Coupling Mechanism and Fatigue Behavior of Vinyl Triethoxysilane-Treated Carbon Black—Styrene–Butadiene Rubber Vulcanizate

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ABSTRACT: When a furnace carbon black was treated with vinyl triethoxysilane (VTEOS) coupling agent, the carboxyl and/or lactone groups of it reacted with the ethoxy group of the coupling agent. The vinyl unsaturation thus grafted to the surface of the treated carbon black underwent crosslinking with the unsaturation present in the backbone of rubber chains during sulphur vulcanization. The vulcanizate containing silane-treated carbon black (STCB) showed a tremendous improvement in the fatigue behavior compared to the vulcanizate containing untreated furnace carbon black (UFCB). This striking difference was explained on the basis of the mechanism of attachment of carbon black to the rubber chains. The STCB anchored to the rubber chains through chemical linkages, whereas the UFCB anchored to the rubber chains by physical means. The chemical linkages of STCB through silane to the rubber chains provided a strong interface, which considerably reduced the chance of failure from the interface, which happened to be the stress concentrating zone, while the physically adhered weak interface of UFCB and rubber chains failed prematurely. The analytical tools employed were infrared spectroscopy, differential scanning calorimetry, and fatigue-to-failure testing. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2235–2241, 2000

Key words: coupling mechanism; fatigue behavior; reinforcement; vinyl triethoxysilane

INTRODUCTION

The use of carbon black to reinforce rubbers[1–5] is an age-old technique. Reinforcement increases the resistances of rubber towards abrasion, tearing, cut growth, flex cracking, and tensile fracture. It is widely believed that the reinforcement is a physicochemical phenomenon.[6–10] However, it was reported by many authors that the reinforcing carbon black loses its reinforcing ability when heated to a high temperature.[11,12] This observation by and large supports the fact that the chemical interactions are quite important in reinforcing rubber vulcanizate by carbon black.

The chemical interactions are developed through chemical groups, and these groups are formed at the time of manufacturing of carbon. Once a carbon black is made, there remains little scope for the modification of chemical groups present in it. The treatment of carbon black with an active chemical compound provides a viable alternative to change the chemical groups present in it; hence, this is a means of altering the reinforcing characteristics. There are reports[13,14] on the surface chemical characteristics modifications of mineral fillers. However, the effort on the modifications of surface groups of carbon black is rare. The mechanisms of attachment of carbon black to the vinyl triethoxysilane is presented here. Its

Table I   Recipe of Mixes Containing Vinyl Triethoxysilane-Treated and Untreated Carbon Black in Parts by Weight

Ingredients	Formulation ID	
	F1	F2
Styrene–butadiene rubber (SBR)	100	100
Carbon black (N330)	40	40
Zinc oxide	5	5
Stearic acid	2	2
CBS	1	1
MBTS	1	1
Sulphur	1.2	1.2
Vinyl triethoxysilane	0	2.73

effect on the reinforcing behavior, as observed through the fatigue-to-failure cycle, is explained on the basis of interfacial bonding.

EXPERIMENTAL

Materials

The materials used were as follows: the styrene–butadiene rubber (SBR; Grade S 1502, 23% styrene containing SBR polymerized by the cold emulsion process) with Mooney (ML 1 + 4 at 100°C) viscosity of 52, from Synthetics and Chemicals, Bariely, India; the high-abrasion furnace carbon black (Grade N330, surface area 53 m^2/g), from Oriental Carbon and Chemicals Ltd., Ghaziabad, India; Vinyl triethoxysilane, of Chemische Fabrik, Fluka AG, West Germany; Mercaptobenzothiazyldisulphide (MBTS) and *N*-cyclohexyl 2-benzothiazylsulphenamide (CBS), from Polyolefin Industry Ltd., Bombay, India; and rubber-grade commercial sulphur, stearic acid, and zinc oxide. Processing aids and stabilizers were avoided.

Processing

The treated carbon black stock was prepared first by drying the UFCB in an open tray at a depth of 7 mm for 1 h in a B-type oven at 125°C following the standard practices of carbon black manufacturer. The dried carbon black was then allowed to cool to a temperature of 80°C, and an accurate 2.73 parts of vinyl triethoxysilane was thoroughly mixed in an exact 40 parts of carbon black.

The mixing[15] of ingredients (see Table I) was performed in a 45-cm-diameter two-roll open mill provided with heating and cooling facilities according to the ASTM D 3182-84. A sheet of 3 mm was cut and left for a maturation time of 24 h at room temperature before moulding so that the ingredients attain equilibrium through diffusion.

A steam-heated single daylight compression moulding press was used for curing of sheets. The moulding time was 6 min at 150°C with 150 kg/cm^2 pressure. The sheets were cooled in running tap water as soon as they were extracted for the mould.

Measurements

Differential Scanning Calorimetry

Approximately 10 mg of accurately weighed samples of both untreated furnace carbon black (UFCB) and silane-treated carbon black (STCB) were run through the differential scanning calorimetry experiment (DSC) with a heating cycle of 10°C/min. The furnace was flushed with nitrogen, and the runs were carried out without disturbing the furnace atmosphere. The instrument used was a DuPont USA 910 attached with a 9900 programmer.

Infrared Spectroscopy

Approximately 10 mg of an accurately weighed sample of UFCB and STCB were taken separately in 10 g of KBr. They were uniformly mixed and pelletized to make a disc of 2 mm for recording infrared (IR) spectra. The vinyl triethoxysilane was taken in an o-ring between two KBr plates. The Perkin–Elmer 783 instrument (USA) was used for this study.

Fatigue-to-Failure Tester

The dumbbell specimens were punched out with a BS-E cutter from the cured and conditioned sheets. The experiment was performed in a Monsanto fatigue-to-failure tester (USA) equipped with automatic data acquisition counter at room temperature with the extension ratios of 1.8, 2.0, 2.2, and 2.4. The fatigue-to-failure cycle reported is the log mean of five data points. The reinforcement factor is defined as the ratio of fatigue-to-failure cycles of STCB containing vulcanizate to the vulcanizate containing UFCB at a particular extension ratio.
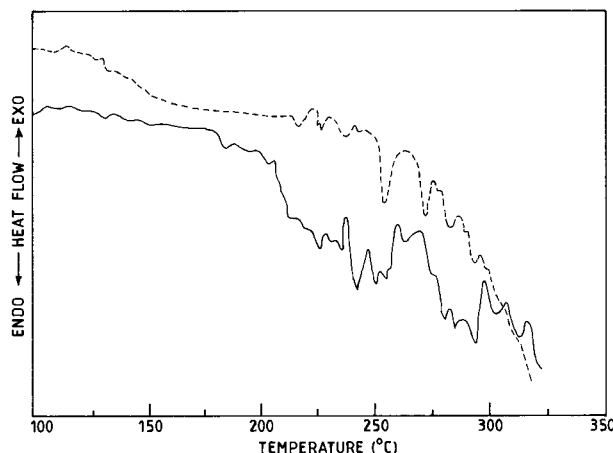
Figure 1   DSC traces of untreated (——) and treated (- - - - -) carbon black containing 2.73 parts vinyl triethoxysilane at a scanning rate of 10°C/min.

RESULTS AND DISCUSSION

DSC Traces of Untreated and Treated Carbon Black

Figure 1 presents the DSC heating traces of untreated and vinyl triethoxysilane-treated carbon black. There are little differences between them up to 200°C, although a distinct shift in baseline could be noticed only in STCB trace near the temperature of 150°C. However, the differences between these traces beyond the temperature of 200°C are quite prominent. They are two broad endothermic peaks at ~ 225 and ~ 275°C, which encompassed few small peak in UFCB traces, whereas the STCB shows two moderately sharp endothermic peaks around 250 and 275°C. A gradual change in baseline could be seen in both the traces in this range of temperature, which may be attributed to the change in specific heat capacity of carbon black[16] with the rise in temperature.

It is interesting to note that the STCB trace does not show any endothermic peak corresponding to the boiling point of VTEOS, which is 139°C, although a change in baseline is seen at 150°C. Both these observations, namely, the absence of sharp endotherm and change of baseline emphasize the presence of VTEOS in the system in a different form but not as physical admixture. Rather, a chemical combination between VTEOS and UFCB to form STCB would better explain the differences in DSC traces of UFCB and STCB.

IR Spectra

The IR spectra of VTEOS, UFCB, and STCB are reproduced in Figure 2. The absorption peaks of VTEOS spectrum are relatively clear, isolated, and almost free of shoulders. However, many absorption peaks of both UFCB and STCB are shouldered, overlapped, and are not clear. Therefore, the main prominent peaks of UFCB and STCB are assigned on the basis of existing literature[16–19] and are listed in Table II.

In the essence of observations based on DSC traces and IR spectra of all the three components, the findings could be tied down as follows.

1. The UFCB contained some bound moisture.
2. The main chemical groups present in the surface of UFCB are carboxyl (—COOH), hydroxyl (—OH), lactone, and vinyl (CH_2=CH—) groups.
3. The VTEOS contained either a little moisture or was partially hydrolyzed, which gave rise to siloxane group (i.e., —SiOH).
4. In the chemical reaction between VTEOS and UFCB, the reacting groups would be —OEt and/or —SiOH of VTEOS and —COOH and/or lactone of UFCB.

In the light of existing literatures,[20,21] the following coupling reactions schemes, that is, Figure 3, schemes (A) and (B) are proposed. Figure 3, Scheme (A), depicts the reaction between carboxyl acid group and the —OEt and/or —SiOH groups and Figure 3, Scheme B, depicts the reaction between the lactone group and —OEt and/or —SiOH groups. These reactions adequately de-
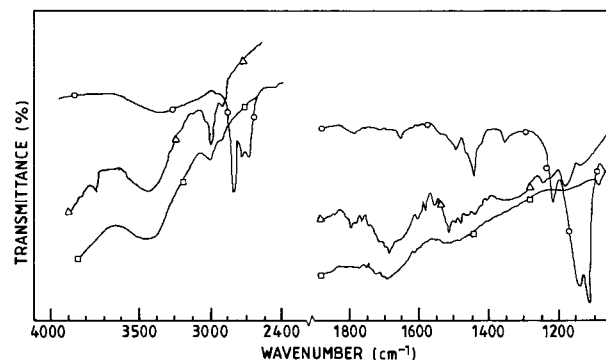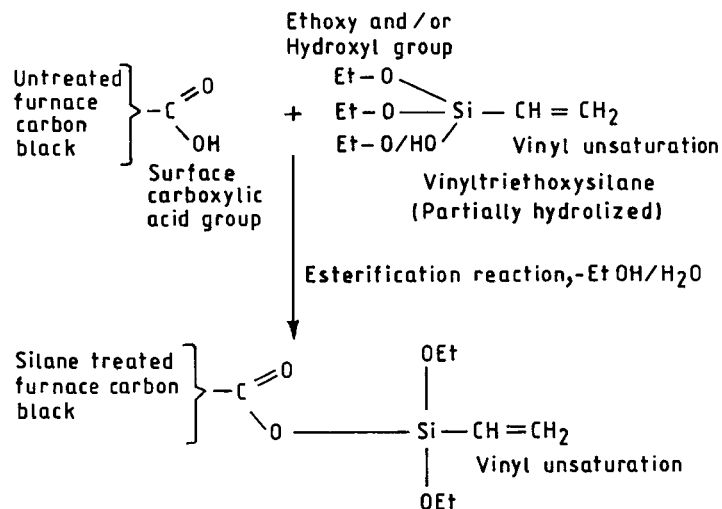

Figure 2   IR spectra of vinyl triethoxysilane (○), unrated carbon black (□), and 2.73 parts vinyltriethoxysilane containing treated carbon black (△).

Table II   Assignment of Infrared Absorption Peaks of Vinyl Triethoxysilane and Untreated and Treated Carbon Black
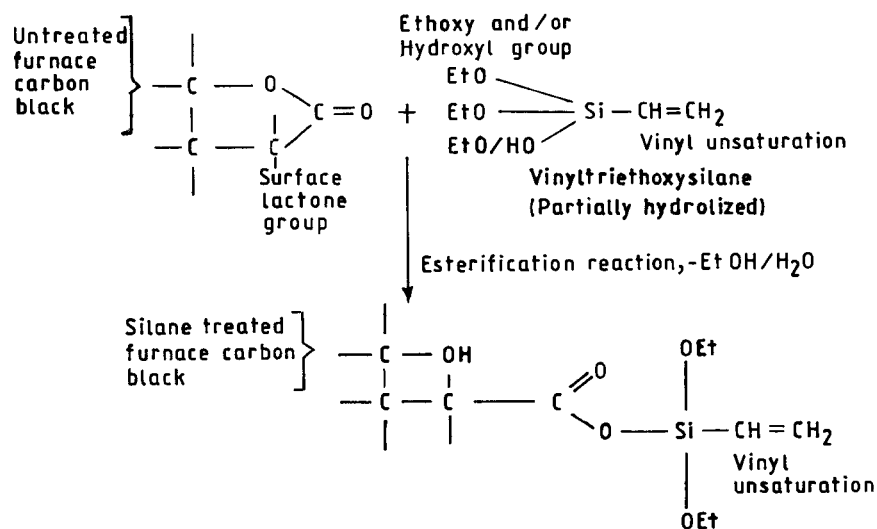
Groups and Absorption Peak Position (cm^{-1})	Vinyltriethoxy Silane (VTEOS) Spectrum	Silane-Treated Carbon Black (STCB) Spectrum	Untreated Carbon Black (UFCB) Spectrum	Remarks
—OH, peak at 3500 (Lide[16])	Present	Present	Present	Presence of some moisture in VTEOS. It may be partially hydrolyzed. Presence of surface hydroxyl group in both STCB and UFCB. Absorption/retention of some moisture is possible.
Vinyl group, peak at 3000 (Lide[16])	Absent	Present	Present	Relatively less vinyl group and strong peak at 2850 cm^{-1} perhaps masked this peak in VTEOS spectrum. The VTEOS treatment increased the altitude of 3000 cm^{-1}, indicating some vinyl groups are transferred from it to UFCB to form STCB.
—SiOH group, peak at 2850 (Schimidbaker and Hassek[18])	Present	Absent	Absent	The —SiOH group is lost in the process of conversion of UFCB to STCB. This group perhaps takes part in reaction and gets converted.
Methylene, peak at 2750 (Lide[16])	Present	Absent	Absent	Large presence of methylene bond in VTEOS. The small dose treatment of UFCB with VTEOS could not manifest this peak.
C=O bond Stretching (Lide[16]) and lactone group, peak at 1800 (Schimidbaker and Hassek[18])	Present; could be attributed to C=O stretching	Present; may be attributed to lactone group	Present; may be lactone group.	Large and modified peak in STCB in comparison to UFCB confirms some transformation due to VTEOS treatment.
Ester carboxyl group, peak at 1700 (Lide[16])	Absent	Present	Present	The comparatively large and modified peak in STCB than UFCB is an indication of conversion of some groups to ester group through chemical reactions.
Vinyl group, peak at 1650 (Lide[16])	Present	Present	Present	The absorption peak is comparatively large in STCB, and this confirms the presence of VTEOS in it.
C—H bending, peak at 1500, (Lide[16])	Present	Present	—	The VTEOS contain large number of C—H bonds. The presence of C—H bending peak in STCB spectrum indicates the presence of VTEOS.
—SiCH$_{2\ group}$, peak at 1450, (Lide[16])	Present	Present	—	Indicates the presence of VTEOS in STCB.
C—OH group, peak at 1350 (Lide[16])	Present	Present	—	This group formed perhaps due to the hydrolysis of —OEt group of VTEOS during the esterification reaction.
—SiCH group, peak at 1235 (Lide[16])	Present	Present	—	Indication of the presence of VTEOS in STCB.
Ethyl group, peak at 1125 (Lide[16])	Present	Present	—	The grafted VTEOS to STCB may perhaps be responsible for the manifestation of this peak in STCB.

scribed the loss/reduction in the absorption peak of ethyl group of STCB due to the dilution effect and the release of ethyl alcohol. Accentu-ation of absorption peak of vinyl group (i.e., at 3000 cm^{-1}) and the appearances of few peaks characterizing the —SiH and —SiCH$_2$ bands

Untreated furnace carbon black
$-C\stackrel{\displaystyle =0}{\diagdown OH}$
Surface carboxylic acid group

+

Ethoxy and/or Hydroxyl group

$\begin{matrix} Et-O \\ Et-O \\ Et-O/HO \end{matrix} \diagup Si-CH=CH_2$
Vinyl unsaturation

Vinyltriethoxysilane (Partially hydrolized)

Esterification reaction,-EtOH/H₂O

Silane treated furnace carbon black
$-C\stackrel{\displaystyle =0}{\diagdown}O \longrightarrow Si-CH=CH_2$

OEt

Si—CH=CH₂
Vinyl unsaturation

OEt

SCHEME (A)

Untreated furnace carbon black
$\begin{matrix} -C-O \\ | \\ -C-C \end{matrix} C=0$
Surface lactone group

+

Ethoxy and/or Hydroxyl group

$\begin{matrix} EtO \\ EtO \\ EtO/HO \end{matrix} \diagup Si-CH=CH_2$
Vinyl unsaturation

Vinyltriethoxysilane (Partially hydrolized)

Esterification reaction,-EtOH/H₂O

Silane treated furnace carbon black
$\begin{matrix} -C-OH \\ | \; | \\ -C-C \end{matrix} \longrightarrow C\stackrel{\displaystyle =0}{\diagdown O} \longrightarrow Si-CH=CH_2$

OEt

OEt

Vinyl unsaturation

SCHEME (B)

Figure 3 The proposed reaction mechanisms [schemes (A) and (B)] between carbon black and vinyl triethoxysilane.

(see Table II) in STCB spectra support the grafting of VEOS in it. However, it is difficult to point out the preference of the reaction schemes (whether Figure 3, Scheme A or Scheme B takes the precedence). It seems that both the schemes prevail and, interestingly, the carbon black is grafted with the unsaturated vinyl group. In course of vulcanization, this vinyl group reported as to take part in sulphur crosslinking[22] reactions and chemically anchored the SFCB to the rubber chains.

Fatigue-to-Failure Behavior

The fatigue-to-failure cycle of vulcanizates containing UFCB and STCB are plotted in Figure 4 against extension ratios. In general, both these curves maintained similar profile notwithstanding the number of cycles to fail were significantly different. The vulcanizate containing STCB showed an improvement in reinforcement factor to 3 at an extension ratios of 1.8. This reinforcement factor of 3 progressively diminished to 1.5 at
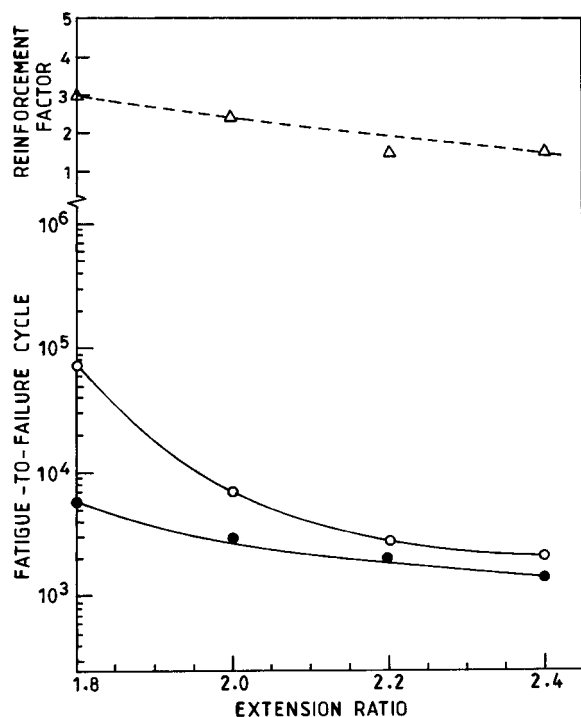
Figure 4 Variations of fatigue-to-failure behavior and reinforcement factor of untreated (●) and 2.73 parts vinyl triethoxysilane containing (○) vulcanizates against extension ratios.

the extension ratios of 2.4. The fatigue to failure, cycles at different extension ratios, and their standard deviation of these vulcanizates are shown in Table III. In general, the vulcanizate containing silane possess lower standard deviation than the vulcanizate containing no silane, and the standard deviation increases with increase in extension ratios.

The improvement in fatigue-to-failure cycle of STCB containing vulcanizate may be attributed to the chemical anchorage between carbon black and the rubber chains through sulphur crosslinking via the grafted vinyl unsaturation of VTEOS and the unsaturation present in the backbone of

rubber chains. This chemical bonding between STCB and rubber chains provides a strong interface. Hence, the chance of failure, which mostly occurs from the interface is greatly reduced. On the contrary, the comparatively weaker interface of the physically bonded UFCB, and rubber chains fails with considerably less fatigue cycles. Furthermore, the incorporation of VTEOS adds some softening action and also improves the dispersion of carbon black[23] in the STCB containing vulcanizate. It was shown in an article,[23] based on scanning electron microscopy and tensile strength that the dispersion of carbon black and its reinforcing behavior were prevalent up to a concentration of 0.91 phr addition of VTEOS. After this concentration of VTEOS, the carbon black conglomerates, and the softening mechanism takes the precedence. These facts in combination with the chemically anchored SFCB to the rubber chains improve the fatigue-to-failure cycle substantially.

The decrease in fatigue cycles, approximately at an equal ratio for both the vulcanizates, with the increase in extension ratios indicates similar failure mechanism. At higher extension ratios, the stress developed at the interface will be greater than the stress induced at lower extension ratios. The higher extensional stress causes an early fatigue-to-failure, although both the vulcanizates showed a decrease of it proportionately.

CONCLUSION

The vinyltriethoxysilane modifies the surface characteristics of carbon black. The vinyl triethoxysilane reacts with the carboxyl and/or lactone groups of the furnace carbon black through its ethoxy group. This chemical combination grafts vinyl unsaturation of vinyl triethoxysilane to the surface of silane-treated carbon black. The vinyl group probably undergoes sulphur

Table III   Fatigue-to-Failure Data and Standard Deviation of Vulcanizates Containing VTEOS and Non-VTEOS Compositions

Properties	Formulation ID							
	F1				F2			
Extension ratio	1.8	2.0	2.2	2.4	1.8	2.0	2.2	2.4
Fatigue failure cycles	56,230	29,510	19,950	13,180	165,960	70,800	26,920	19,500
Standard deviation	1.93	2.15	2.55	2.95	1.51	1.75	2.05	2.50

crosslinking during vulcanization and provides a strong interface between carbon black and rubber chains. Unlike the weaker physical bonding between untreated carbon black and rubber chains, the chemically bonded interface of treated carbon black and rubber chains withstands substantially higher number of fatigue-to-failure cycles. The softening action and improvement in dispersion of carbon black due to the presence of VTEOS further improves the fatigue life rubber composition based on treated carbon black.

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