172 in clay-filled natural rubber has been proposed as given below:

(a)

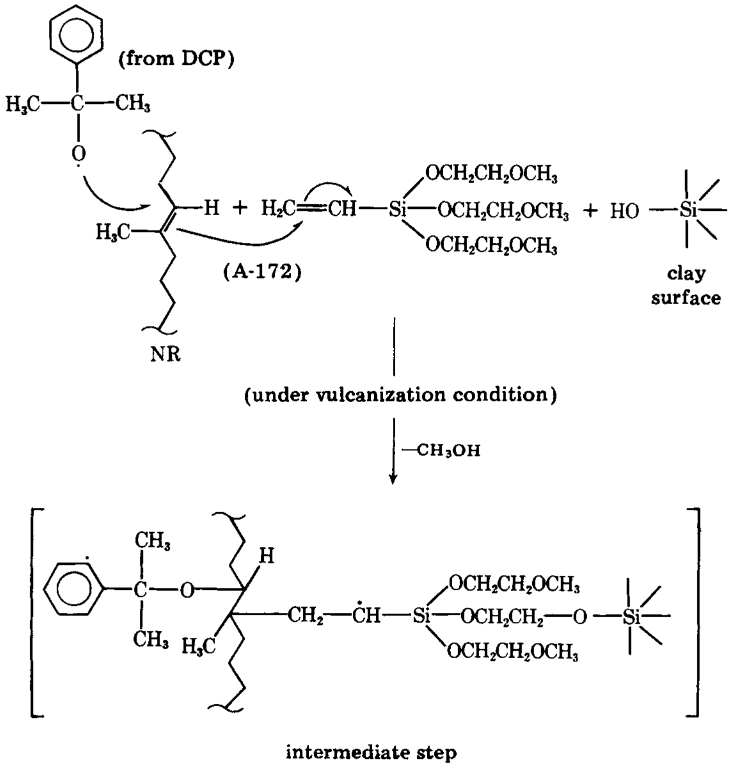


(b)

(i) in the sulfur vulcanization system



(ii) in the DCP vulcanization system



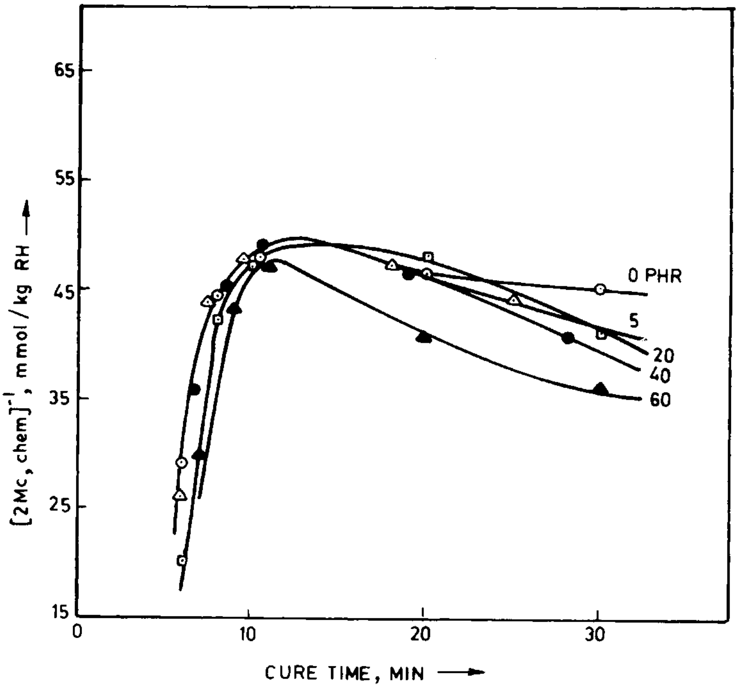


Fig. 6. Plot of total chemical crosslinks [2Mc, chem]$^{-1}$ vs. cure time in the presence of clay alone in the sulfur system.

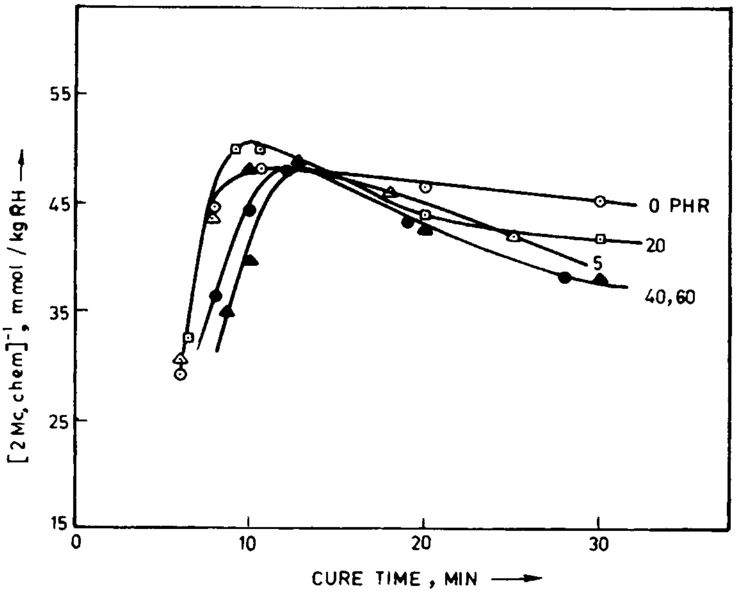


Fig. 7. Plot of total chemical crosslinks [2Mc, chem]$^{-1}$ vs. cure time in the presence of clay and A-172 in the sulfur system.

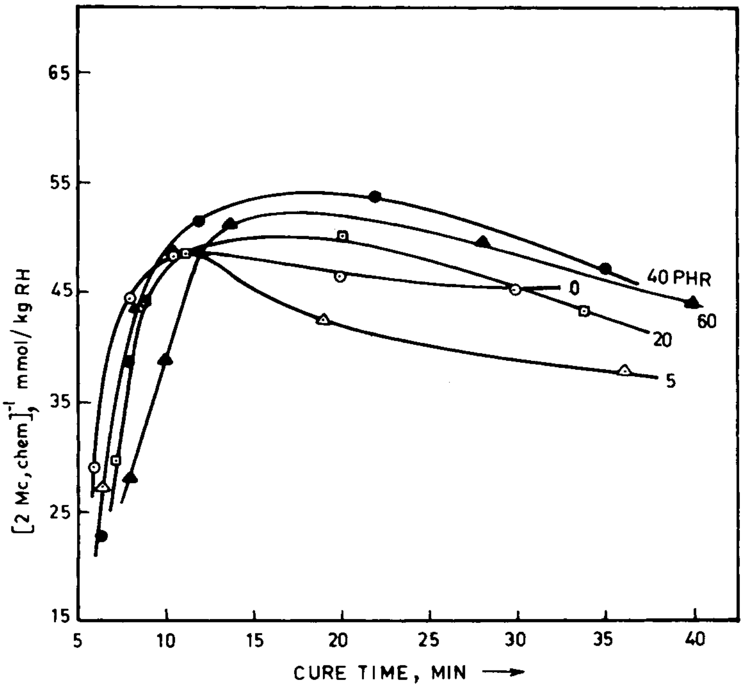


Fig. 8. Plot of total chemical crosslinks [2Mc, chem]$^{-1}$ vs. cure time in the presence of clay and Si-69 in the sulfur system.

According to this reaction mechanism, it is found that, in the sulfur vulcanization system, a single molecule of Si-69 can couple free radically with each olefinic unit of elastomer molecule, and also with two units of clay through condensation of its ethoxy groups and surface —OH groups of clay resulting in the formation of ether linkages with a greater ease than that of A-172 which can interact with the elastomer through its vinyl group rather with a great difficulty since the dipole is hardly induced both in vinyl group and elastomer under these circumstances. However, in the DCP vulcanization system, the cumyloxy radical facilitates in creating free radical on the tertiary carbon, which may undergo interaction with the vinyl group of A-172. The resultant product thus formed, having free radical on methene carbon, may continue further coupling reaction.

The order of reinforcing activity in the sulfur vulcanization system (no additive < A-172 < Si-69) and in the DCP vulcanization system (no additive < A-172) can thus be understood.

Network Structure and Kinetics of Crosslinking

Sulfur System

The variation of total chemical crosslinks [2Mc,chem]$^{-1}$ and polysulfidic crosslinks at different cure times are shown in Figures 6–11. The results of the network structure of the vulcanizates at the respective optimum cure times are shown in Table V.

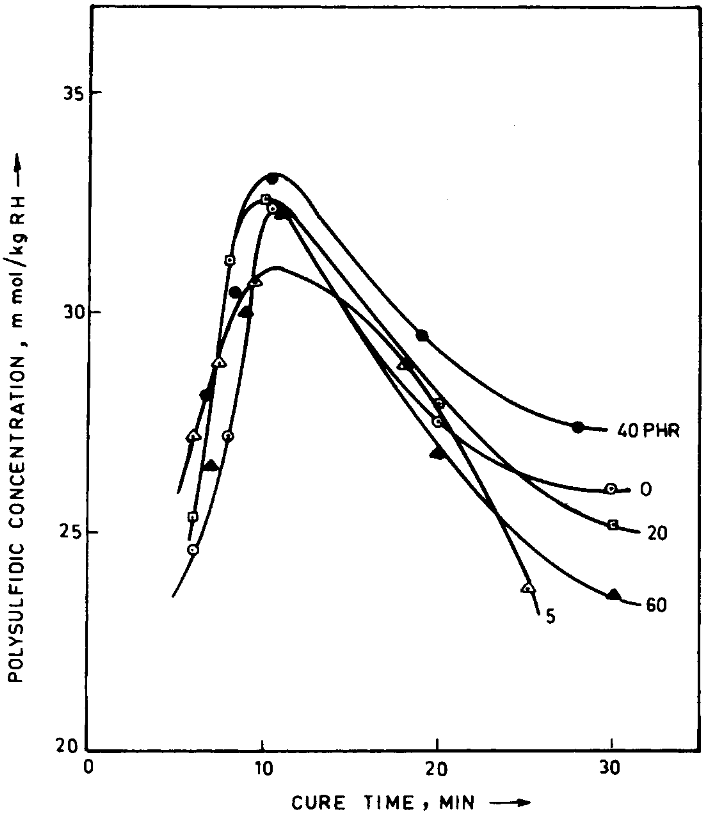


Fig. 9. Plot of polysulfidic crosslinks vs. cure time in the presence of clay alone in the sulfur system.

In the case of clay mixes with no additive (mixes B–E) both crosslink density and polysulfidic crosslinks pass through maxima with increase in cure time. But, at higher loading, the rate of decrement of total chemical crosslinks and polysulfidic crosslinks beyond the maximum becomes higher. At optimum cure time, total chemical crosslinks and polysulfidic crosslinks almost remain constant on the addition of filler. In the case of mixes with A-172 (mixes F–I), similar changes in total crosslink density and polysulfidic crosslinks are observed with increase in cure time, whereas, in the case of mixes with Si-69 (mixes J-M), the mode of changes is different. The increase of filler loading to 40 and 60 phr tends to increase the crosslink density and polysulfidic crosslinks at prolonged cure times. This appears to be due to the reversion resistance properties of Si-69, which is markedly manifested at higher filler loading and also rebuilding of exactly as many polysulfidic crosslinks as have just disappeared during overcure.[27] The less crosslink destruction processes in the mixes with Si-69 are also evident from the lower and constant F values (Table V).

It is also evident in Table V that the network structure is not affected significantly by the presence of coupling agents and addition of filler. The coupling bond or polymer filler attachment, as evident from Figure 12, passes through a maximum in the region of optimum cure times for all mixes. But at a particular

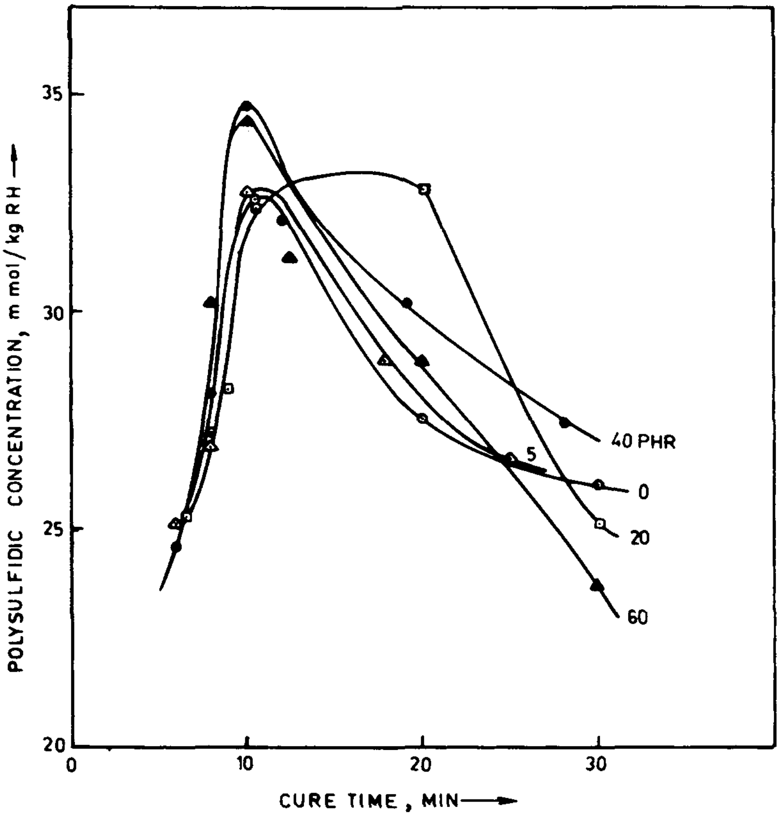


Fig. 10. Plot of polysulfidic crosslinks vs. cure time in the presence of clay and A-172 in the sulfur system.

filler loading as seen from Figure 13, the order of magnitude of coupling bond of the mixes is as follows:

no additive < A-172 < Si-69

Peroxide System

In this case, unlike sulfur vulcanization, total chemical crosslink density does not pass through a maximum, but marches with increase in cure time[28] (Figs. 14 and 15). In the case of mixes without A-172, it is found from Figure 14 that, at higher filler loading and at prolonged cure times, the rate of increment of crosslink density decreases. However, in the case of mixes with A-172, it is found from Figure 15 that, at prolonged cure times, the crosslink density of highly filled mixes (40 and 60 phr) are more as compared to mixes having a lower level of clay, although the rate of increase of crosslink density at prolonged cure times is almost similar to that of mixes without A-172. At optimum cure time, the total chemical crosslinks are almost the same in all the mixes, as is evident from Table VI. Hence the presence of A-172 and the addition of filler do not have any significant effect on the network structure of peroxide cured vulcanizate. Unlike sulfur

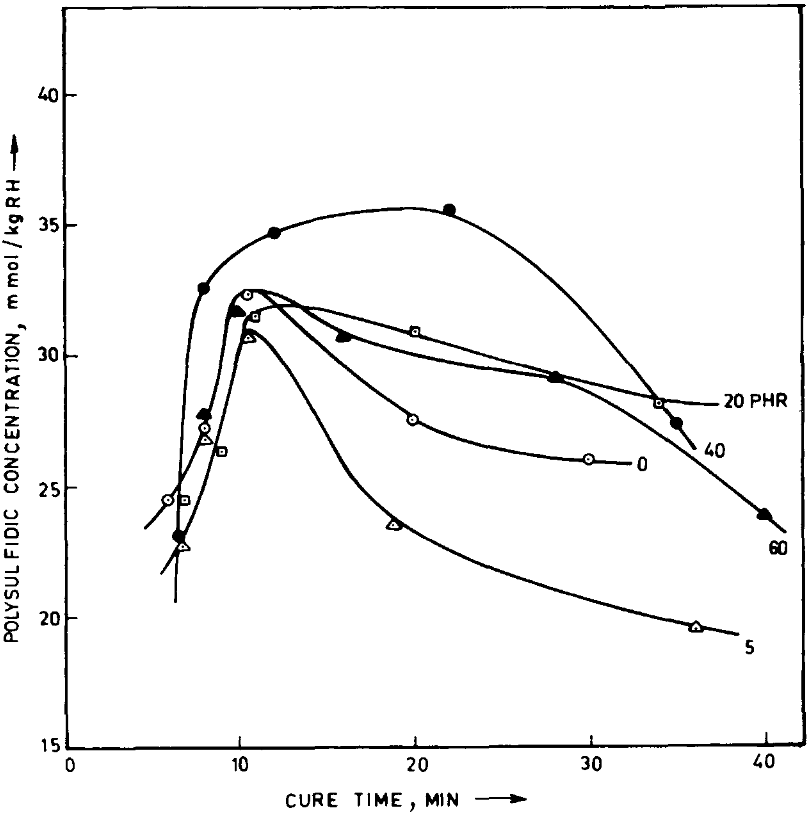


Fig. 11. Plot of polysulfidic crosslinks vs. cure time in the presence of clay and Si-69 in the sulfur system.

vulcanization, the coupling bond of peroxide-cured vulcanizate also does not pass through a maximum with increase in cure time (Fig. 16). It is evident from Figure 17 that the coupling bond increases with filler loading and, at any level of filler, the amount of the coupling bond of the mix containing A-172 is higher than that of the mix with no coupling agent.

Technical Properties

Sulfur System

Technical properties of the vulcanizates, as shown in Table VII, indicate that the properties largely associated with improved reinforcement, viz., tensile strength, modulus, and tear strength, are only marginally higher for the mxies with Si-69 and A-172 than that of mixes without additive.

A higher modulus is observed in the mix with Si-69 than in that with A-172 whose modulus is again higher than that of the mix without additive. Modulus of a vulcanizate is a property which is solely governed by the total amount of chemical crosslinks and coupling bonds (polymer–filler attachment). As is seen from Table V, chemical crosslinks are almost the same in all the mixes, so that

TABLE V

Chemical Characterization of Sulfur-Cured Vulcanizates

		No additive			A-172				Si-69				
	Clay(phr):	5	20	40	60	5	20	40	60	5	20	40	60
Mix	A	B	C	D	E	F	G	H	I	J	K	L	M
Total chemical crosslinks, $[2M_c, \text{chem}]^{-1}$ (mmol/kg RH)	48.1	48.0	47.6	49.1	47.4	48.1	49.5	48.2	48.8	48.2	48.7	51.4	51.2
Polysulfidic crosslinks (%)	67	64	68	67	68	68	65	66	64	64	65	68	60
Network combined sulfur $[S_c] \times 10^{-2}$ (mmol/kg RH)	7.0	7.1	7.0	6.8	6.8	6.9	6.6	6.2	6.1	7.1	7.1	6.8	6.6
E, atoms/chemical crosslink	14.6	14.7	14.2	14.1	13.9	13.6	13.8	12.6	12.8	14.7	14.6	13.2	12.9
F, Sulfide ion/chemical crosslink	0.7	1.0	1.0	1.2	1.1	0.6	0.8	0.9	0.9	0.9	0.9	0.9	0.9
Free sulfur concentration (mmol/kg RH)	47	25	28	40	42	59	86	123	132	28	30	59	69

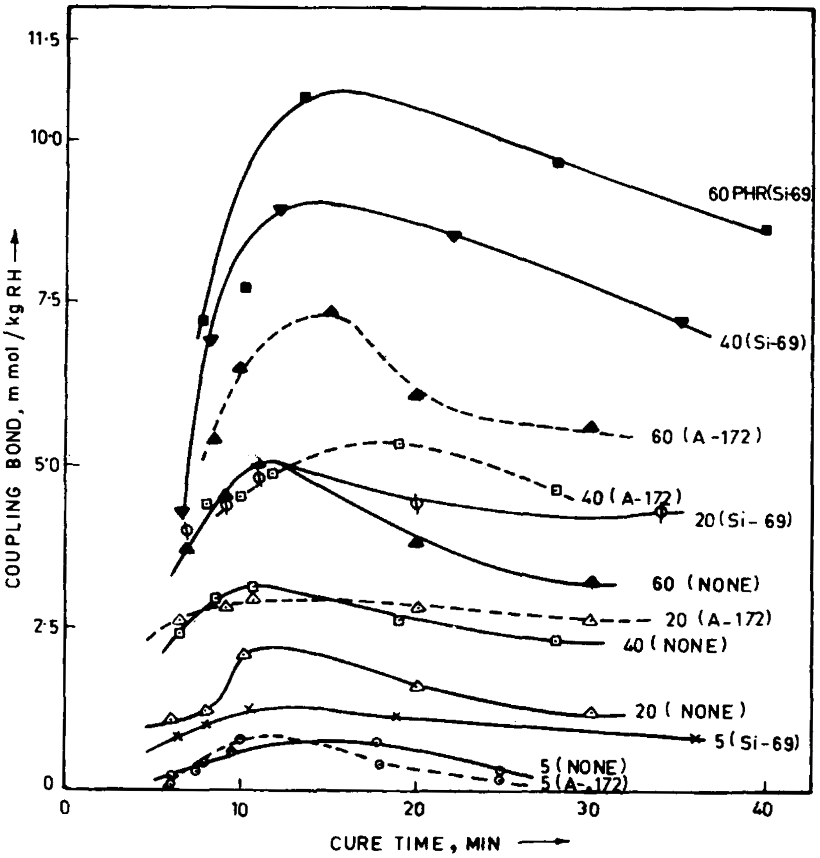


Fig. 12. Variation of coupling bond with cure time in the presence of (a) clay, (b) clay with A-172, and (c) clay with Si-69, in the sulfur system.

amount of coupling bonds becomes responsible for a higher modulus of mixes with Si-69 and A-172 than that of the mix without additive. We have earlier seen that the amount of coupling bonds follow the order

Si-69 > A-172 > no additive

The difference in values of tensile strength between mixes with additive and without additive is not much. It must be realized that for strain-crystallising rubbers like NR, the enhancement of tensile strength is not a criterion for reinforcement. Tear strength of vulcanizates follows a similar pattern like modulus.

Elongation at break varies inversely with the total amount of chemical crosslink density and coupling bonds. Since the crosslink density is almost constant in the mixes, elongation at break follows the order Si-69 < A-172 < no additive. The order is reverse of the order of coupling bond. Technical properties after ammonia swelling as reported in Table VIII also confirms this observation.

As hardness of vulcanizate largely depends on the amount of chemical cross-

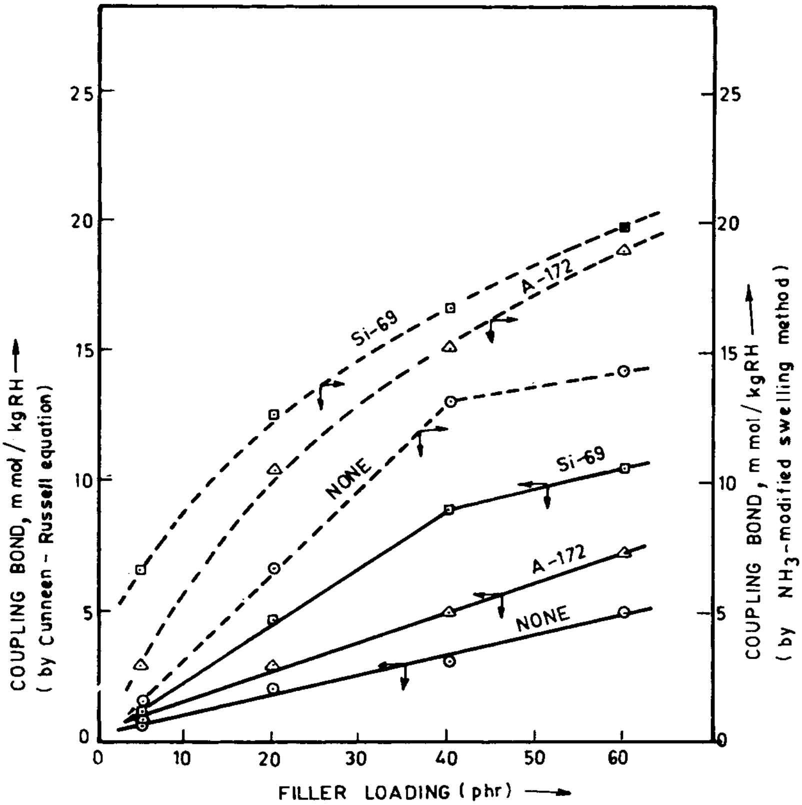


Fig. 13. Variation of coupling bonds [measured by (i) Cunneen–Russell equation and (ii) ammonia-modified swelling method] with filler loading in presence of (a) clay, (b) clay with A-172, and (c) clay with Si-69, in the sulfur system.

links and polymer filler attachment, the order of hardness of the mixes is: no additive < A-172 < Si-69.

Polymer–filler interaction controls the compression set property of vulcanizate: the higher the interaction, the lower the compression set. The results of Table VII show the lowest compression set of mixes with Si-69 and the highest compression set for the mix with no coupling agent.

About abrasion resistance, no marked improvements are noticed. The mixes containing Si-69 and A-172 have slightly more abrasion resistance than the mix containing no coupling agent. Among all the three type of mixes, flex cracking resistance (Table VII) is higher in the mixes containing A-172 than that in the mixes without additive, which resistance in turn is higher than the mixes having Si-69.

Heat buildup and dynamic set properties are good indication of polymer–filler interaction in filled mixes. From Table VII, it is found that heat buildup and dynamic set are lowest in mixes with Si-69 among the three types of mixes.

Table VII shows further that coupling agents have little impact on the rebound resilience whereas higher loading of filler decreases the rebound resilience in all cases, as expected.

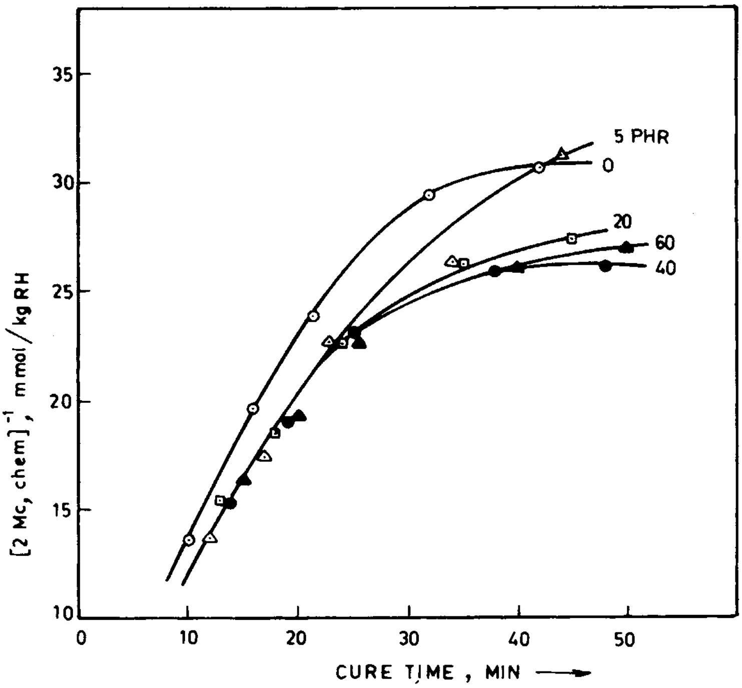


Fig. 14. Plot of total chemical crosslinks [2Mc, chem]$^{-1}$ vs. cure time in the presence of clay alone in the peroxide system.

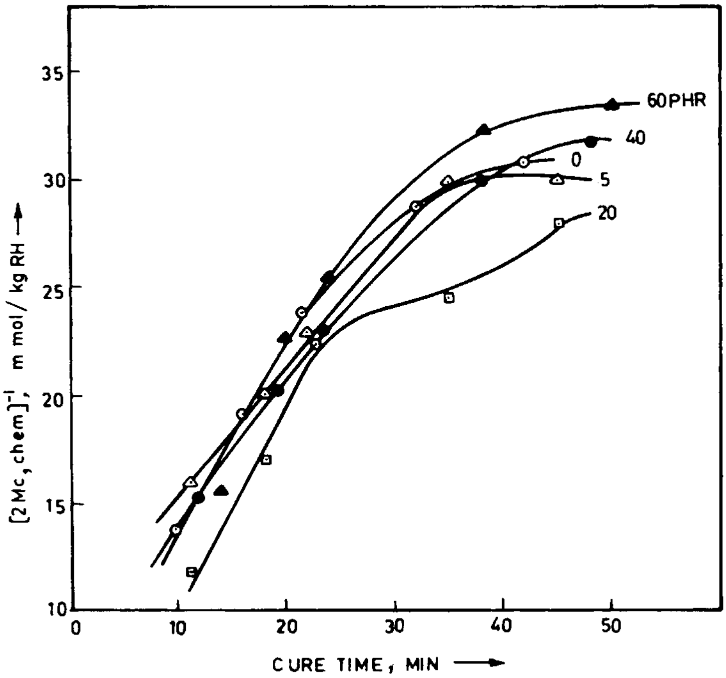


Fig. 15. Plot of total chemical crosslinks [2Mc, chem]$^{-1}$ vs. cure time in the presence of clay and A-172 in the peroxide system.

TABLE VI
Chemical Characterization of Peroxide-Cured Vulcanizates

		No additive				A-172			
Clay(phr):		5	20	40	60	5	20	40	60
Mix	N	O	P	Q	R	S	T	U	V
Total chemical crosslinks, [2Mc, chem]$^{-1}$ (mmol/kg RH)	23.8	22.7	22.6	23.1	22.9	22.9	22.4	22.8	25.6

Peroxide System

Technical properties of the vulcanizates cured by DCP are shown in Table IX. As compared to sulfur-cured vulcanizates, the difference in values of properties (that is, those mainly govern reinforcement, viz., tensile strength, tear strength,

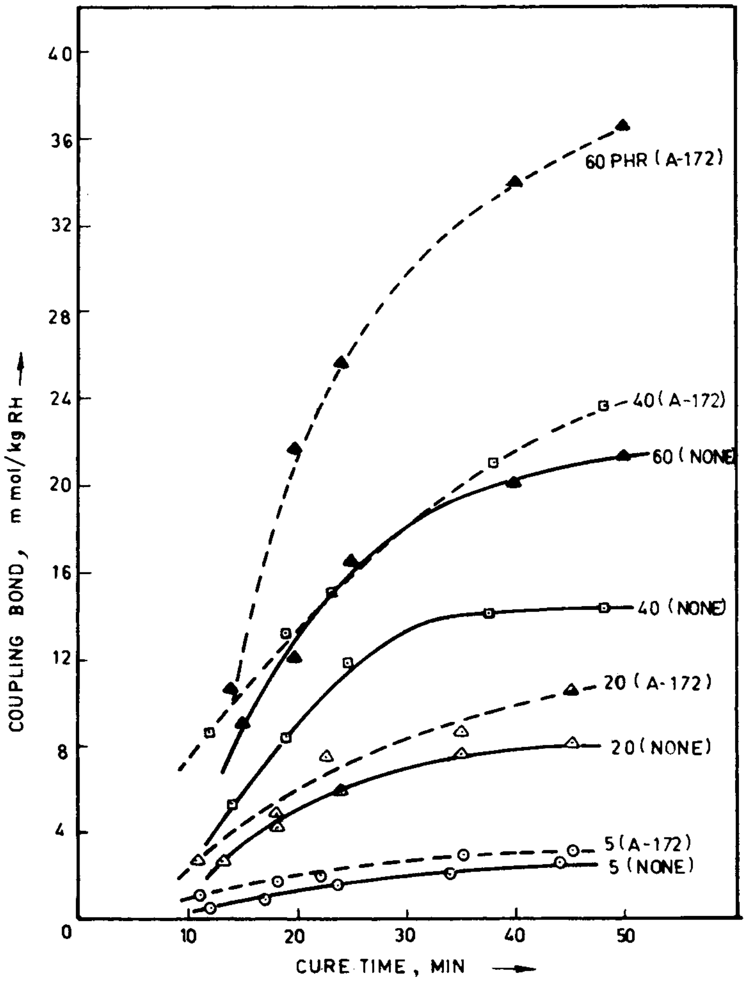


Fig. 16. Variation of coupling bond with cure time in the presence of (a) clay and (b) clay with A-172, in the peroxide system.

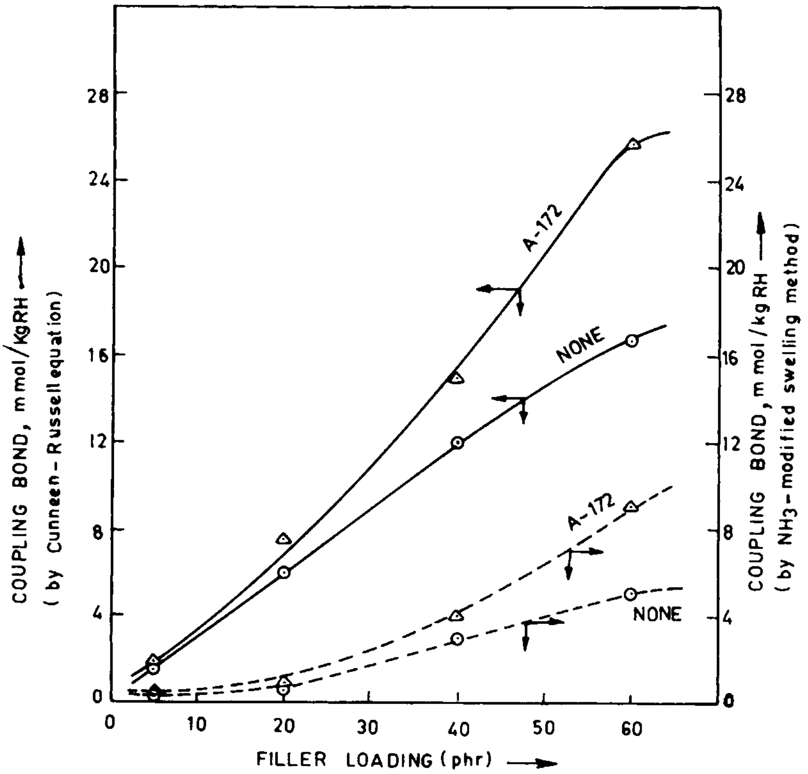


Fig. 17. Variation of coupling bonds [measured by (i) Cunneen–Russell equation and (ii) ammonia-modified swelling method] with filler loading in presence of (a) clay and (b) clay with A-172, in the peroxide system.

modulus, and abrasion resistance) between the mixes with and without A-172 is considerably higher in the DCP-cured system. This indicates higher polymer–filler interaction in mixes with A-172 cured by DCP.

Elongation at break is lower in mixes with A-172 than that in those without A-172 due to higher proportion of coupling bonds in the former case (Figures 16 and 17). The results of Table VIII also support the higher values of tensile strength, tear strength, modulus, and abrasion resistance and the lower values of elongation at break for the mixes containing A-172.

Hardness and rebound resilience are higher in the mixes having A-172 than in those without A-172 due to the higher percentage of coupling bond.

Properties like compression set, dynamic set, and heat buildup, which are very much dependent on polymer–filler interaction, are lower in the mixes containing A-172 than that of mixes without A-172, indicating higher polymer–filler interaction in the former case.

Flex cracking resistance is better with A-172.

Scanning Electron Microscopy Studies

In order to understand the failure mechanism in both sulfur and peroxide vulcanization systems, we have studied the mode of failure by tension and tear at 40 phr clay level of SEM.

TABLE VII
Physical Properties of Sulfur-Cured Vulcanizates

		No additive				A-172				Si-69			
	Clay(phr):	5	20	40	60	5	20	40	60	5	20	40	60
Mix	A	B	C	D	E	F	G	H	I	J	K	L	M
Modulus 300% (MPa)	1.7	2.2	2.9	4.2	5.8	2.3	3.3	5.1	7.2	2.6	3.9	5.6	7.7
Tensile strength (MPa)	26.3	24.7	23.4	23.5	23.1	25.9	26.2	26.0	21.9	25.4	24.8	24.5	21.3
Elongation at break (%)	700	690	670	650	590	675	640	620	555	660	630	610	540
Tear strength (kN·m^{-1})	35.7	34.9	30.6	30.3	29.5	34.1	33.1	30.9	29.7	36.7	36.5	37.5	37.6
Hardness, shore A	45	46	48	51	55	46	48	50	56	46	49	54	58
Compression set (%)	39	48	56	58	62	44	50	57	59	43	47	50	55
Abrasion loss (cc/1000 rev)	3.1	2.6	2.1	1.8	1.8	2.5	1.9	1.8	1.7	2.5	2.0	1.8	1.8
Flex cracking resistance (kilocycles)	90	65	52	31	22	78	55	36	25	52	35	24	19
Heat buildup (ΔT°C)	3	5	7	10	15	5	7	9	13	4	6	7	11
Rebound resilience (%)	88	86	84	80	74	86	84	80	74	86	84	80	74
Dynamic set (%)	1.1	1.4	1.7	2.5	3.2	1.2	1.3	2.0	2.2	1.2	1.2	1.3	1.7

TABLE VIII
Percent Retained in Properties of Vulcanizates After Ammonia-Modified Swelling

	Sulfur System				DCP system				
	No additive		A-172	Si-69	No additive			A-172	
Clay(phr):	0	40	40	40	0	40	60	40	60
	A	D	H	L	N	Q	R	U	V
Tensile strength (%)	98	91	83	76	96	75	78	55	55
Modulus 300% (%)	95	79	59	58	95	86	91	81	86
Tear strength (%)	98	75	77	74	96	93	89	71	77
Elongation at break (%)	100	100	105	105	100	115	110	120	115

Tensile Fracture Surface

Fractured surfaces of sulfur cured mixes, that is, mix D (clay alone) and mix L (clay with Si-69), are shown in Figures 18(A) and 18(B), respectively. Figure 18(A) shows vacuoles on the surface caused by dewetting of the clay filler in the rubber matrix. The tensile strength of this mix is also relatively poor (Table VII). By the incorporation of silane coupling agent, dewetting is reduced as evident by the absence of vacuoles [Fig. 18(B)].

In the case of peroxide cured mixes, the fracture surface [Fig. 18(C)] of mix Q (clay alone) shows smooth surface with vacuoles. However, the fracture surface [Fig. 18(D)] of mix U (clay with A-172) shows the absence of vacuoles and more rough surface having coiled tear lines. The tensile strength of mix U is also higher than that of mix Q (Table IX).

Tear Fracture Surface

The fractographs in Figure 19 are views of the tear fracture surface. In the case of sulfur cured vulcanizates, the fractured surface [Fig. 19(A)] of mix D (clay alone) shows more vacuoles as compared to fracture surface [Fig. 19(B)] of mix

TABLE IX
Physical Properties of Peroxide-Cured Vulcanizates

		No additive				A-172			
	Clay(phr):	5	20	40	60	5	20	40	60
Mix	N	O	P	Q	R	S	T	U	V
Modulus 300% (MPa)	1.1	1.2	2.5	4.2	5.2	1.9	3.3	6.6	9.8
Tensile strength (MPa)	12.2	12.3	10.0	13.6	15.6	12.4	11.2	14.0	16.9
Elongation at break (%)	660	650	500	480	460	600	470	440	390
Tear Strength (kN·m^{-1})	17.4	18.3	25.7	26.7	25.2	20.4	27.2	28.2	26.8
Hardness, shore A	37	38	43	49	53	39	45	50	55
Compression set (%)	5	10	14	16	21	6	7	9	12
Abrasion loss (cc/1000 rev)	3.8	4.1	4.0	3.5	3.3	3.9	3.2	2.9	2.6
Flex cracking resistance (kilocycles)	65	45	33	19	12	56	50	24	20
Heat buildup (ΔT°C)	4	6	8	10	12	6	7	8	10
Rebound resilience (%)	81	78	76	72	69	80	78	74	71
Dynamic set (%)	0.3	0.5	0.6	0.8	1.0	0.3	0.5	0.7	0.8

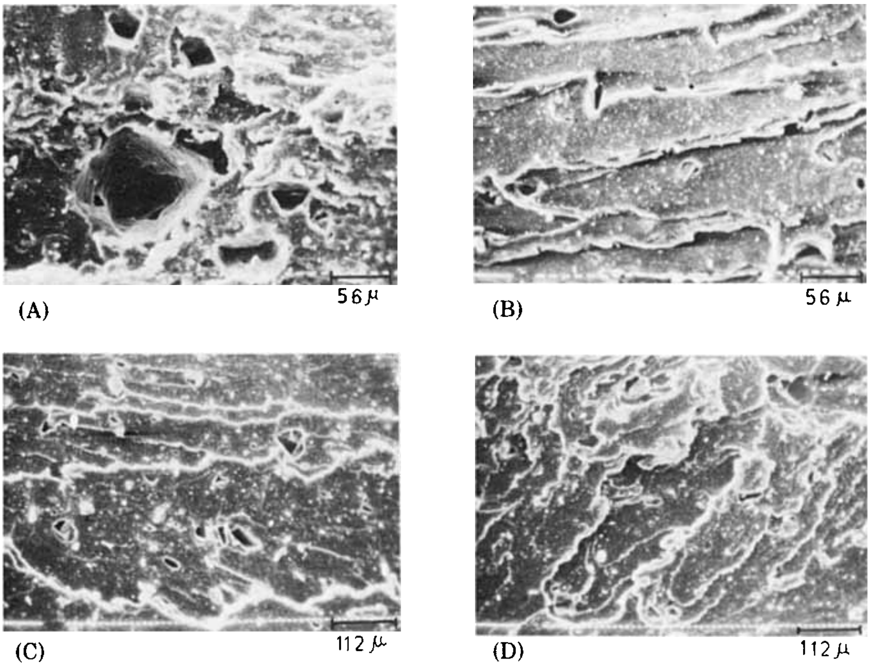


Fig. 18. SEM photographs of tensile fracture surfaces: (A) the presence of vacuoles on the surface of mix D; (B) reduced dewetting of filler on the surface of mix L; (C) smooth surface with vacuoles of mix Q; (D) rough surface with coiled tear lines of mix U.

L (clay with Si-69). It is also evident from Table VII that mix L containing Si-69 gives rise to higher tear resistance.

In the case of peroxide cured mixes, the fractograph [Fig. 19(C)] of mix Q (clay alone) shows vacuoles (that is, more dewetting of filler) and more cracks on the surface than that of mix U (clay with A-172), as shown in the Figure 19(D). The tear lines of mix Q are almost steady in nature. Incorporation of A-172 changes the fracture mode from steady tear to stick-slip tear resulting in increase in tear resistance.[29–31]

CONCLUSIONS

The effect of clay in NR in the presence of silane coupling agents (Si-69 and A-172 in sulfur vulcanization and A-172 in peroxide vulcanization systems) has been analyzed by studies on network structure, technical properties of vulcanizates, and scanning electron micrographs of fracture surfaces. Improved technical properties associated with reinforcement in presence of Si-69 and A-172 have been explained on the basis of higher proportions of coupling bonds in Si-69 and A-172 mixes. Lower values of compression set, dynamic set, and heat buildup of mixes containing Si-69 and A-172 show enhanced polymer–filler attachments (or coupling bonds) in these mixes.

Coupling agents do not have any pronounced effects on the network structure of rubber vulcanizates. Analyses of results obtained from mixes containing A-172

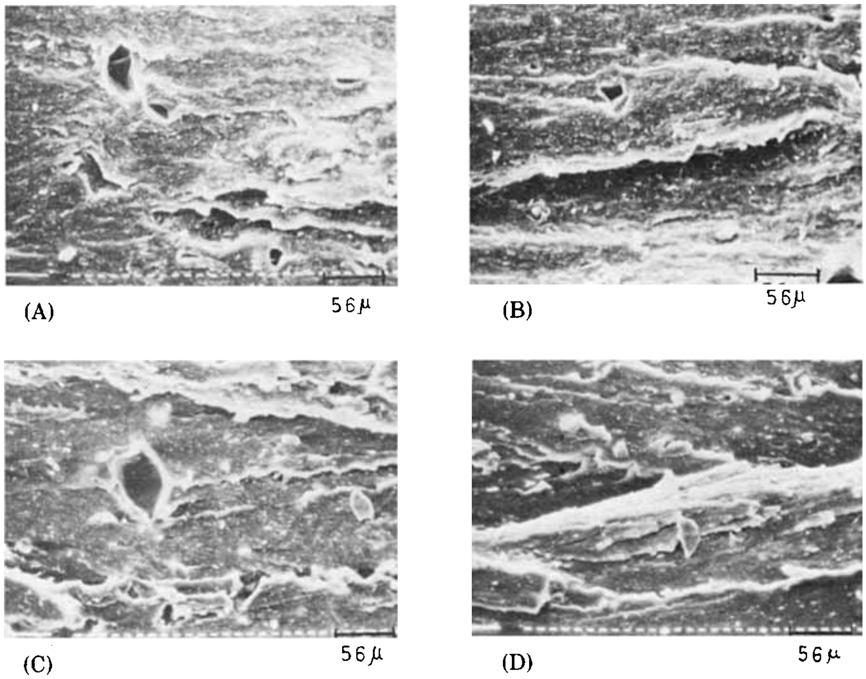


Fig. 19. SEM photographs of tear fracture surfaces: (A) vacuoles formation on the surface of mix D; (B) less vacuoles with tear lines on the surface of mix L; (C) the presence of cracks and dewetting of filler on the surface of mix Q; (D) Tear accompanied by stick-slip process of mix U.

cured by both sulfur and DCP show higher polymer–filler interaction in the DCP system.

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