1026-1265/2002

Mechanical Properties and Aging Behaviour of Styrene-butadiene-vinyltriethoxysilane Coupled Carbon Black Vulcanizates

Kamal Kumar and Suryya K. Rana*
Department of Textile Technology, Indian Institute of Technology Delhi
New Delhi-110 016, India

Received 26 November 2000; accepted 15 October 2002

ABSTRACT

Addition of vinyltriethoxysilane (VTEOS) in carbon black provides beneficial effects by improving various mechanical properties of styrene-butadiene rubber (SBR) vulcanizates. In addition to this, the incorporation of (VTEOS) strikingly improves their aging behaviour. This experiment was carried out to understand the behaviour of SBR vulcanizates due to the addition of VTEOS in the range of 0 to 2.73 phr. Evaluation of properties was made through compression moulded sheets as per standard industrial practices. The VTEOS increases the fatigue-to-failure (FTF) cycles of the vulcanizate containing 2.73 phr of VTEOS by three times at an extension ratio of 1.80, which is the maximum value of FTF reported here, in comparison to the vulcanizate containing no VTEOS. However, the other mechanical properties namely tensile, tear, compression, resilience and hardness show an improvement at around 0.5 to 1 phr of VTEOS. The aging behaviour of vulcanizates at this 0.5 phr of VTEOS is comparatively better. It was seen that the VTEOS plays the roles of coupling agent and softener. It acts as a coupling agent up to 0.5 phr and beyond it acts as softener. A small amount above this coupling action is beneficial for many uses. It appears that the optimal dosage of addition of VTEOS to this system to be around 0.5 to 1 phr.

Iranian Polymer Journal, 11 (5), 2002, 287-293

Key Words:
coupling agent,
aging behaviour,
styrene-butadiene rubber,
fatigue-to-failure behaviour.

INTRODUCTION

Two important aspects of rubber for the estimation of suitability for a particular use are the mechanical properties and aging behaviour [1-6]. Mechanical properties are indicative of the application range whereas, the aging behaviour indicates its life spun.

Among mechanical properties, the fatigue is an indication for deciding applications under cyclic stress and strain. Ranging from truck tires to shoe soles and engine mounting, this property approximately predicts

(*)To whom correspondence should be addressed.
E-mail: s_k_rana@hotmail.com

the life under cyclic stress-strain. The life is again severely affected on the presence of different atmosphere namely ozone or oxygen, which is evaluated in accelerated testing known as aging. It is believed that the physico-chemical bonding between carbon black and the rubber is instrumental in improving the mechanical properties of the vulcanizates.

In this study effort was made to institute chemical bonding between carbon black and rubber through coupling agent, i.e. VTEOS. It was reported [7-9] that the VTEOS hinged to the carbon black through ethoxy groups and the vinyl group of it attached to the rubber. This interface provided by the VTEOS is expected to be stronger than the physico-chemical linkage and improved many mechanical properties. Improvements in various mechanical properties are presented here.

EXPERIMENTAL

Materials

Followings were the materials used (Table 1) in this study: The 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 carbon black used was high abrasion type furnace black (Grade N 330) with BET surface area of 53 m^2/g. It was 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 in order to avoid interferences with the reactive silane-coupling agent.

Processing

Carbon black stocks were prepared by heating untreated furnace carbon black (UFCB) in a B-type oven on open trays over a depth of 7-mm at 125°C for 1 h. These stocks 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. The uniformity of the dispersion of VTEOS is checked quantitatively through infrared (IR) spectra by taking samples throughout the batches. These treated stocks were kept in airtight containers for making mixes.

The mixing of the ingredients and SBR were done according to ASTM D 3182-74. A two-roll mill of a diameter of 18 inches equipped with heating and cooling facilities was used for this study. About 3 mm-thickness sheets were cut and left for a maturation time of 24 h before moulding was performed.

The moulding was carried out in a direct steam heated single daylight hydraulic type moulding press. The platen size of the press was 0.5 x 0.5 mm^2 and the moulding was performed at 150°C for 6 min at a pressure of 150 kg/cm^2. This moulding time was arrived through rheometric study [7]. The test pieces so made were rapidly cooled under running tap water as soon as they were taken out of the mould.

Measurements

Hardness

The hardness of the samples was measured as per ASTM D 3182-74 conditioned according to ASTM D

Table 1. Formulations of various vulcanizates.

Ingredient ID	F_1	F_2	F_3	F_4	F_5	F_6
Styrene-butadiene rubber	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
CBS	1	1	1	1	1	1
MBTS	1	1	1	1	1	1
Sulphur	1.2	1.2	1.2	1.2	1.2	1.2
Vinyltriethoxysilane	0	0.22	0.45	0.91	1.82	2.73

1339. The instrument used for this measurement was Croydon CR 9, H.W.Wallace Co Ltd. (Germany).

Compression Set

Samples were conditioned at 25% RH at 24 ± 2°C for 3 days for the measurement of compression set. The samples were compressed to a height of 25% of their original height and kept for 22 h at a temperature of 70°C. The compressed height was measured after the samples were released and allowed a relaxation period of 24 h as per ASTM D 395-85. The compression set is calculated according to the formula:

$$\text{Compression set (\%)} = [(H_o - H_f)/(H_o - H_c)] \times 100$$

Where, H_o, H_f and H_c are the original, final and the compressed height of the sample, respectively.

Fatigue-to-failure Test

The dumb-bell specimens were punched out with a BS-E cutter from cured and conditioned sheets. The experiments were conducted with various extension ratios in a fatigue-to-failure tester, Monsanto, USA.

Tensile Test

Dumb-bell shaped ASTM C type specimens were punched out from a 2 mm conditioned sheet. The tensile testing was carried out according to the standard ASTM D 412-51 T. Two ink marks were put at the neck part of the specimen and were held between the two grips of the Universal tensile tester, Zwick, Japan.

The load was measured to pull apart a sample to 100, 300% and at the break. Stress-at-100 and 300% is reported as the modulus at 100 and 300%, respectively and the stress-at-failure is reported as tensile strength. The stress and elongation are calculated as follows:

$$\text{Stress (kg/cm}^2) = \text{F (kg) / A (cm}^2)$$
$$\text{Elongation-at-break (\%)} = [(L - L_o) / L_o] \times 100$$

Where, F is the measured load to draw the sample, A is the original area, L is the length between two inch marks at the time of deformation and L_o is the original length between the two ink marks of the sample.

Tear Test

Tear test was carried with ASTM B type of specimen punched out from a conditioned sheet of 2 mm observing the procedure described in ASTM D 624-73. The samples were cut with a notch of 0.5 mm depth and the testing was performed in the Zwick Universal tensile tester, Japan. The tear strength is calculated as follows:

$$\text{Tear strength (kg/cm)} = \text{F (kg) / 2t (cm)}$$

Where, F is the maximum load required tearing the sample and t is the thickness of the specimen.

Abrasion Resistance

Samples of 16 mm diameter were cut from a thick moulded and conditioned sheet prepared as per ASTM D 3182-74 with the special cutting tool supplied with the equipment. The samples were made to rub on the specified rough surface for a defined length of traverse at a particular contact load. The loss in volume to complete the traverse of rough surface is reported as abrasion resistance. The instrument used was Thueringer Industriewerk (AP-40, 613-20R, 34/84), Rauenstein, W. Germany.

Resilience

The resilience was determined by using a Dunlop falling weight resilience tester. Compression moulded samples in the form of button of 12.7 mm diameter and 10 mm thickness were used for the determination of resilience by falling weight method. The percentage

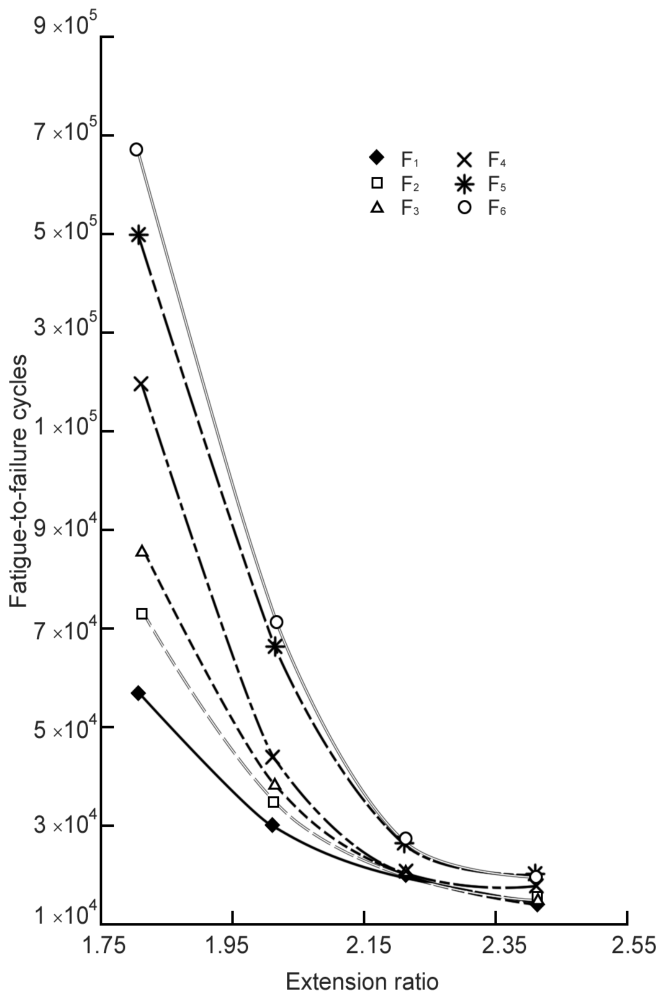
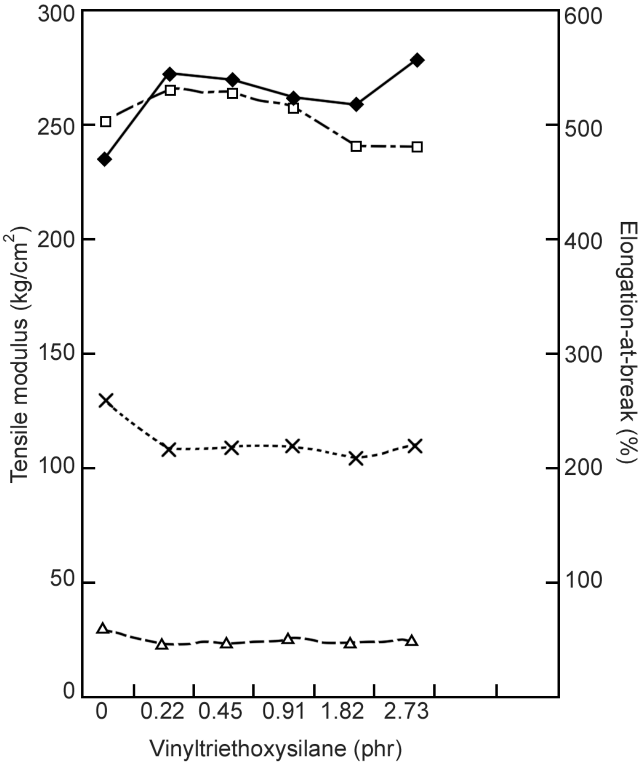


Figure 1. Plot of fatigue-to-failure cycles against VTEOS content.



(□) Tensile strength; (△) Modulus at 100% elongation; (×)Modulus at 300% elongation; (◆) Elongation-at-break.

Figure 2. Plot of tensile properties against VTEOS content.

rebound in height of the load dropped on the specimen is reported as resilience:

$$\text{Resilience (\%)} = [h/h_o]\times 100$$

Where, h is the rebound height and h_o is the falling height of the weight on the sample.

Aging

The punched out tensile samples were suspended from a port for aging and were kept for specified periods at 125°C in a B-type oven with air circulation facility. Samples were taken out after completion of desired exposure time and put on hold for 24 h so that the samples were acclimatized before testing were carried out. The tensile strength, moduli at 100% and 300% and the elongation-at-break were evaluated as the procedure described in tensile test section.

RESULTS AND DISCUSSION

Fatigue-to-failure Behaviour

The variations of FTF cycles of vulcanizates containing UFCB treated with 0-2.73 phr VTEOS are shown in Figure 1 at different extension ratios.

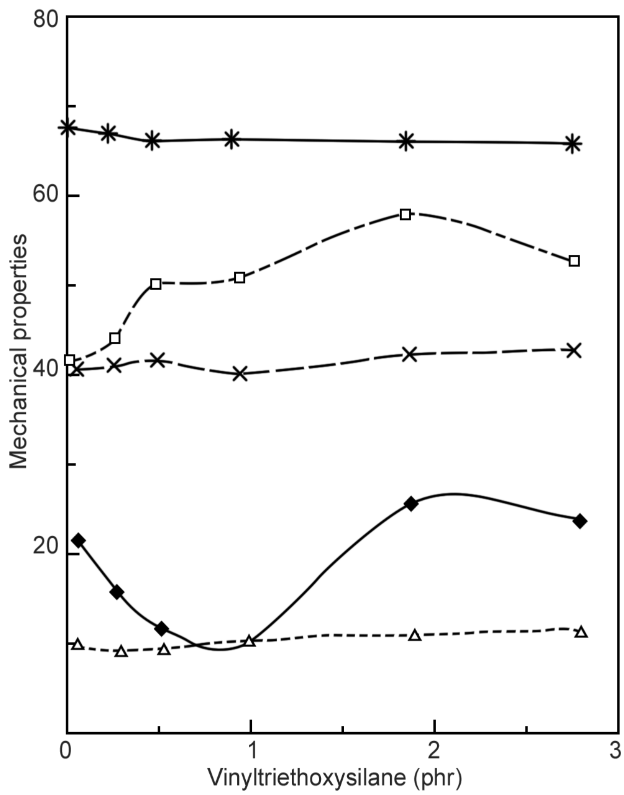
A systematic increase in FTF cycles with the increase in VTEOS content is apparent in all the cases. The increase in FTF value is phenomenal for the vulcanizate containing 2.73 phr VTEOS at an extension ratio of 1.80 than the vulcanizate containing no VTEOS.

In general, the FTF curves are much steeper at lower extensions than at higher extensions. At higher extension ratios, it is expected that some physical damage would have been introduced which leads to premature (i.e., lower number of failure cycles) FTF cycles.

Un-aged Tensile Behaviour

The tensile strength, elongation-at-break and moduli at 100 and 300% elongation are shown in Figure 2. At a cursory glance, the variations of these properties with the concentration of VTEOS are non-linear.

Both the tensile and elongation-at-break pass through maxima at about 0.5 phr of VTEOS. Although, the tensile strength almost gradually decreases after attaining the maximal, the elongation-at-break maintains nearly constant value up to 1.5 phr VTEOS and



(◆) Compression set(%); (□) Tear strength(kg/cm); (△) Abrasion resistance (cc/1000); (×) Resilience (% rebound); (✱) Hardness (shore A).

Figure 3. Plot of different mechanical properties against VTEOS content.

then showed considerable increase at 2.73 phr of VTEOS. The moduli show similar but reverse trend to the tensile and elongation-at-break signifying greater effect of VTEOS elongation-at-break than that of the tensile strength. On other words, incorporation of VTEOS eases the deformation behaviour of the vulcanizates comparatively better than the load bearing capacity.

It was reported [9] that the VTEOS forms linkage between carbon black and polymer. The VTEOS linkage is quite flexible. This is expected to be a better flexibility than the physical adsorption of polymer chain to the surfaces of the non-treated carbon black. Therefore, the increase in concentration of VTEOS introduces more flexible chemical bonding and it may so happen with some of the physical bonds due to adsorption, which are replaced by it. Perhaps at around 0.5 phr of VTEOS a subtle balance between physical and chemical bonding seems to be established. Correspondingly, the maxima of both the elongation and tensile have been observed at this content of VTEOS. As beyond this percentage of VTEOS content, perhaps the excess VTEOS acts as softener. Due to this reason the tensile strength decreases beyond 0.5 phr of VTEOS addition.

However, the elongation-at-break increases as a result of its softening action.

Other Mechanical Properties

The variation of abrasion resistance, compression set, resilience, tear strength and hardness on the change of VTEOS content are shown in Figure 3. The effect is very prominent on compression set and tear strength, whereas others remain almost unaffected.

The abrasion resistance is minimal at around 1 phr of VTEOS. There is about 10% drop in loss due to abrasion. In effect, the abrasion behaviour of the vulcanizate around 1 phr VTEOS is better by 10% which would provide better life to the vulcanizates against abrasion. Perhaps, the balancing of coupling action and the softening actions, which is attributed for the observed behaviour of tensile strength, is responsible for this.

At lower percentage addition of VTEOS, the tensile strength is better along with good elongation-at-break that seems the contributing factor in improving the abrasion loss. However, at higher VTEOS uses, as the tensile strength decreases, the vulcanizates may not be able to withstand the cutting and wear behaviour resulting in the increase in abrasion loss. The tear strength,

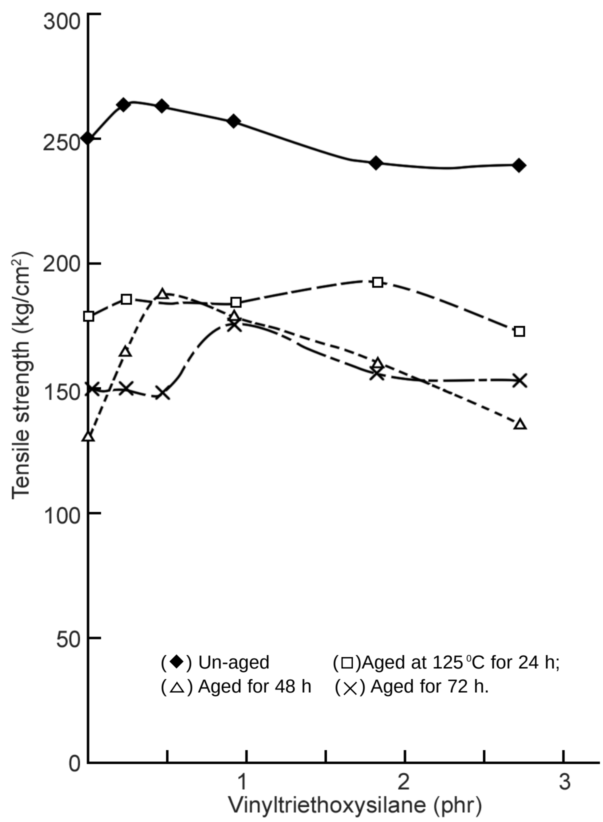


Figure 4. Plot of tensile strength against VTEOS concentration.

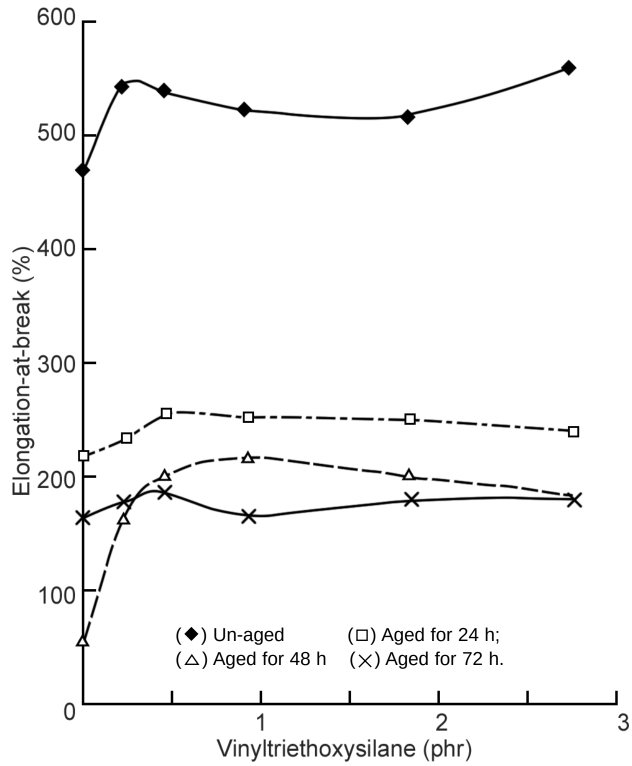


Figure 5. Plot of elongation-at-break against VTEOS concentration with different aging time.

on the other hand, shows two stages of improvement. Around 20% increase is seen around a VTEOS content of 0.5 phr and another improvement of about 8% in its value is observed around 2 phr of VTEOS content. A slight decrease could be noticed afterwards. The compression set decreases by a value of 50% from its non-incorporated VTEOS value in the range of 0.5 to 1.0 phr. This advantage diminishes in compression set value is lost above this percentage addition of VTEOS. There are a marginal improvement of about 6% in the resilience and hardness around 0.5 to 1 phr VTEOS contents.

Aged Tensile Properties

Figures 4 and 5 show of aging on the tensile strength and elongation-at-break, respectively against VTEOS content at different exposure time lengths of aging.

It is apparent from the Figure 4 that the drop in tensile strength is quite sharp on aging exposure. The tensile curve of un-aged samples is reproduced for comparison. This sharp drop in tensile strength could be attributed to the non-incorporation of anti-oxidants and anti-ozonants on account of simplifying the study of the behaviour of the coupling agent. It is expected that this sharp fall in the tensile strength could be resisted on the incorporation of these ingredients in the formulations.

The tensile curve of aged samples for 24 h at 125℃ shows a tendency for resisting deterioration due to aging. The aging behaviour of the VTEOS containing vulcanizates at little above 1 phr content is about 10% better than the VTEOS free vulcanizate. The effect on the incorporation of VTEOS in vulcanizates is much prominent at 48 h of exposure time. One can observe a phenomenal resistance toward aging of vulcanizates containing approximately 0.5 phr of VTEOS. This improvement in tensile strength is about 40% higher than the corresponding VTEOS free sample. A similar behaviour is observed for 72 h exposure time.

The effect of aging on the incorporation of VTEOS on the elongation-at-break is presented in Figure 5. Similar phenomenon is observed as that of the tensile strength (Figure 4).

Briefly, the trend in improvement is also noticed around an exposure time of 24 h. Exposure time of 48 h showed a tremendous improvement in aging behaviour as the elongation-at-break of vulcanizate around 0.5 phr VTEOS is about 250% higher than the corresponding VTEOS free samples. Although the elongation-at-break at 72 h exposure is not all that better when compared to the exposure time of 48 h, it is interesting to note that the improvement in aging behaviour is sharply noticed up to the VTEOS content of 0.5 phr.

Therefore, the VTEOS plays two roles [7-10]: (i) It reacts with the surface reactive groups of the carbon black and; (ii) it also acts as a softening agent. It seems that about 0.5 phr is sufficient to react with the surface reactive groups of the carbon black. Excess to this amount of the VTEOS, it remains as softener in the system. There are properties such as FTF and un-aged mechanical properties in which the effect of both the parts of the VTEOS becomes additive or show little deterioration. For instance, the FTF showed continuous improvement (Figure 1), whereas the tensile strength showed continuous improvement up to 0.5 phr, and thereafter the trend was unclear due to this reason.

The VTEOS contains unsaturations in the form of vinyl groups. The excess added from this quantity that needed for the reacting carbon black surface groups does not help in improving the aging properties. This phenomenon is nicely reflected on the elongation-at-break behaviour of the vulcanizates. The improvement in the aging behaviour perhaps arises from the reduction of unsaturation groups of the SBR chain.

CONCLUSION

Incorporation of VTEOS improves the FTF cycles all through the studied concentration ranges. Around 2.73 phr of incorporation, it increases the FTF cycles by three times over its vulcanizate containing no VTEOS at an extension ratio of 1.80. The extension ratio also determines the FTF cycles. Lower extension ratios provide higher FTF cycles. It is seen that the VTEOS plays roles both as coupling agent and as a softener. Up to a content of 0.5 phr it behaves as coupling agent and above this percentage addition, the excess amount manifests its function as a softener. This is clear from the aging studies through the elongation-at-break. Other mechanical properties showed increase in their magnitude at around 0.5 to 1 phr of VTEOS content. The aging of vulcanizate with 0.5 to 1 phr of VTEOS is superior to the vulcanizates containing either more than this range or no VTEOS at all. It appears that the addition of VTEOS little in excess than the required (i.e., 0.5 phr) amount is beneficial. This excess amount remains present in the system as softener and improves many mechanical properties of the un-aged vulcanizates.

REFERENCES

1. Rana S.K., "Curing characteristics and mechanical properties of vinyltriethoxysilane coupled carbon black/styrene butadiene vulcanizates", *J. Appl. Polym. Sci.*, **69**, 1719-1725 (1998).
2. Nakajima N. and Harrell N., "Effect of extending oil on viscosity behavior of elastomers", *Rubb. Chem. Technol.*, **56**, 784-807 (1983).
3. Edwards D.C. and Sato K., "Interaction of silica with functionalized SBR", *Rubb. Chem.Technol.*, **53**, 66-79 (1980).
4. "Reinforcement of Elastomers", G. Kraus, Ed. , Interscience Publishers, New York (1965).
5. "Rubber Technology", M. Morton, Ed.,Van Nostrand Reinhold Company, New York (1973).
6. "Natural Rubber Science and Technology ", A.D. Roberts, Ed. Oxford, London (1988).
7. "Rubber Technology and Manufacture", C.M. Blow and C. Hepburn , Ed., Butterworths, London (1975).
8. Rana S.K., M.Sc. Thesis, "Studies on the effect of the coupling agent in SBR-carbon black composite vulcanizates", Delhi University, Delhi (1989).
9. Rana S.K., "Coupling mechanism and fatigue behavior of vinyltriethoxysilane treated carbon black/styrene butadiene rubber vulcanizate", *J. Appl. Polym. Sci*., **78**, 2235 -2241 (2000).
10. Rana S.K. and Chandra R., "Mechanistic study of fatigue behavior of vinyltriethoxysilane coupled carbon black/styrene butadiene rubber vulcanizate", *J. Appl. Polym. Sci.*, **78**, 25-34 (2000).