

Mechanistic Study of Fatigue Behavior of Vinyltriethoxysilane-Coupled Carbon Black/Styrene-Butadiene Rubber Vulcanizate

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ABSTRACT: The increase in fatigue to failure (FTF) cycles by three times was observed for styrene-butadiene rubber (SBR) vulcanizate containing carbon black treated with 2.73 phr vinyltriethoxysilane (VTEOS) over the untreated furnace carbon black (UFCB) vulcanizate at an extension ratio of 1.80. There could be several factors responsible for such a phenomenal increases in FTF; however, specifically the chemical reactions associated with this are investigated. The UFCB contains carboxylic and lactone groups on its surface besides other groups. On treatment with VTEOS, the ethoxy or silanol group(s) of it reacts with the carboxylic and lactone groups of UFCB. This provides an interface between the particulate UFCB and the flexible rubber matrix unlike UFCB, which adsorbs polymer in absence of VTEOS. Furthermore, the vinyl group thus attached to the UFCB takes part in vulcanization reaction and increase in the degree of cross-linking. In addition, the VTEOS substantially reduces the formations of weak polysulphidic linkages. The added flexible interface increased cross-linking and reduced polysulphidic linkages seem to be mainly responsible to the significant improvement of FTF behavior. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 25–34, 2000

INTRODUCTION

Rubbers finds use in many fields due to their superior behavior on repetitive applications. For example, the tread of tire undergoes cyclic stress-strain while rolling and the sole of shoes flex repetitively on use. This repetitive stress-strain property is known as fatigue. The improvement in fatigue is directly associated with the increase in longevity of an intended product.

The addition of vinyltriethoxysilane (VTEOS) to untreated furnace carbon black (UFCB) substantially improved the fatigue to failure (FTF) behavior. Improvement in simple physical adhe-

sion of carbon black (CB) to rubber may not be the right answer for almost three times increase of observed FTF.^{1–7} Besides the physical phenomenon, it seems one need to consider the chemistry behind the silane treatment. In this article, an attempt was made to explore the possible mechanisms of coupling and the association of SCB to the rubber to the network.

EXPERIMENTAL

Materials

Following were the materials used (Table I) in this study: The styrene-butadiene rubber (SBR) (Grade S 1502) was a cold-emulsion polymer with 23% styrene content and Mooney [1 + 4 @ 100°C] viscosity 52, which was a product of Synthetics and Chemicals, Bariely, India. The CB that was

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Table I Recipe of Mixes Containing UFCB and SFCB Containing Different Concentrations of VTEOS

Ingredients	FORMULATIONS					
	F1	F2	F3	F4	F5	F6
SBR	100	100	100	100	100	100
Carbon black	40	40	40	40	40	40
Zinc Oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
CBS	1	1	1	1	1	1
MBTS	1	1	1	1	1	1
Sulphur	1.20	1.20	1.20	1.20	1.20	1.20
Vinyltriethoxysilane	0.00	0.22	0.45	0.91	1.82	2.73
Total weight	150.20	150.42	150.65	151.11	152.02	153.93

used was high-abrasion furnace CB (Grade N 330) with BET surface area of 53 m²/g, a product of Oriental Carbon and Chemicals Ltd, Ghaziabad, India. The VTEOS (LR Grade) was a product of Chemische Fabrik, Fluka AG, Germany. The mercaptobenzothiazyl disulphide and N-cyclohexyl 2-benzothiazylsulphenamide (Rubber Grade) were the products of Polyolefin Industries Ltd, Mumbai, India. Commercial rubber manufacturing grades of sulphur, stearic acid, and zinc oxide were used in compounding. Processing aids were not used to avoid any interference with the reactive silane-coupling agent.

Processing

CB stocks were prepared⁸ by heating UFCB in a B-type oven on open trays over a depth of 7 mm at 125°C for 1 h. These stock were then allowed to cool to 80°C temperature. The required doses of VTEOS were then slowly injected to the UFCB in a rotating container. These treated stocks were kept in airtight containers for making mixes.

The mixing of the ingredients and SBR were done according to American Society for Testing and Materials (ASTM) D 3182-74 in an 18-in. diameter two-roll open mill equipped with heating and cooling facilities. A sheet of 3-mm thickness was cut and left for a maturation time of 24 h before molding.

The molding was carried out in a direct steam heated single daylight hydraulic type molding press. The platen size of the press was 0.5 × 0.5 mm² and the molding was performed at 150°C for 6 min at a pressure of 150 kg/cm². The test pieces made this way were rapidly cooled under running tap water as soon as taken out of the mold.

Measurements

Curemetry

Two discs of about 50-mm diameter were punched out from the 3-mm mixed sheet and were put around the conical rotor of the rheometer (Monsanto, USA). The tests were performed at 150°C in accordance with ASTM D 2705 and the graphs were recorded simultaneously. The properties evaluated were initial torque, optimum torque, final torque, thermoplasticity, and cure rate. The optimum torque is the torque that is just 0.9 times to the difference between the initial and final torque and the time taken to achieve this optimum torque is the optimum cure time. The cure rate is the percentage of the reciprocal to the difference between optimum cure time and the time taken to raise just two units above the initial torque. Thermoplasticity is the difference between optimum torque and initial torque.

Differential Scanning Calorimeter

Samples of about 10 mg were accurately weighed for each run and were scanned in a differential scanning calorimeter (DSC), Du Pont 910, with 9900 programmer (Du Pont, USA). The runs were taken in a self-generating atmosphere. The peak temperatures of the first and second peaks are reported as vulcanization and conversion temperature respectively and the heats of transition of the first and second peaks are reported as the heat of vulcanization and heat of conversion, respectively.

IR Spectroscopy

Approximately 10 mg of samples of treated and untreated CB were mixed thoroughly with 10 g of

KBr separately. Pellets of 2-mm thickness were made for IR measurements. VTEOS was placed in between the KBr plates separated by an O-ring. The traces were recorded on an IR instrument (Perkin Elmer 783, USA).

FTF Test

The dumb bell specimens were punched out with a BS-E cutter from a cured and conditioned sheet. The experiments were conducted with various extension ratios in a FTF tester (Monsanto, USA).

Volume Fraction and Bound Rubber

Samples of 10-mm diameter were punched out from a cured sheet of 2-mm thickness and were allowed to swell in 100-mL benzene at $24 \pm 2^\circ\text{C}$ for 3 days. The volume fraction of rubber is calculated from the original weight, swollen weight, and de-swollen weight.⁹

About 0.3 g of mix was placed in 100 cc of toluene in each case in a tight enclosure for 7 days. The gelled part of the mix was separated by filtration, dried, and weighed. The bound rubber is calculated by employing the standard procedure.

RESULTS AND DISCUSSION

FTF Behavior

The variations of FTF cycles of vulcanizates containing UFCB treated with 0–2.73 phr VTEOS are shown in Figure 1 at four extension ratios. A systematic increase in FTF cycles with the increase in VTEOS content is apparent in all the cases. The increase in FTF value is phenomenal for the vulcanizate containing 2.73 phr VTEOS at an extension ratio of 1.80 than the vulcanizate containing no VTEOS. In general, the FTF curves are much steeper at lower extensions than at higher extensions. At higher extension ratio, it is expected that some physical damage may be introduced which leads to premature FTF failure cycles.

IR Spectroscopy

The IR spectra of UFCB, SFCB, and VTEOS in the desired frequency regions are shown in Figure 2. Although the spectra of UFCB and SFCB resemble each other, there are few regions of dissimilarity. The spectrum of VTEOS is quite sharp

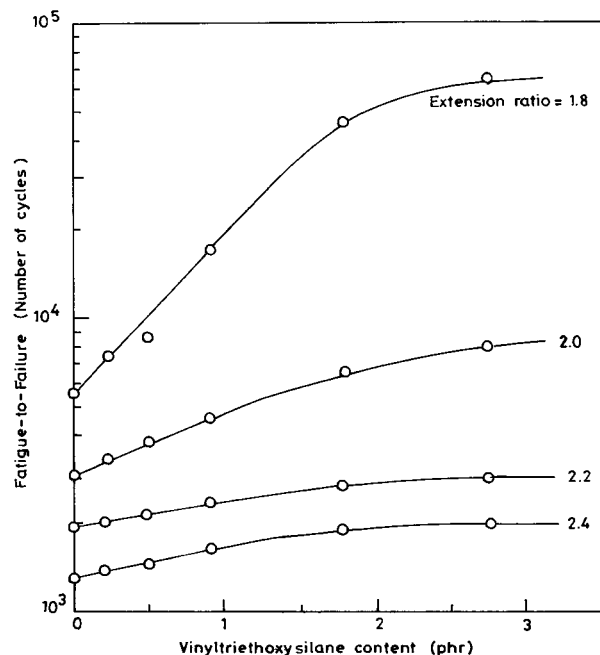


Figure 1 Plot of fatigue to failure cycles against vinyltriethoxysilane at 1.8, 2.0, 2.2, and 2.4 extension ratios.

and different from the above two. The absorption peaks of these spectra are assigned^{10–15} to the presence of different groups and the approximate reasons for the manifestations are given in Table II.

DSC Study of UFCB and SFCB

Figure 3 presents the DSC traces of UFCB and SFCB treated with 2.73 phr of VTEOS in the temperature range of 100–350°C. There is a continuous shifting of base line throughout. The difference between the traces up to the temperature of 200°C is small; it is prominent beyond 200°C. At 150°C, one may notice a distinct change in base line in SFCB trace when compared against the trace of UFCB. There are two broad endothermic peaks, one is approximately at 225 and the other at 275°C. The second peak encompasses few small peaks in the case of UFCB, however the peaks for SFCB at these two temperatures are moderately sharp.

It is interesting to note that there is no endothermic peak at 139°C in the DSC trace of SFCB, which is the boiling point of VTEOS. This indicates that the VTEOS is not present as a simple physical admixture. The endothermic shifting of baseline of SFCB trace at 150°C may be attrib-

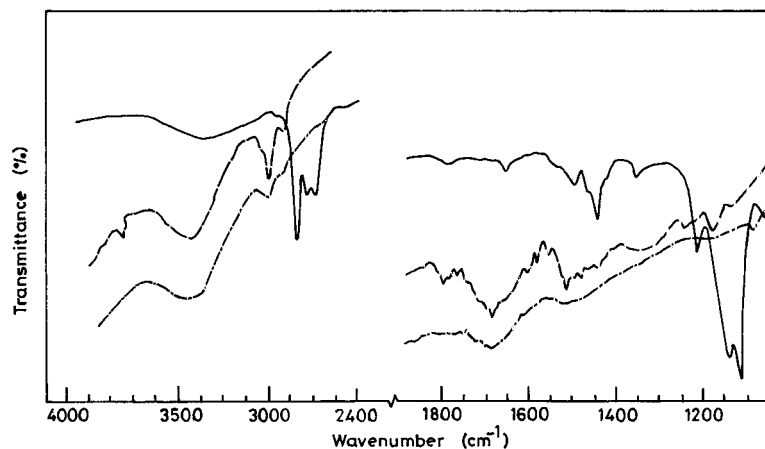


Figure 2 IR spectra of vinyltriethoxysilane (—), untreated furnace carbon black (---) and furnace carbon black treated with 2.73 phr of vinyltriethoxysilane (-·-).

uted to the release of the unreacted part of VTEOS. The chemically combined VTEOS may be responsible for the significant modification of the DSC trace of SFCB in the temperature range of 200–350°C.

Coupling Mechanism

The observations of IR and DSC of UFCB, SFCB and VTEOS could be summarized as:

1. main chemical groups present in UFCB are carboxylic (-COOH), lactone, hydroxyl (-OH) and vinyl (-HC=CH₂);
2. treatment of UFCB with VTEOS increases the number of vinyl group in SFCB;
3. appreciable modification of ester group is observed in STCB compared to UFCB;
4. ethyl group is clearly noticeable in STCB spectrum compared with UFCB spectrum;
5. no endothermic peak is seen in DSC trace of STCB corresponding to the boiling point of VTEOS;
6. significant differences between the DSC traces of UFCB and STCB are seen at higher temperature ranges.

From these observations one may infer that either carboxyl or lactone or both groups of UFCB chemically combine with the ethoxy and/or hydroxyl groups of VTEOS. Figure 4 (scheme A&B) presents the coupling mechanisms.^{16–18} Scheme A in Figure 4 shows the reaction between the -COOH group with the ethoxy/hydroxyl groups. On the other hand, Scheme B in Figure 4 presents

the reaction between the lactone group and ethoxy/hydroxyl groups.

It is difficult to determine which of these mechanisms is predominant. Because the increase in hydroxyl peak at 3500 cm⁻¹ is almost negligible, which could have been the confirmation that Scheme B is predominant, it may be believed that the coupling scheme is primarily as shown in Scheme A.

Curemetric Study

Figure 5 shows the curemetric traces of mixes containing UFCB treated with 0–2.73 phr of VTEOS at an isothermal run temperature of 150°C. These curemetric traces resemble each other and the decreasing trend of final torque with the increase in VTEOS content is clearly discernible. Figure 6 presents the quantitative variation of curing parameters, e.g., initial and final torque, induction time, cure rate, and thermoplasticity against the VTEOS content. The variations of bound rubber and volume fraction of rubber are also shown for comparison.

The effect of VTEOS could be noticed in changing the vulcanization reaction of SBR in tow stages namely the initial and final curing. The parameters characterizing the initial stage of cure, i.e., the initial torque, induction time, cure rate, and thermoplasticity increases up to 0.91 phr of VTEOS content with a tendency of plateauing beyond this concentration, whereas the final cured stage parameter, i.e., the final torque, shows the opposing effect to that of the initial cure stage. It is interesting to note that the variations of initial curing parameters match well to

Table II IR Absorption Peaks of UFCB, SFCB, and VTEOS

Absorption Frequency in cm^{-1} and Responsible Chemical Groups	UFCB Spectrum	VTEOS Spectrum	SFCB Spectrum	Remarks
3500, $\text{—OH}^{10,11}$	Present	Present	Present	Presence of surface hydroxyl group in both UFCB and SFCB. Peak is broad due to the presence of hydrogen bond. ¹² Perhaps little hydrolysis of VTEOS resulted in the manifestation of this peak.
3000, Vinyl ^{10,11}	Present	Absent	Present	UFCB contains ethyl groups as a result of its manufacturing process. The strong group at 2850 cm^{-1} perhaps masked this peak. The intensity of this peak is higher in SFCB compared to UFCB.
2850, —SiOH^{13}	Absent	Present	Absent	Appearance of this peak in VTEOS spectrum may be assigned to its partial hydrolysis. Absence of this peak in UFCB means the absence of this group. No manifestation of this group in SFCB may hint at the involvement of this group in chemical reaction.
2750, Methylene ^{10,11}	Absent	Present	Absent	Present in the VTEOS spectrum because of large presence of methylene bond. This bond is comparatively small both in UFCB and in SFCB due to the small dose addition of SFCB in it.
1800, —C=O stretching ^{10,13}	Present	Present	Present	The group responsible for this absorption band in VTEOS is difficult to assign. The presence of this group in UFCB indicates the presence of lactone ^{14,15} group. On VTEOS treatment this peak modified in SFCB hints at the chemical transformation.
1700, Ester ^{10,11}	Present	Absent	Present	This group is not present in VTEOS. Perhaps the manifestation of this peak in UFCB is an indication of the presence of —COO— group. ¹⁴ This group might have reacted with VTEOS, which causes to intensify and modify this peak.
1650, Vinyl ^{10,11}	Present	Present	Present	All of them contain this group. The comparatively larger peak in SFCB than UFCB would confirm the attachment of VTEOS in UFCB.
1500, —C—H bending ^{10,11}	Absent	Present	Present	The VTEOS contains large number of C—H bonds. Manifestation of this peak in SFCB spectrum with no peak in UFCB hints presence of VTEOS in SFCB.
1450, $\text{—SiCH}_2^{10,11}$	Absent	Present	Present	Do
1350, $\text{—COH}^{10,11}$	Absent	Present	Present	Do
1235, $\text{—SiCH—}^{10,11}$	Absent	Present	Present	Do
1125, Ethyl ^{10,11}	Absent	Present	Present	Do

the variation of bound rubber whereas the variations of final curing parameter matches qualitatively to the variations of volume fraction rubber.

The incorporation of VTEOS increases the unsaturation of SFCB, which in turn increases the affinity of it towards the unsaturated SBR back-

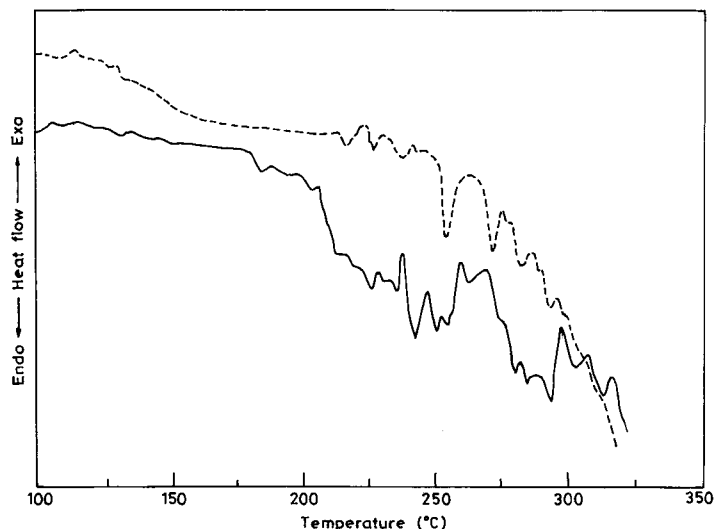


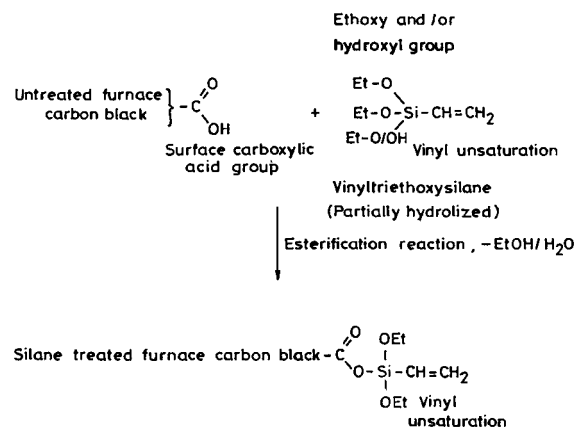
Figure 3 DSC traces of untreated carbon black (—) and carbon black treated with 2.73 phr of vinyltriethoxysilane (---).

bone. Therefore, the holding capacity of the UFCB increases on treatment with VTEOS. This is reflected in the increase of initial torque. The increase in induction time helps in maintaining lower torque, which is noticed in the increase in thermoplasticity.

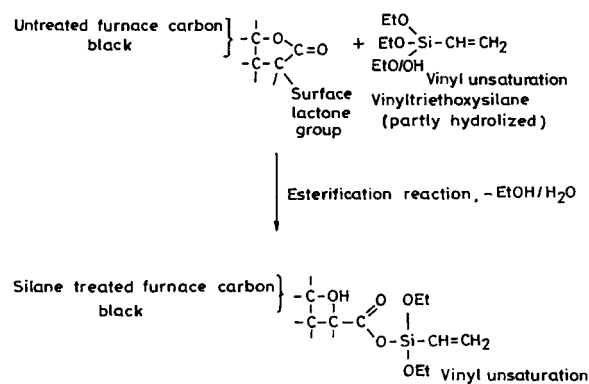
DSC Study of Mixes

The DSC traces of mixes containing UFCB and SFCB with different concentrations of VTEOS are reproduced in Figure 7. In general, there are two prominent endothermic peaks present in the trace. The first one appears at around 250°C and the other at 370°C; the first peak may be attributed to the vulcanization and the second peak to the polysulphidic to monosulphidic conversions and to the resulphuration.¹⁸ The peak temperatures and the heat of transitions are plotted against VTEOS concentrations in Figure 8.

The vulcanization temperature remains constant at 250°C, whereas the heat of vulcanization increases twice compared with that of the mix containing UFCB, with a value of 40 J/g at a VTEOS concentration of 0.91 phr and maintains the value thereafter. The nearly constant vulcanization temperature indicates the mechanism of vulcanization is similar and the temperature of the larger heat of vulcanization signifies an increase of the extent of reaction. The trends of volume fraction rubber is apparently opposite to what was expected. Perhaps the liquid nature of VTEOS makes the SBR accessible to the ingestion of hydrocarbon.



Scheme A



Scheme B

Figure 4 Coupling mechanisms of vinyltriethoxysilane with furnace carbon black.

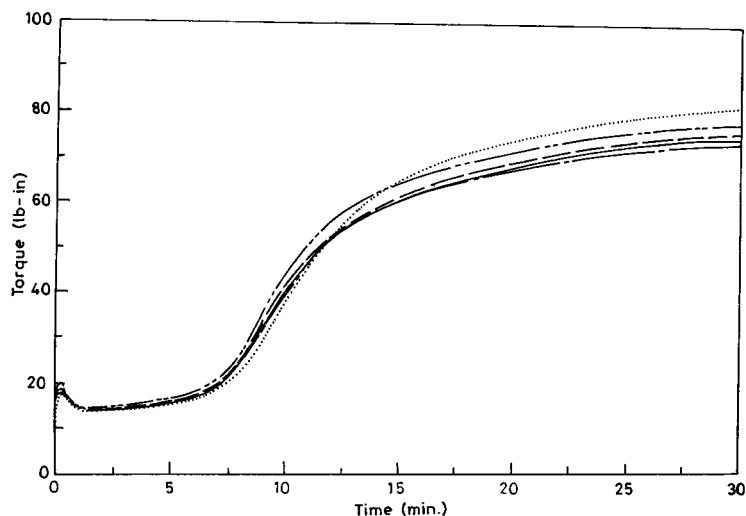


Figure 5 Curemetric traces of mixes containing untreated carbon black (. . .) and treated carbon black containing different concentration of vinyltriethoxyethane (phr): 0.22 (_ . _ .), 0.45 (- - -), 0.91 (_ _ _), 1.82, and 2.73 (. _ .).

It can also be seen from Figure 8 that the conversion temperature increases from 350°C to 370°C for the mix containing UFCB corresponding to a VTEOS concentration of 0.91 phr. The conversion temperature plateaus beyond this con-

centration of VTEOS. However, the heat of conversion approaches a maximum around a VTEOS concentration of 0.91 phr and slowly decreases thereafter. The increasing conversion temperature means encountering stronger sulphur bonds

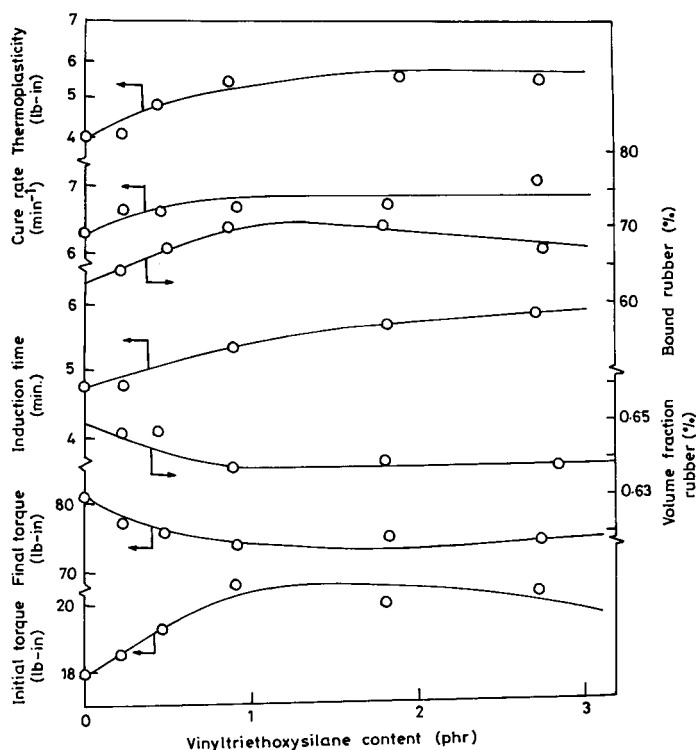


Figure 6 Plot of initial and final torque, induction time, thermoplasticity, cure rate, volume fraction rubber, and bound rubber against vinyltriethoxysilane content.

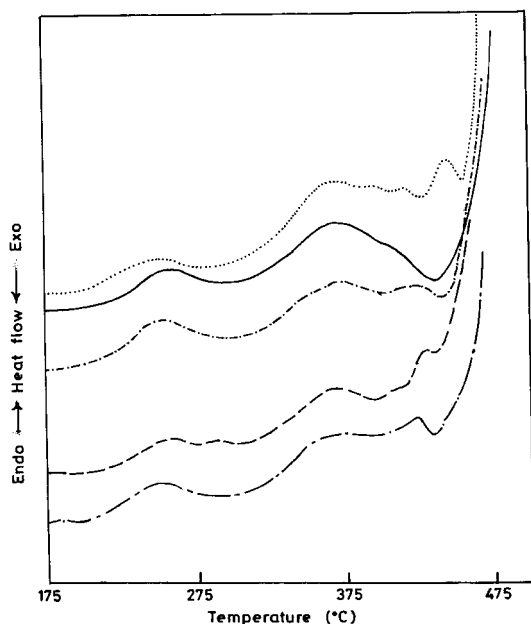


Figure 7 DSC traces of mixes containing untreated (...) and furnace carbon black treated with different concentration of vinyltriethoxysilane (phr): 0.22 (—), 0.91 (— · —), 1.82 (— —), and 2.73 (— · — · —).

that formed at the vulcanization step itself. This indicates that the vulcanization mechanism is similar and the presence of VTEOS helps in for-

mation of more thermally stable monosulphidic bonds compared with polysulphidic linkages.

Mechanism of Vulcanization

The observations described above and in the essence of established mechanism of vulcanization¹⁹⁻²² a simplified vulcanization scheme (Fig. 9) is proposed to elucidate the effect of VTEOS. The scheme for STCB illustrates only the effect of carbonyl group, as it is the major groups present on the surface of CB. The effect of lactone is similar and the degree of effectiveness of C=O is expected to be interfere due to the presence of -OH group (see Fig. 4).

It is believed that in the presence of zinc oxide, accelerator, and accelerator activator the vulcanization reaction predominantly proceeds through the cationic path (i.e., formation of polysulphenyl ion as active species). The reactive polysulphenyl ions formed in situ at the time of vulcanization. These polysulphenyl ions attack the unsaturations of bound fragment of part of SBR (Fig. 9, Scheme B, III) and also the vinyl group of silane fragment in the case of STCB (Fig. 9, Scheme A, I) besides reacting with the unbound polymer part. The reaction between polysulphenyl ions and bound rubber and/or attached vinyl unsaturation to the STCB is likely to be more probable due to the induced in-homogeneity in the chain. This

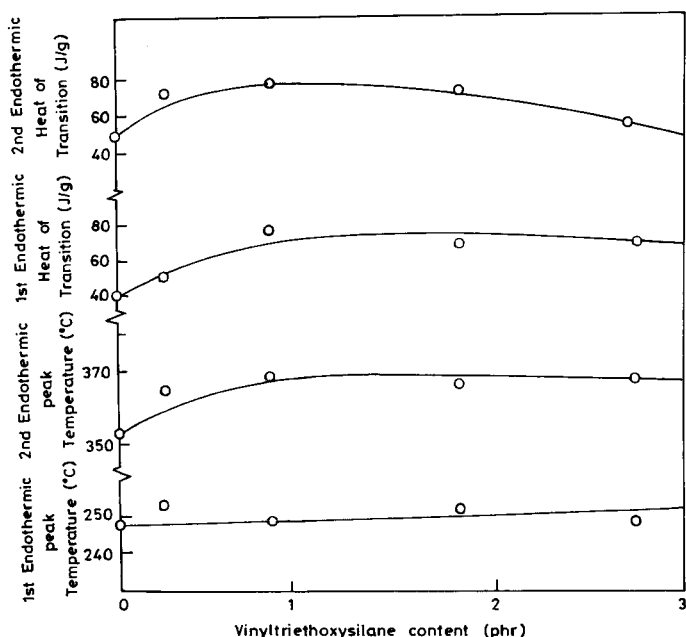


Figure 8 Plot of peak temperatures and heat of transitions of mixes containing different concentration of vinyltriethoxysilane.

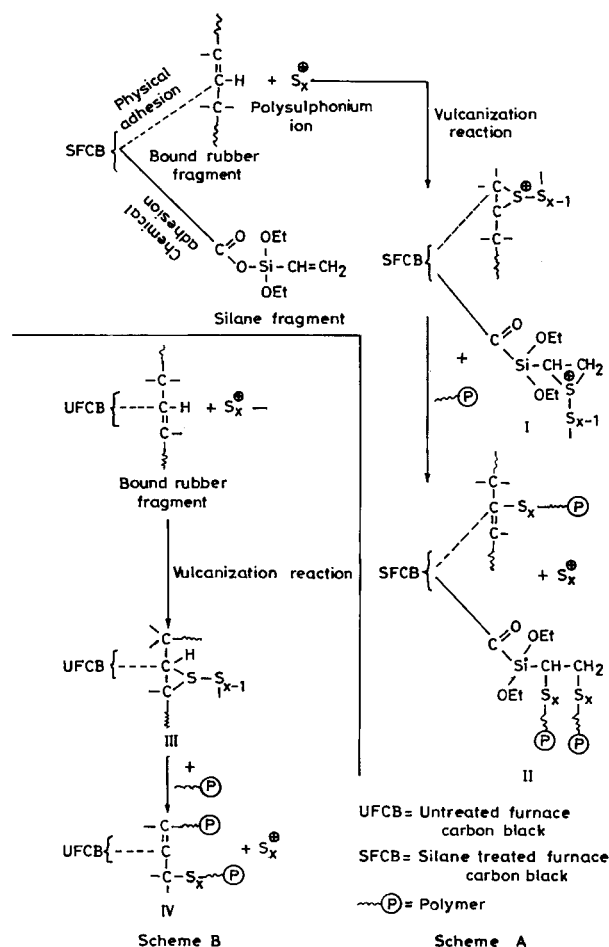


Figure 9 Vulcanization schemes of styrene-butadiene rubber in presence of untreated and vinyltriethoxysilane treated carbon black.

induced in-homogeneity occurs as a result of adsorption of polymer chains by the CB. The reaction between polysulphenyl ions and unbound polymer also takes place. Finally, these intermediates react with polymers and give rise to the network structures (shown in Figure 9, Schemes A,B).

The presence of C=O group in the STCB vulcanizate differentiates itself from the mix containing UFCB. The electron pulling effect of C=O group is responsible for attracting more polysulphenyl ion; more such complexes are formed and the vulcanization proceeds faster. Due to this fact the availability of sulphur to make a polysulphur bridge is reduced and the tendency to form polysulphidic link reduces, which manifests in the reduced heat of conversion and increased heat of vulcanization. The reason for the increase of in-

duction time is not clear. However, the interesting part is that it increases the process safety of the mix.

CONCLUSION

The UFCB reacts with the VTEOS primarily through carboxylic groups to form STCB. The grafted vinyl group of STCB takes part in the vulcanization reaction and attaches itself to the SBR network structure. The nucleophile carboxylic group, present in the STCB, makes the vulcanization proceed faster by attracting more positively charged polysulphenyl ion. As larger numbers of active polysulphenyl ions involve in the vulcanization reaction, the chances of formation of polysulphidic linkages decrease in the case of STCB. For a given amount of sulphur more crosslinks are formed and more number of links effectively shares the applied load due to FTF extension. At the same time the interface of STCB and SBR are chemically bonded with flexible linkages. The flexible chemical anchorage of STCB to the polymer, decreased polysulphidic linkage, and higher degree of cross-linking is reflected in the phenomenal increase in FTF behavior. The increase in dispersion of carbon black and softening effect are also two effects noticed earlier⁶ may also be counted towards this increase in FTF.

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