

Curing Characteristics and Mechanical Properties of Vinyltriethoxysilane-Coupled Carbon Black/Styrene-Butadiene Rubber Vulcanizates

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Received 22 May 1997; accepted 3 September 1997

ABSTRACT: Styrene-butadiene rubber (SBR) vulcanizates containing 0 to 2.73 parts of vinyltriethoxysilane (VTEOS) per hundred parts of rubber (phr) were prepared, keeping the other ingredients weight constant. The mixes were tested for their curing behavior by a curemeter. The vulcanizates were analyzed through a Universal tensile tester, fatigue-to-failure tester, and scanning electron microscope mainly for mechanical properties and correlation. An increase in induction time and decrease in cure time, each by 10%, was noticed by the incorporation of 2.73 phr of VTEOS. The tensile strength and elongation at break improved significantly up to 0.5 phr of VTEOS and either a small improvement or deterioration of these properties was observed beyond this concentration of VTEOS. The fatigue-to-failure cycle at four extension ratios showed a gradual and appreciable improvement. It is noteworthy to mention that the vulcanizate containing 2.73 phr VTEOS possessed about a threefold increase in the fatigue-to-failure cycle compared to its non-VTEOS vulcanizate. However, this distinction of the fatigue-to-failure cycle progressively decreased with increase in the extension ratios. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1719–1725, 1998

Key words: vinyltriethoxysilane; fatigue-to-failure; coupling mechanism; reinforcement

INTRODUCTION

Rubbers are seldom used without fillers and their incorporation improves many desired mechanical properties besides making them cost-effective. The degree of improvement in physical properties, also known as the degree of reinforcement,^{1–4} depends on the physical and chemical characteristics of the filler.

The mechanism of reinforcement is a complex physicochemical phenomenon.^{5,6} However, an increase in the number of polymer chains to sustain an applied load is a widely accepted mechanism. Carbon black, when used as a filler, establishes a

large number of physical interlinking points among the polymer chains. These interlinks help to distribute the stress to the relatively unstrained chain segments from the overstressed areas. The chains thus would be equally strained and the load-bearing capacity of the vulcanizate increases.

The roles played by chemical groups of carbon black toward the reinforcement are still not clear,^{7,8} although some reports showed that treatments leading to the passivation^{9–11} of surface-active groups of carbon black eventually diminish the reinforcing ability. The chemical state at which the surface groups manifest reinforcement deserves more attention. In an earlier work, the mechanism of attachment of carbon black to the rubber chains through VTEOS was reported.¹² In

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

Ingredients	Formulation ID					
	F1	F2	F3	F4	F5	F6
Styrene-butadiene rubber (SBR)	100	100	100	100	100	100
Carbon black (N330)	40	40	40	40	40	40
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Pilcure CBS	1	1	1	1	1	1
Pilcure MBTS	1	1	1	1	1	1
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2
VTEOS	0	0.22	0.45	0.91	1.82	2.73

this article, the effect of such bridging on the curing characteristics, fatigue-to-failure cycle, and tensile properties is explored.

EXPERIMENTAL

Materials Used

The materials used were (i) styrene-butadiene rubber [grade S 1502, 23% styrene containing cold emulsion polymer, 52 Mooney viscosity (ML 1 + 4 at 100°C)] of Synthetics and Chemicals, Bariely, India; (ii) high-abrasion furnace carbon black (grade N330, surface area 53 m²/g) of Oriental Carbon and Chemicals Ltd., Ghaziabad, India; (iii) vinyltriethoxysilane (VTEOS) of Chemische Fabrik, Fluka AG, Germany; (iv) Pilcure MBTS (i.e., mercaptobenzothiazyl disulfide) and Pilcure CBS (i.e., *N*-cyclohexyl-2-benzothiazylsulfenamide) of Polyolefin India Ltd., Bombay, India; and (v) rubber-grade commercial sulfur, stearic acid, and zinc oxide.

Compounding

Carbon Black Stock Preparation

The carbon black was first dried in an open tray at a depth of 7 mm for 1 h in a B-type oven. The carbon black was allowed to cool to a temperature of 80°C. The VTEOS was then uniformly mixed with carbon black by dosing VTEOS from a fine nozzle in a rotating container in the required quantity. These stocks were kept in airtight containers for subsequent use.

Mixing

The mixing of ingredients was performed¹³ in an 18-in. diameter two-roll open mill provided with heating and cooling facilities, according to ASTM D 3182-74. The formulations of different compounds are presented in Table I. A sheet of 3 mm

was cut and left for a maturation time of 24 h before molding was carried out.

Molding

A direct steam-heated single daylight hydraulic compression-molding press was employed for the molding of sheets and buttons. The molding temperature was maintained at 150°C, and pressure, at 150 kg/m², for both the cases. But the sheets and buttons were cured for 6 and 15 min, respectively. They were chilled rapidly under running tap water after being extracted from the mold.

Measurements

Curemetry

Two punched discs of about 50-mm diameter and 3-mm thickness were put around the conical rotor in a Monsanto Rheometer 100 (U.S.A.) in accordance with ASTM D 2705. The torque versus time was recorded (i.e., the curemeter trace) isothermally at 150°C. The minimum and the maximum torques of a trace are reported as the initial and final torques, respectively. The 0.9 times difference between the final and initial torques is the optimum torque, which, in turn, is required to evaluate the cure rate. The cure rate is the percent of the reciprocal of the time taken to achieve the optimum torque from the torque just two units above the initial torque.

Fatigue-to-Failure Testing

Dumbbell specimens were punched out with a BS-E cutter from a conditioned sheet of 2 mm thickness cured for an optimum curing time. Experiments were performed in a Monsanto fatigue-to-failure tester (U.S.A.) equipped with automatic

data acquisition counters. The fatigue-to-failure cycle reported is the log mean of five data points for a particular vulcanizate.

Tensile Testing

Tensile testing was carried out according to ASTM D 412-51 T, with ASTM-C dumbbell-type punched specimens from 2-mm-thick compression-molded and conditioned sheets. The tensile strength and elongation at break are calculated as

$$\text{Tensile strength (kg/cm}^2\text{)} = F/A$$

$$\text{Elongation at break (\%)} = [(L - L_0)/L_0] \times 100$$

where F is the load required to break; A , the initial area; L_0 , the initial distance between two ink marks; and L , the separation of the ink marks at the time of break. The tensile stress at 100 and 300% elongation are reported as moduli at 100 and 300%, respectively. The tensile tests were carried out in a Zwick universal tensile tester, Japan. The average of five samples is reported as tensile data in each category.

Scanning Electron Microscopy

The microphotographs were taken from the fatigue-to-failure fractured surfaces shaded with silver by a vacuum-deposition technique. The samples were collected right at the tester just after breakage. The samples were kept in an airtight container so as to keep the fractured surface free of contamination. The micrographs were taken in a JEOL JSM-840 (Japan) scanning electron microscope, keeping the tilt angle at zero degrees.

RESULTS AND DISCUSSION

Curemetric Study

Figure 1 reproduces the curemetric traces of mixes containing 0–2.73 phr of VTEOS subjected to isothermal heating at 150°C. Qualitatively, these traces resemble each other and the differences among them are quite small. These traces occupied the position one above the other, except for some discrepancies in the initial portion of it as the VTEOS content decreases.

The quantitative variations of these traces in the initial parts—which are characterized by the initial torque, induction time, and cure rate, and

the final parts—which are characterized by the final torque, are plotted in Figure 2. The initial and final torque curves are nonlinear and opposite in trends of variations. While the initial torque increases up to 20 lb in. from 18 lb in., the final torque decreases from 80 lb in. to 72 lb in. around 1 phr of VTEOS content with respect to the mix containing no VTEOS. However, beyond 1 phr of VTEOS content, both the torques remain almost constant. The induction time and the cure rate manifest quite a linear increase with the increase in VTEOS content up to the maximum range of incorporation. The induction time increases from 4.75 to 5.75 min and the cure rate increases from 6.35 to 6.90 min⁻¹ as the VTEOS content increases from 0 to 2.73 phr. The induction time and cure rate were expected to have a direct effect on the molding characteristics of the mixes. On the one hand, the increase in induction time prolongs the cure safety of the VTEOS containing mixed stocks, and on the other, the increase in cure rate shortens the vulcanization time, thus increasing the productivity.

Fatigue-to-Failure Behavior

The variations in the fatigue-to-failure cycle of the vulcanizates against VTEOS content are shown in Figure 3 at 1.8, 2.0, 2.2, and 2.4 extension ratios. A systematic increase in the fatigue-to-failure cycle is apparent from the curves (Fig. 3) as the VTEOS content increases in all four extension ratios. These curves maintain a steep curvilinear increase at lower extension ratios (i.e., at 1.8 and 2.0 extension ratios) and almost a flat curvilinear increase at higher extension ratios (i.e., at 2.2 and 2.4 extension ratios) as the concentration of VTEOS increases. These differences in the fatigue-to-failure cycle toward the extension ratios perhaps lie in the vulcanizates behavior at low and high deformations. Interestingly, the three-fold rise in the fatigue-to-failure cycle, for 2.73 phr VTEOS in the vulcanizate at the 1.8 extension ratio, in comparison to the non-VTEOS vulcanizate, makes the incorporation of VTEOS in a recipe an attractive proposition.

Scanning Electron Microscopy

Figure 4(a–c) presents microfractographs of the fatigue-to-failure surfaces of vulcanizates containing 0, 0.22, and 0.91 phr of VTEOS. These photographs show uniformly spread dark and light spots of various sizes. The light and dark

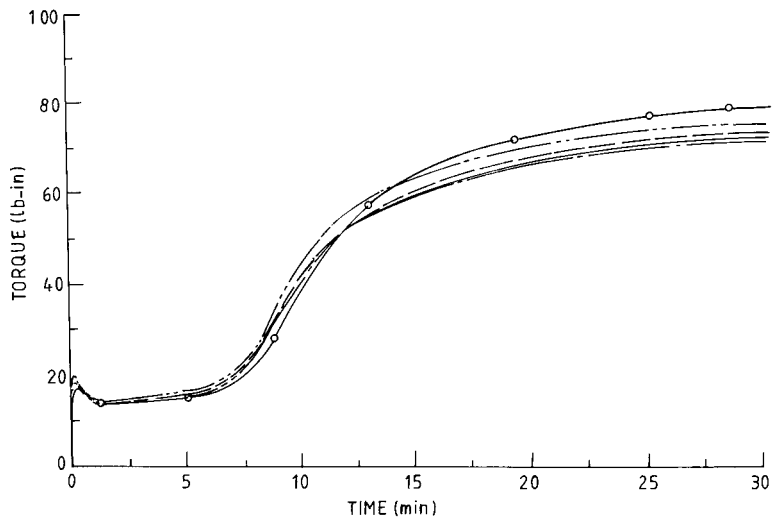


Figure 1 Curemeter traces of SBR/carbon black mixes at 150°C containing (—○—) 0, (-----) 0.22, (—) 0.45, (— — —) 0.91, (— · — ·) 1.82 and 2.73 phr of VTEOS.

spots in the range of 12–20 μm represent aggregation, whereas the black spots in the range of 75–100 μm represent the clustering of carbon black.^{14–16} The light spots are bulges of carbon black aggregates/clusters present in the side of surface under examination. However, the dark spots are holes¹⁶ formed either due to the migration of carbon black aggregates/clusters to the

other side of fracture surface or due to the splattering of carbon black at the time of failure.

The size and number of aggregates are greatly reduced by the incorporation of 0.22 phr of VTEOS [Fig. 4(b)] in comparison to its non-VTEOS vulcanizate [i.e., Fig. 4(a)]. Few clusters are also seen at this composition [Fig. 4(b)]. It is interesting to note that the appearance of

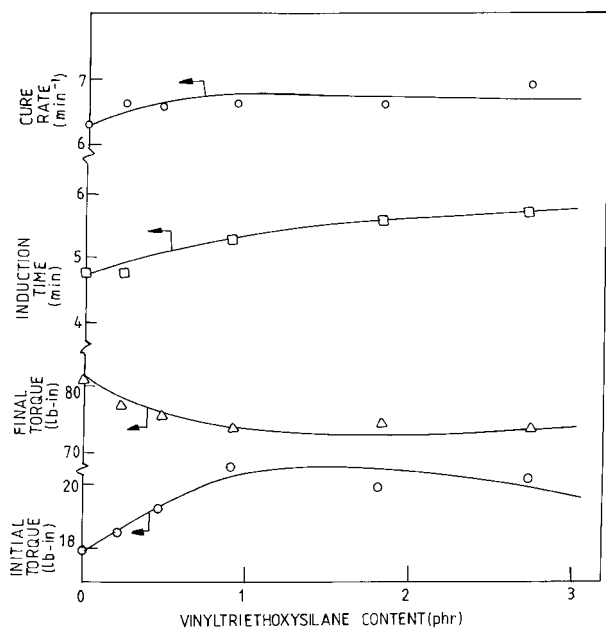


Figure 2 Plot of initial and final torques, induction time, and cure rate at 150°C of SBR/carbon black mixes against VTEOS content.

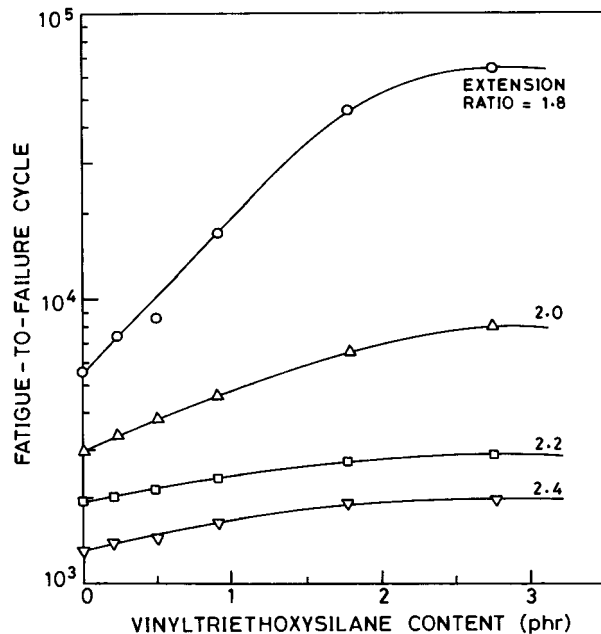
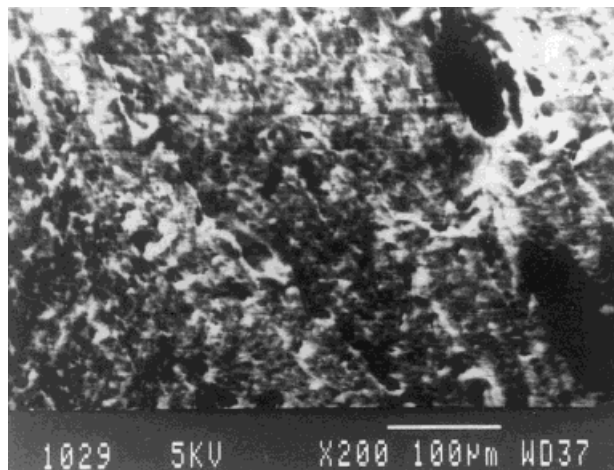
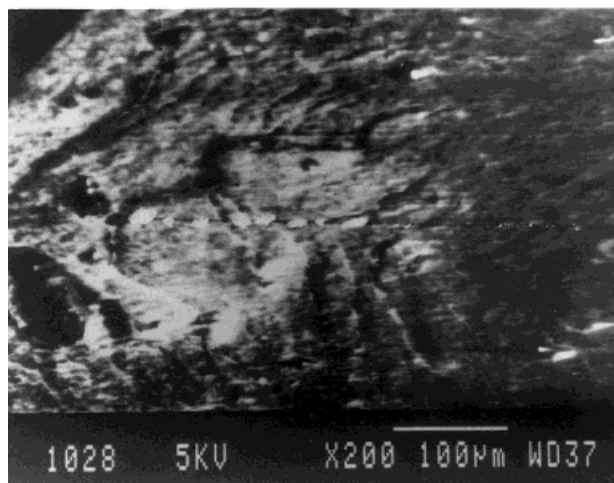


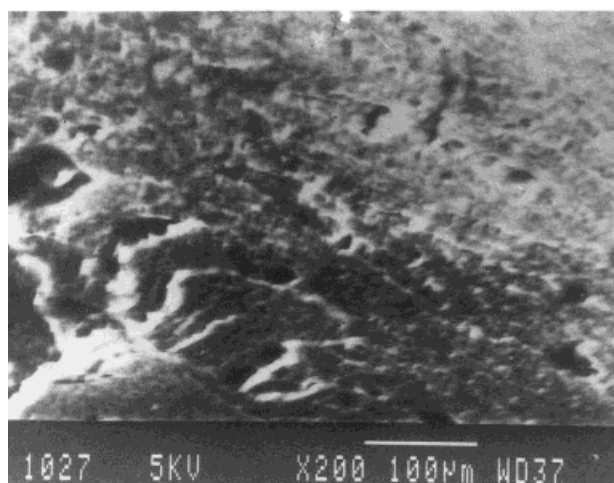
Figure 3 Plot of fatigue-to-failure cycles of SBR/carbon black vulcanizates against VTEOS at 1.8, 2.0, 2.2, and 2.4 extension ratios.



(a)



(b)



(c)

Figure 4 Microfractographs of fatigue-to-failure surface of SBR/carbon black vulcanizates containing (a) 0, (b) 0.22, and (c) 0.91 phr of VTEOS.

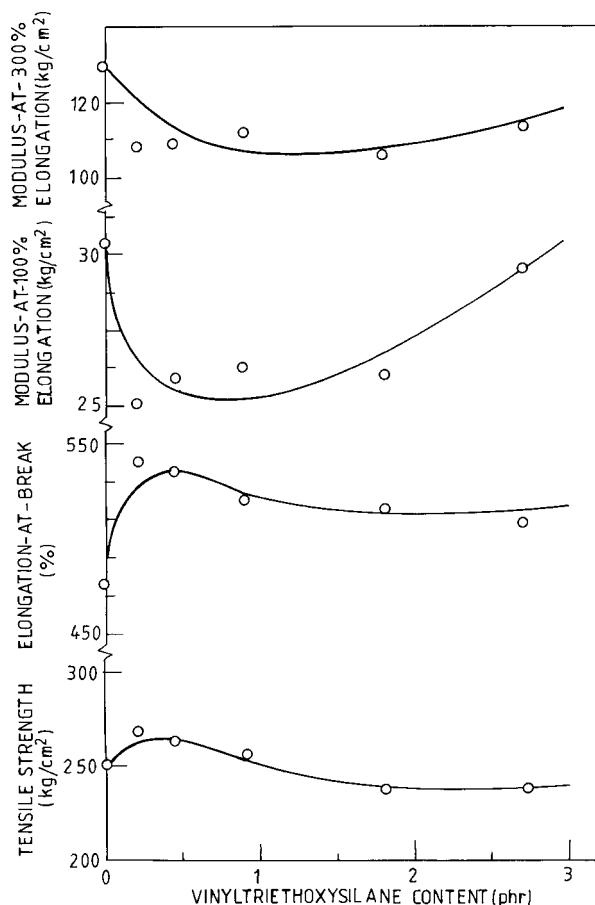


Figure 5 Plot of tensile strength, elongation at break, and moduli at 100 and 300% extension of SBR/carbon black vulcanizates against VTEOS content.

cracks along the extension axis are indicative of the tearing path deviation¹⁷ at this composition, which perhaps manifests a change in the mode of failure. Further addition of VTEOS up to 0.91 phr reduces the size of the aggregates and improves the dispersion of carbon black as is manifested through the more even distribution of light and dark spots [Fig. 4(c)]. Notwithstanding that some clusters either still remain or reappear, the failure surface of this 0.91-phr-containing vulcanizate is rather complex. A gradual change from the simple to complex failure surface may also be noticed as the VTEOS content increases from 0 to 0.91 phr.

Tensile Behavior

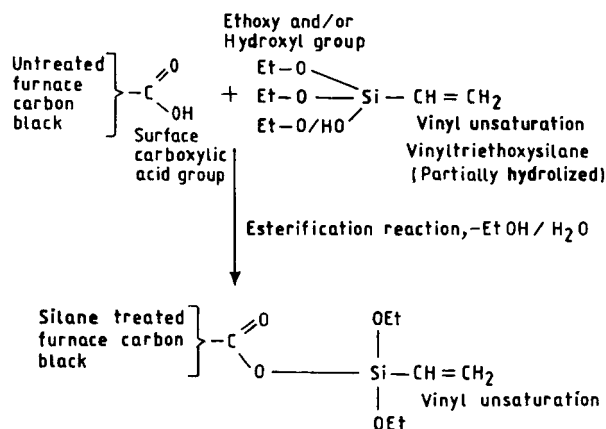
The tensile strength, elongation at break, and moduli at 100 and 300% elongations change nonlinearly with VTEOS content (Fig. 5 and Ta-

Table II Tensile Properties (Standard Deviation) of Vulcanizates Containing VTEOS-Treated and Untreated Carbon Black

Properties	Formulation ID					
	F1	F2	F3	F4	F5	F6
Tensile strength (kg/cm ²)	284 (1.30)	267 (0.98)	262 (1.50)	256 (1.60)	239 (0.75)	239 (1.20)
Elongation at break (%)	464 (3.25)	539 (2.56)	535 (2.78)	519 (2.70)	514 (2.50)	508 (2.70)
Modulus at 300% elongation (kg/cm ²)	129 (1.26)	108 (1.16)	109 (1.35)	111 (1.35)	106 (1.25)	113 (1.22)
Modulus at 100% elongation (kg/cm ²)	31 (1.15)	25 (1.09)	27 (0.95)	28 (1.05)	27 (1.20)	29 (1.15)

ble II). Both the tensile strength and elongation at break pass through a maximum corresponding to 0.5 phr VTEOS content and then decrease gradually. Although the tensile strength decreases to a little lower value, the elongation at break still maintains a significantly higher value at 2.73 phr of VTEOS as compared to its non-VTEOS vulcanizate. The moduli follow the opposite trend to that of the tensile strength and elongation at break. The opposite effect on the moduli perhaps indicates a greater influence of VTEOS on the elongation characteristics than on the tensile stress at around 0.5 phr VTEOS content. However, this effect on the moduli almost nullifies at high-dose (i.e., 2.73 phr) use of VTEOS, perhaps due to the relatively greater reversal of the stress characteristic than of the elongation behavior.

The VTEOS covalently attached itself to the carbon black surface through a condensation reaction of ethoxy (or hydroxyl groups in the case of partially hydrolyzed VTEOS) groups of VTEOS

**Figure 6** Probable coupling reaction scheme between VTEOS and carbon black.

and carboxylic and/or lactone groups of carbon black and was reported in a recent article¹² in the essence of existing literature.^{18,19} One of the probable reaction schemes between VTEOS and carbon black is reproduced in Figure 6. It is discernible from the reaction scheme that the unsaturated vinyl group becomes anchored to the carbon black. The treated carbon black improves the interaction²⁰ between itself and the SBR chains through the unsaturation present in its backbone. This specific interaction helps in distributing carbon black in the polymer matrix at low concentrations of VTEOS. However, at higher concentrations (i.e., beyond 0.5 phr VTEOS content), the liquid nature of VTEOS imparts a slippage action in the treated carbon black. The higher VTEOS-dosed carbon blacks avoid a shearing action by slipping past through the roll nip at the time of mixing and become agglomerated. The reappearance or reorganization of some carbon black clusters and/or aggregates²¹ thus results. The increase in initial torque up to 1 phr and the decrease of it beyond this concentration may reinforce the belief of interaction at a low concentration and slippage at a high concentration of the incorporation of VTEOS.

The attached vinyl groups of the treated carbon black and the unsaturation present in SBR react with the sulfur to form sulfur crosslinks at the time of vulcanization.^{12,13} These sulfur crosslinks provide a strong interface between SBR and carbon black via the VTEOS bridges. Therefore, the observed increase in tensile strength and elongation at break around 0.5 phr VTEOS content may be due to the sulfur crosslink formed between SBR chains and the treated carbon black. The high initial torque of treated carbon black around this composition exerts more shearing action on carbon black. Hence, a comparatively larger number

of physical bonds are also expected to be formed between the polymer and carbon black together, achieving a better dispersion of treated carbon blacks. These factors help in the the manifestation of additional reinforcement in the tensile properties. However, the reinforcement is less prominent at higher doses of VTEOS (see Fig. 5) because of the predominance of its softening action. At higher doses, the VTEOS-treated carbon blacks show reorganization to form clusters/agglomerates which adversely affect the tensile strength. Although a progressive decrease in the elongation at break beyond 0.5 phr VTEOS is evident, it maintains a sufficiently higher value of 530% at 2.73 phr VTEOS content, while the non-VTEOS vulcanizate fails around 475%. The decrease in the final torque of mixes with increase in VTEOS content may hint at the softening action of VTEOS at higher doses.

CONCLUSIONS

On treatment, the VTEOS covalently attached itself to the carbon black. The treated carbon black shows both enhanced interaction and slippage behavior to those of the rubber depending upon the quantity of VTEOS used. While the interaction plays a vital role at lower doses, the slippage behavior comes into prominence at higher doses of VTEOS addition. The vinyl unsaturation of the VTEOS anchored to the carbon black seems to increase the interaction through the unsaturation present in the polymer backbone. The improved interaction helps in better dispersion of the carbon black. In contrast, at relatively high quantity, the fluid nature of VTEOS imparts slippage behavior to the treated carbon blacks. The treated carbon blacks with higher doses of VTEOS slip through the shearing action of the mixing devices. Thus, some reorganization of carbon black clusters and/or aggregates results at the higher dose use.

About a 10% increase in induction time and cure rate is noticed around a 1-phr VTEOS-containing mix in comparison to the non-VTEOS containing mix. The increase in induction time adds to the scorch safety and the increase in cure rate shortens the curing time.

The fatigue-to-failure cycle of vulcanizates noticeably increases throughout the addition of VTEOS. A strong interface and finer dispersion of carbon black combined with the softening ac-

tion of VTEOS seem to be responsible for this increase.

The tensile strength and elongation at break increase up to 0.5-phr VTEOS content. Beyond this concentration of VTEOS, both the tensile strength and elongation at break are seen to be decreased gradually. The effect of VTEOS is more prominent in the elongation at break than in the tensile stress at lower doses. But at higher doses of VTEOS use, the comparative effect on the elongation at break has been balanced by a similar effect on the tensile stress.

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