Reinforcing Effect of Silica on the Properties of Styrene Butadiene Rubber–Reclaim Rubber Blend System

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ABSTRACT: Incorporation of silica into styrene butadiene rubber (SBR)–reclaim rubber (RR) blend system was carried out by sol–gel technique and conventional method. A well known silica coupling agent bis(3-triethoxysilyl propyl) tetrasulfide was found to affect the curing characteristics and mechanical properties of SBR/RR vulcanizate. Here, the effect of RR on silica reinforcement was studied for different SBR/RR blend system. Silica incorporation by conventional mechanical mixing in absence of TESPT showed a much higher tensile properties than that of silica incorporated by the in situ sol–gel reaction of tetraethoxy silane both in presence and absence of TESPT. Studies of equilibrium swelling in a hydrocarbon solvent were also carried out. ATR study indicates that RR forms bond with silica particles due to the presence of active functional site on RR. The amount of silica incorporated by sol–gel reaction was determined through thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) studies further indicate the coherency and homogeneity in the silica filled SBR/RR vulcanizate. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 957–968, 2006

Key words: sol–gel; silica; reclaim rubber; thermogravimetric analysis (TGA); reinforcement

INTRODUCTION

Reclaim rubber (RR) is a degraded mass obtained after reclaiming of vulcanized rubber by a suitable agent following a suitable process. Almost in all commercial applications, RR is used as a component of a blend with fresh rubber. In a recent review article, Adhikari et al. [1] have successfully discussed various process of reclaiming. Kligensmith[2] used cryoground butyl rubber with fresh virgin rubber in 5–15% level. De et al. studied the physical properties of natural rubber–RR,[3] styrene butadiene rubber (SBR)–RR,[4] and natural rubber/polybutadiene rubber–RR[5] blend system.

In general, inorganic fillers are mixed with rubber for the reinforcement of rubber network. Besides carbon black, silica is the other important and economical[6] reinforcing filler used in the rubber industry. Silicas have been lacking in one prerequisite for all rubber reinforcing capability, i.e., strong silica–rubber bonding. Moreover, silica does not provide the same level of reinforcement when compared to carbon black of the same particle size. To overcome these limitations, silane coupling agents are used with silica for the reinforcement of rubber vulcanizates.

Mechanical mixing is a useful processing technique for the preparation of silica/rubber composite or silica-filled rubber vulcanizates. Instead of conventional mixing, the in situ silica filling by sol–gel reaction of tetraethoxy silane (TEOS) has been reported as a novel technique to reinforce the rubber vulcanizates.[7–11] The reaction of TEOS occurs in two steps, the hydrolysis and the condensation reaction, to produce SiO_2. It was reported that in sol–gel process inorganic glasses are formed in the vulcanizate at low temperatures.[7,8] Mark et al.[8,11,12] and Ikeda et al.[10] studied the in situ silica incorporation by sol–gel technique for silicone rubber and polyisobutylene.[13] Ikeda and coworkers carried out the in situ silica reinforcement of styrene–butadiene rubber,[14–17] butadiene rubber,[18,19] epoxidised natural rubber,[20] and acrylonitrile butadiene rubber,[21,22] where the sol–gel silica was generated in the rubber vulcanizates, i.e., the sol–gel reaction of TEOS was conducted in the chemically crosslinked rubber. Kohjiya et al.[23] also reported incorporation of silica into the rubber matrix in an alternative way. Here, in situ silica filling was carried out before curing, and the physical properties of the in situ silica filled vulcanizates were studied and compared with

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those of the conventional silica–filled vulcanizates. Yo-shimi et al.[24] reported the in situ silica filling in the rubber latex, and showed the usefulness of their method for the reinforcement of rubber vulcanizates.

In this study, reinforcement of silica in styrene–butadiene rubber (SBR)–RR blend system is described. Introduction of silica in the SBR/RR vulcanizates is carried out by sol–gel technique and by conventional method. The mechanical properties of in situ silica-filled vulcanizates were compared with those of the conventional silica filled vulcanizates. Further, the effect of TESPT on these two systems was investigated.

EXPERIMENTAL

Material

GRT, purchased from local market, was used. The GRT was an unclassified ground rubber from the tread and sidewalls of passenger and truck tires. The ground particles were of various sizes ranging from a few millimeters to 100 μm. SBR 1502 (Synthetics and Chemicals Ltd.), tetramethyl thiuram disulfide (TMTD) (ICI, India), zinc oxide (S. D. Fine Chem., India), stearic acid (Loba Chemie, India), sulfur (S. D. Fine Chem., India), spindle oil (MCI, India), and toluene (S. D. Fine Chem. India) were used as received. TEOS was obtained from Acros Organics, NJ, USA, and the TESPT reagent was obtained commercially. The silica used was Ultrasil VN-3, whose specific surface area is about 200 m^2/g. The catalyst for the sol–gel reaction was n-butylamine (SRL, India).

Experimental procedure

Preparation of RR

One hundred grams of ground rubber was mixed with 2.75 g TMTD and 10 mL spindle oil. The mixture was then mechanically milled in an open two-roll mill and milling was carried out at a friction ratio of 1.2 for 40 min at near ambient temperature. It has been found that with progress of milling the materials become soft and sticky and the band formation occurs on the roll.

Preparation of SBR–RR vulcanizates

Mixing of fresh SBR, various proportion of RR and compounding ingredients, was carried out at room temperature on an open two-roll mixing mill. The cure characteristics of the rubber compounds were determined with the help of a Monsanto Oscillating Disc Rheometer, R-100 at 160°C. All cure curves were observed to level off in the region of 60 min, where the torque–time gradient of each sample was constant or did not change significantly.

The compounded rubber stock were then placed in a mold and pressed between the platens of a hydraulic press (Carver, Model 2518). The samples were cured at 160°C temperature and at applied pressure of 5000 psi for the respective optimum cure times ($t = t_{90}$) obtained from rheographs. After curing, the sheet was taken out of the mold and immediately cooled under tap water to restrict from further curing.

Preparation of sol–gel vulcanizate

The sol–gel vulcanizates (SGVs) were prepared by soaking the cured sheets in TEOS for 48 h at 30°C. After soaking, the swollen sheets were immersed in a 10% aqueous solution of n-butylamine for 24 h at this same temperature. The catalyst solution was then removed, and the sheets were heated at 50°C for 72 h for drying and further dried in a vacuum oven at 50°C to constant weight.

Characterization of the vulcanizate

A Hounsfield, model H10 KS tensile testing machine, was used to measure the modulus, tensile strength, and elongation at break of the vulcanizate as per ASTM D 412–51T at room temperature (25 ± 2°C) at a uniform speed of separation 500 mm/min. Hardness (shore A) of the vulcanizates were measured by a Hirosima Hardness Tester as per ASTM D 1415–56T. The values reported were based on the average of five measurements for each sample.

Equilibrium swelling experiments of the vulcanizates was performed in toluene at room temperature. Here, the samples were allowed to swell for 72 h in toluene. Crosslinking value of the composite was measured with the following equation[25]

$$\frac{1}{Q} = \frac{W_S - W_D}{\left(\dfrac{W_0 \times 100}{W_F}\right)}$$

and crosslinking value = 1/Q, where W_S, W_D, W_0, and W_F are swollen weight, dried weight, weight of the original sample, and formula weight, respectively. Formula weight (W_F) is the total weight of rubber plus compounding ingredients based on 100 parts of rubber.

The volume fraction (Vrf) of a rubber network in the swollen phase and is given by the equation by Ellis and Welding.[26]

$$V_{\text{rf}} = \frac{\left(\dfrac{W_2}{d_2}\right)}{\left(\dfrac{W_1}{d_1}\right) + \left(\dfrac{W_2}{d_2}\right)}$$

where W_1 is the weight fraction of solvent, d_1 is the density of the solvent, W_2 is the weight fraction of

TABLE I
Mix Formulation and Curing Characteristics of Rubber Compounds Prepared for Insists Silica Formation

	1	2	3	4	5	6	7	8	9	10
Ingredients (phr)										
Styrene–butadiene rubber (SBR)	80	70	60	50	40	80	70	60	50	40
Reclaim rubber (RR)	20	30	40	50	60	20	30	40	50	60
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
TMTD	1.61	1.335	1.06	0.785	0.51	1.61	1.335	1.06	0.785	0.51
TESPT	–	–	–	–	–	5	5	5	5	5
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Curing Characteristics										
Optimum cure time (t_{90}, min)	5.5	5.25	4.75	4.5	4.25	21	19.5	19	18	17
Scorch time (t_{s2}, min)	0.5	1.0	1.0	1.0	1.0	0.5	0.5	0.5	0.5	0.5
Extent of cure (dNm)	58	56	55.5	55.6	54.2	92.6	111	108	109	104
Cure rate index (min^{-1})	20	23.5	26.7	28.6	30.8	4.9	5.3	5.4	5.8	6.1
Mechanical properties										
100% modulus (MPa)	1.59 (1.61)	1.62 (1.63)	2.10 (2.16)	2.13 (2.41)	2.28 (2.84)	1.29 (1.72)	1.34 (1.88)	1.65 (2.57)	1.65 (3.08)	2.45 (3.59)
200% modulus (MPa)	2.25 (2.95)	2.31 (3.22)	3.08 (4.31)	3.19 (4.59)	3.32 (5.02)	–	–	–	–	–
Tensile strength (MPa)	2.781 (7.11)	2.974 (7.43)	3.835 (8.44)	4.573 (9.12)	5.017 (8.28)	1.94 (9.90)	2.24 (10.62)	2.43 (11.31)	2.66 (11.51)	3.07 (11.67)
% elongation at break	377 (417)	382 (353)	345 (323)	427 (307)	445 (305)	255 (187)	240 (182)	235 (172)	220 (157)	220 (143)
Hardness (shore A)	60 (63)	65 (68)	64 (70)	62 (73)	60 (75)	64 (82)	65 (84)	69 (85)	71 (89)	71 (91)
Crosslinking value (1/Q)	(0.352)	(0.399)	(0.433)	(0.455)	(0.479)	(0.795)	(0.862)	(0.922)	(0.977)	(1.073)

Data in the parentheses represents the mechanical properties after sol–gel reaction.

	1′	2′	3′	4′	5′	6′	7′	8′	9′	10′
Ingredients (phr)										
Styrene–butadiene rubber (SBR)	80	70	60	50	40	80	70	60	50	40
Reclaim rubber (RE)	20	30	40	50	60	20	30	40	50	60
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
TMTD	1.61	1.335	1.06	0.785	0.51	1.61	1.335	1.06	0.785	0.51
TESPT	–	–	–	–	–	5	5	5	5	5
Silica	16.95	14.62	14.58	14.52	11.57	10.99	18.11	18.87	19.15	20.34
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Curing characteristics										
Optimum cure time (t_{90}, min)	3.5	3.25	2.75	2.5	2.25	21	17.5	16.5	18	19
Scorch time (t_{s2}, min)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Extent of cure (dNm)	52	44.5	49	49.5	49	92	93.6	95.2	100	105
Cure rate index (min^{-1})	33.3	36.4	44.4	50	57.1	4.9	5.9	6.25	5.7	5.4
Mechanical properties										
100% modulus (MPa)	1.02	1.10	1.35	1.46	1.70	1.90	2.32	2.93	3.20	4.24
200% modulus (MPa)	1.60	1.86	2.52	2.63	3.21	–	–	–	–	–
Tensile strength (MPa)	12.57	12.54	11.63	8.30	8.13	5.54	5.44	5.39	5.33	5.29
% elongation at break	697	673	567	440	403	180	167	156	153	120
Hardness (shore A)	60	62	66	67	68	67	70	72	74	75
Crosslinking value (1/Q)	0.24	0.27	0.32	0.35	0.40	0.43	0.47	0.55	0.59	0.67

polymer in the swollen specimen, and d_2 is the density of the polymer.

Thermo gravimetric analysis (TGA)

The TGA of the vulcanizate was carried out by using a TGA 50, Shimadzu, Japan, thermogravimetric analyzer in nitrogen (flow rate 50 mL/min). All these analysis were carried out at heating rate of 10°C/min. The filler and the silica contents were also determined accordingly, using the TGA method reported earlier.[27] The values reported were based on residual contents at 800°C.

Scanning electron microscopy (SEM)

To study the dispersion of silica for both in situ silica-generated vulcanizate and externally silica-added vulcanizate, SEM studies were done on a JEOL, JSM 5800. The failure behavior was also analyzed using SEM. The samples were broken in liquid nitrogen and the phase morphology was examined.

RESULTS AND DISCUSSION

Tables I and II show the recipes employed to investigate the effect of TESPT and RR on the curing characteristics and mechanical properties such as 100 and 200% modulus, tensile strength, elongation at break, and hardness of SBR/RR vulcanizates.

It is observed that the TESPT containing vulcanizate had longer optimum cure time (t_{90}) and significantly

higher extent of cure ($\tau_{max} - \tau_{min}$). This is due to the fact that during crosslinking reactions fragmented TESPT was first grafted onto the rubber and participated in the crosslinking reaction, which may also form bond with RR, containing active functional sites[28,29] and consequently increases optimum cure time (t_{90}) of the vulcanizates. Because of high crosslink density of the vulcanizates, the materials become stiff and extent of cure ($\tau_{max} - \tau_{min}$) will be higher.

Mechanical properties of sol–gel versus conventional system without TESPT

The silica-filled vulcanizates prepared by sol–gel technique and conventional process by adding external silica were designated as the sol-gel vulcanizates (SGVs) and the conventional vulcanizates (CVs). The gum vulcanizates (given in Table I) were treated to the sol–gel process, which has been described in the experimental section. In this process, the vulcanizates were swollen in TEOS to incorporate a significant amount of silica to the SBR/RR vulcanizates. The filler contents before and after the sol–gel reactions were measured, and the silica contents of the SGVs were determined accordingly. The results are shown in Table III in which the recipes of gum and silica filled vulcanizates for the two systems such as SGVs and CVs are reported. The filler content of pure RR vulcanizate with same amount of compounding ingredients is also measured. The amount of filler obtained for the vulcanizate is mainly due to zinc oxide. This is confirmed by theoretical calculation based on recipes and

TABLE III
Filler and Silica Content of RR and Silica-Filled Vulcanizates

Gum vulcanizates		Silica-filled sol–gel vulcanizates			Silica-filled conventional vulcanizates	
Sample	Filler (wt %)	Sample	Filler (wt %)	Silica (wt %)	Sample	Silica (wt %)
SBR	4.8	SBR/RR = 80/20	21.1	16.95	SBR/RR = 80/20	16.90
RR	9.8	SBR/RR = 70/30	19.6	14.62	SBR/RR = 70/30	14.57
		SBR/RR = 60/40	21.2	14.58	SBR/RR = 60/40	14.51
		SBR/RR = 50/50	20.0	14.52	SBR/RR = 50/50	14.43
		SBR/RR = 40/60	17.9	11.57	SBR/RR = 40/60	11.50

TGA data where an error of about 3–4% was observed. The silica content obtained from TGA analysis in CVs and SGVs are comparable.

It is found that in SBR/RR vulcanizates incorporation of silica is decreased with increase in the RR content in absence of TESPT. This is due to the fact that with increase in the RR content crosslink density of SBR/RR vulcanizates increases; therefore, when this sample is immersed in TEOS for in situ silica formation less amount of TEOS is penetrated into the vulcanizate and consequently silica formation decreases.

The modulus at 100 and 200% elongation, tensile strength, elongation at break, hardness, and crosslinking value of SGVs and CVs are shown in Tables I and II (compare mix 1–5 with 1'–5'). From the results, it is evident that 100 and 200% modulus increases with increase in the RR content both for SGV and CVs. But the value of 100 and 200% modulus for SGVs are higher than that of CVs, which can be corroborated from crosslinking value data. This means that the vulcanizates containing silica, introduced by sol–gel techniques, had higher stiffness and ultimately it is converted to a brittle material, which is reflected in tensile strength value. Hashim et al.[17] reported that the reinforcing efficiency of silica by sol–gel technique is higher than that of the CVs due to nanosilica formation during sol–gel reaction. A peculiar behavior is observed in our experiment. Although modulus values are higher for SGV, tensile strength values are drastically reduced in case of SGVs as compared with the CVs. It is also evident from the result that crosslinking values of CVs are much lower than that of the SGVs (Fig. 1). The higher tensile strength value of CVs may be due to the formation of chemical bond between external silica and the active functionality of
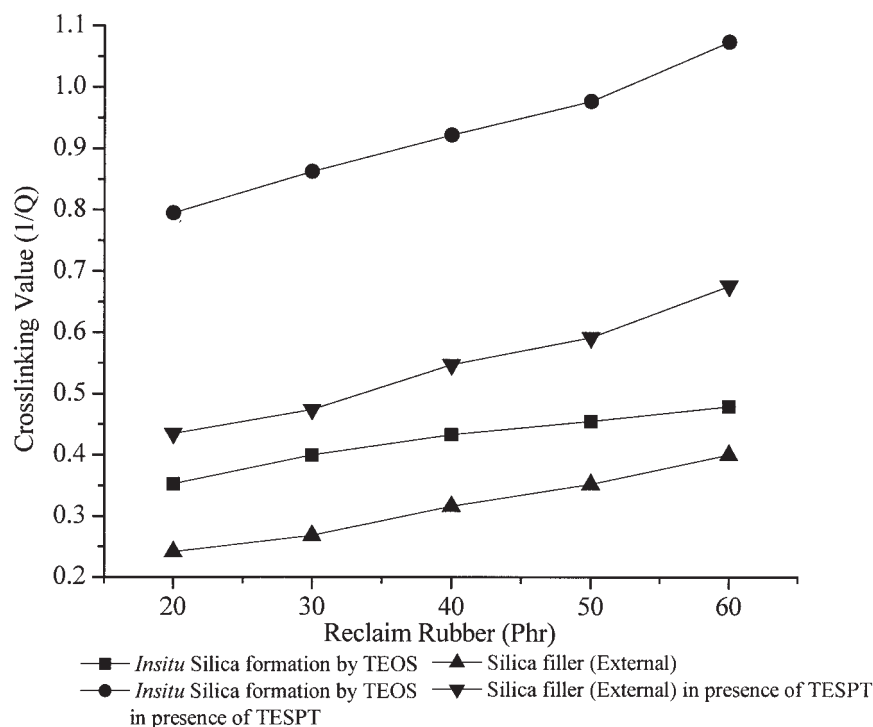

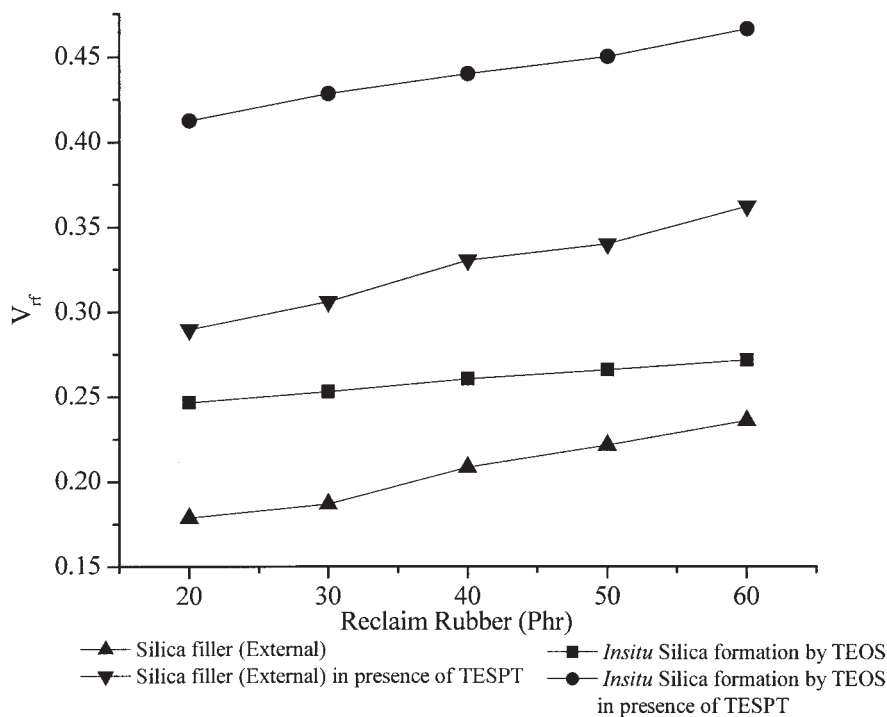**Figure 1** Effect of RR on crosslinking value of various SBR/RR SGVs and CVs.

Figure 2 Effect of RR on V_{rf} value of various SBR/RR SGVs and CVs.

RR.[28,29] In case of SGVs, no chemical bond formation occurs between rubber and filler, but the nanosize particles are well dispersed into the matrix, i.e., there is no chance of agglomerate formation. Therefore, stress can easily be transmitted from one portion to another. Since the silica contents of the SGVs and the CVs are considered to be comparable and the dispersion of silica in both the cases are more or less homogeneous, the higher reinforcing efficiency of CVs are mainly due to chemical bond formation. But for each individual vulcanizates, the different trend of tensile strength value with RR content was observed. In case of SGVs, tensile strength increases with increase in RR content but for CVs tensile strength decreases with increase in RR content. In both the cases, elongation at break decreases with increase in the RR content. This is due to the fact that with increasing crosslinking value, materials become stiff and therefore chain mobility decreases. Hardness also increases with increase in the RR content for both SGVs and CVs. Because of higher stiffness of SGVs, the hardness value is higher for those vulcanizates. Usually, an increase in stiffness due to an increase in the degree of cure or the filler content results in decreased elongation at break. Figure 2 shows the volume fraction (V_{rf}) of a rubber network in the swollen phase versus RR content in SBR/RR vulcanizates. From this figure, it is evident that for both the cases V_{rf} increases with increase in the RR content, but for SGVs the V_{rf} values are much higher compared to that of the CVs. Thus, crosslinking values of SGVs are higher than that of the CVs (Fig. 1).

Mechanical properties sol–gel versus conventional system with TESPT

Here, SGVs and CVs were prepared in presence of TESPT. It should be noted that in both the cases the silica particles were chemically bound to the rubber network. The only difference in terms of their preparation was in the mode of silica and TESPT incorporation into the system. In the case of SGVs, the TESPT was first grafted onto the rubber. As the TEOS grew into silica particles during sol–gel process, they became bonded with rubber due to the reaction between the grafted alkoxy silyl groups and the silanol groups on silica. This is schematically represented in Scheme 1. Therefore, a significant difference in morphology, degree of crosslinks, and distribution of crosslink bonds occur between two systems such as SGVs in presence and absence of TESPT.

It has been found that in the presence of TESPT silica content increases with increase in the RR content. The uniqueness of TESPT is that it can be considered part of the cure system, since it contains sulfur, and therefore should also be treated as a cocuring agent when sulfur cure system are used. From the sulfur crosslinking mechanism, the S_8 ring opens during vulcanization and reacts with the allylic hydrogens or the double bonds of the rubber to form sulfur crosslinks. By the same chemistry, it is possible for the sulfur bridges of TESPT to be broken and to be reacted with the rubber. The alkoxy silyl end groups provide the reaction sites for the silica to form a silica rubber-
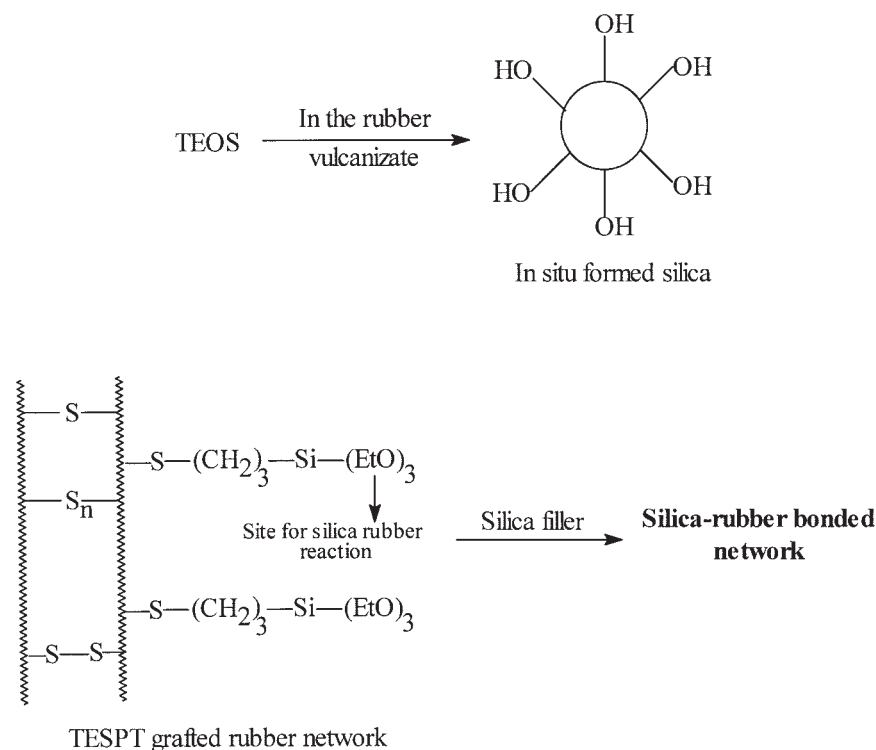
Scheme 1   Formation of silica–rubber-bonded network during sol–gel process.

bonded network. RR contains some stable radicals;[28] therefore during the time of curing, these stable radicals may also couple with sulfur radical generated from TESPT. As a result, fragmented TESPT, as a pendant, is formed on the backbone of rubber chain. Therefore, silica content increases with increase in RR in the presence of TESPT.

Tables I and II (compare mix 6–10 with 6′–10′) show the modulus at 100% elongation, tensile strength, elongation at break, hardness, and crosslinking value of SGVs and CVs. It is seen from the results that 100% modulus increases with increase in the RR content both for SGVs and CVs. The reason for higher 100% modulus may be due to higher crosslinking value of rubber vulcanizates, arising out of the gel present in RR and newly form chemical bonds between the alkoxy silyl groups attached with rubber chain and the silanol groups on silica, which is also corroborated by crosliking value data. As crosslinking value increases in the rubber matrix, chain mobility decreases and more load is required for 100% elongation. But the extent of increase of 100% modulus is higher for CVs because of agglomeration of silica particles into the rubber matrix. Tensile strength also increases with increase in the RR content for SGVs, but the reverse trend is observed for CVs. The tensile strength values of all the different SBR/RR vulcanizates are higher for SGVs than that of the CVs. The agglomerated silica in the vulcanizates remains present as weak sites for stress transmission to its surrounding (continuous ma-

trix), resulting in a lower tensile strength. The elongation at break decreases with increase in the RR content for both the vulcanizates. Hardness also increases with increase in RR content for both the vulcanizates. The extent of increase is higher for SGVs than that of the CVs. The higher stiffness of SGVs is mainly due to higher crosslinking value of the vulcanizates (Fig. 1). In Figure 2, the volume fraction (V_{rf}) of a rubber network in the swollen phase is plotted against RR content. Here for both the vulcanizates V_{rf}, values increases with increase in the RR content. But the absolute values of V_{rf} for each of the sol–gel SBR/RR vulcanizates are much higher than that of the conventional SBR/RR vulcanizates. Thus in presences of TESPT, crosslink density of SGVs are greater than that of the CVs.

TGA of SGVs

Thermal degradation of GRT reclaim and different SBR/RR SGVs in inert atmosphere were analyzed and corresponding results are given in Figures 3(a) and 3(b). The temperature interval of degradation stages evaluated from DTG curves, temperature of the stages maximum rate of degradation, sample weight loss at the temperatures, and char residue values are listed in the Table IV. The thermal degradation in inert gas atmosphere of reclaim GRT occurs in three temperature regions.
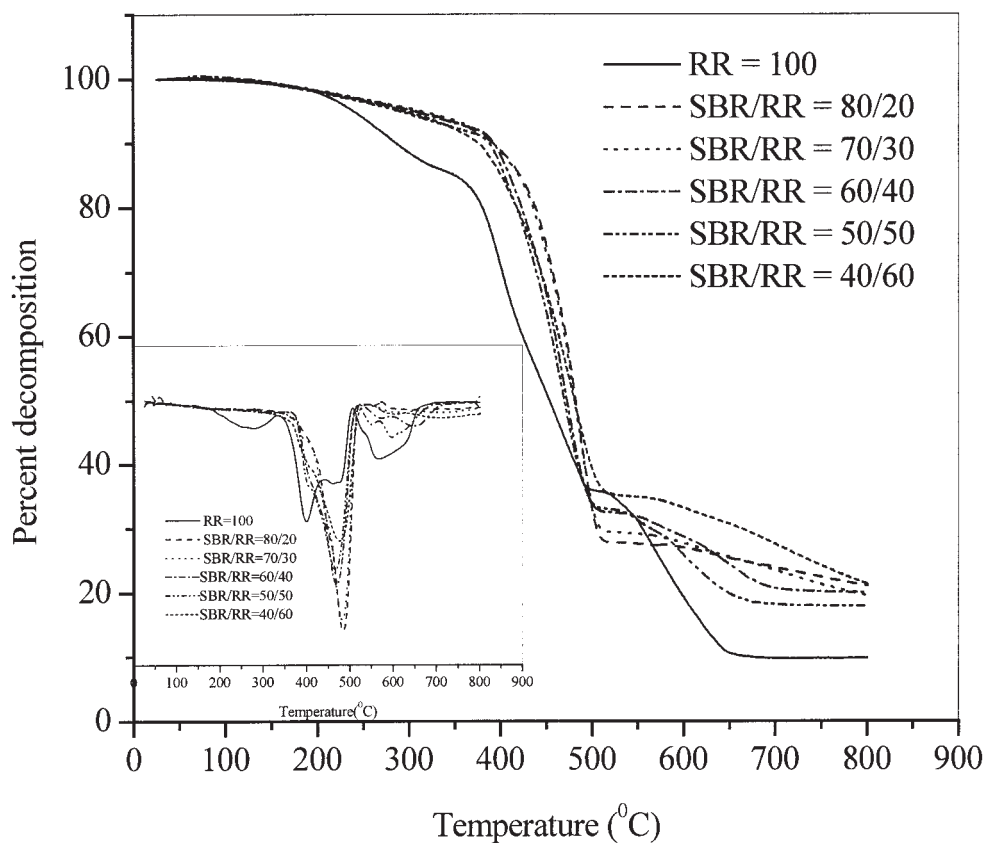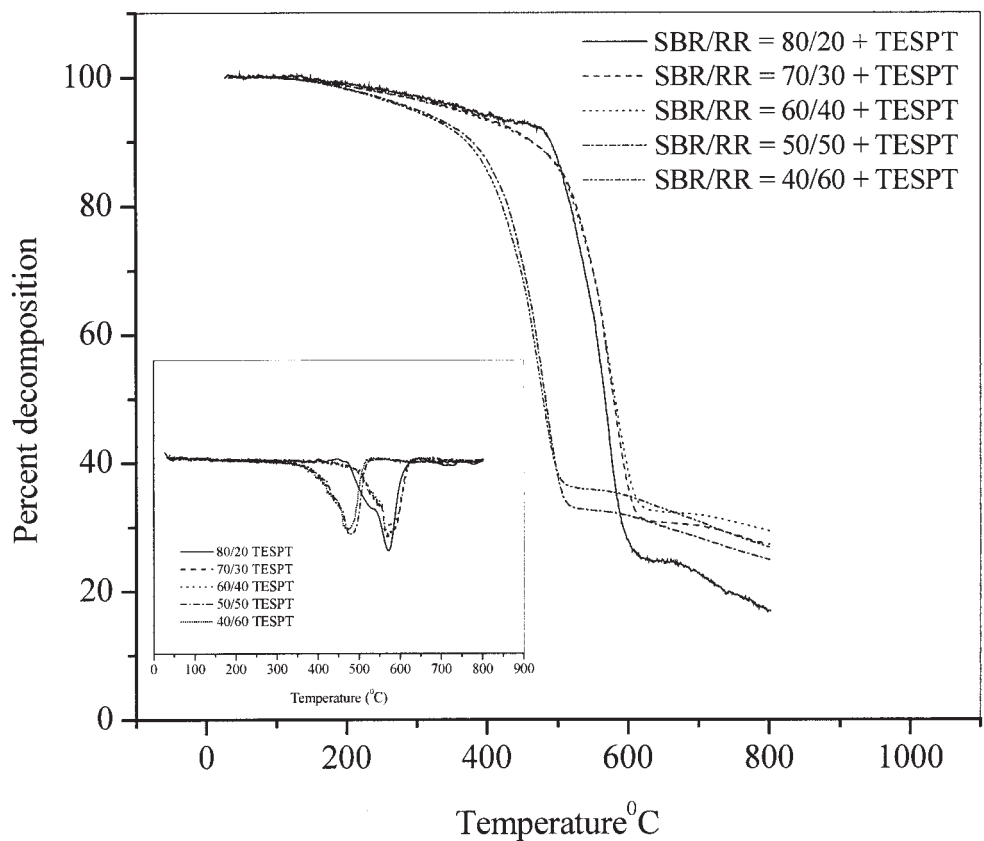
Figure 3   (a) TGA of SBR/RR SGVs in presence of TESPT (b) TGA of SBR/RR SGVs in absence of TESPT.

TABLE IV
Degradation Temperature at Various Stages and % Weight Loss of SBR/RR Vulcanizates

Sample code	1st degradation				2nd degradation				3rd degradation			
	Start	Peak	End	% wt loss	Start	Peak	End	% wt loss	Start	Peak	End	% wt loss
Without TESPT												
RR = 100	33.6	274.5	334.4	14.06	334.4	399.4	507.5	50.14	507.5	569.9	715.2	26.07
SBR/RR = 80/20	45.7	–	326.8	5.71	334.5	484.9	522.5	66.12	522.5	650.3	763.1	5.82
SBR/RR = 70/30	31.4	187.7	344.3	6.26	344.3	482.2	524.3	64.31	524.3	675.5	795.6	9.73
SBR/RR = 60/40	33.6	–	369.5	7.73	369.5	466.9	517.4	59.74	517.4	653.6	780.6	12.47
SBR/RR = 50/50	33.6	–	366.9	8.32	366.9	464.4	514.8	58.61	514.8	597.3	770.4	15.13
SBR/RR = 40/60	51.1	–	349.4	7.81	349.4	477.2	529.8	57.06	529.8	–	793.0	13.43
With TESPT												
SBR/RR = 80/20 + TESPT	36.1	–	452.4	7.03	452.4	575.4	627.6	68.14	627.6	–	793.0	7.64
SBR/RR = 70/30 + TESPT	38.7	–	416.9	7.08	416.9	572.4	642.6	62.21	642.6	–	793.0	3.35
SBR/RR = 60/40 + TESPT	48.6	–	440.5	8.57	440.6	562.6	638.1	58.95	638.1	–	792.3	2.92
SBR/RR = 50/50 + TESPT	41.79	–	356.8	8.04	356.9	482.9	537.6	59.22	537.6	–	795.6	7.74
SBR/RR = 40/60 + TESPT	45.28	–	336.6	7.17	336.6	474.1	534.3	56.9	534.3	–	792.3	8.85

In inert atmosphere, weight loss of the rubber sample at 1st low intensity stage can be related mainly to thermal decomposition of vulcanization crosslinks (sulfur links), decomposition of links formed by ZnO, stearic acid, and partial breakage of rubber backbone. Intensive thermal depolymerization process occurs at the 2nd stage with maximum rate of weight loss at 399.4°C. The weight loss slows down at 3rd stage. Above 800°C, sample weight becomes constant. The 1st stage degradation does not occur in SBR/RR SGVs both in presence and absence of TESPT. From the results, it is evident that with increase in the proportion of RR thermal stability of the vulcanizates decreases, but the extent of decrease in the 2nd stage degradation is very less with increase in the proportion of RR. But the thermal stability of TESPT containing SGVs is much higher compared to that of the former. However, the degradation in the 3rd stage initially increases with increase in the proportion of RR that reaches to a maximum and then decreases for SGVs without TESPT.

IR analysis

In this investigation, IR analysis was performed to assess the incorporation of silica via sol–gel technique. From IR spectra of ground rubber, it is observed that there is intense peak at 3426 cm^{-1}. This is due to the presence of absorbed moisture in ground rubber. But this peak almost vanishes after reclamation with TMTD only. This observation indicates that after reclaiming with TMTD, ground rubber forms some new linkages (bonds) with TMTD, which reduce its moisture absorption capacity. The same observation is also observed for the other spectrum.

All spectra show peak about 2900 cm^{-1} due to the asymmetric C—H stretching of hydrocarbon rubber back bone. Peak appears at 1000–1100 cm^{-1} is due to Si—O—Si stretching, which is completely absent in ground rubber and reclaim sample. But the intensity of this peak increases with the incorporation of TESPT during compounding of rubber. This is due to the fact that the fragmented TESPT, which is already bound to rubber backbone, can easily form bond with the other end with incoming silica. As a result, number of Si—O—Si linkages increases in TESPT contain sample compared to those of other samples.

The characteristic peak at 955–960 cm^{-1} is due to the presence of silanol ended silica chains in the rubber matrix. This is an indication of incomplete reaction of silanol within the rubber matrix. But the peak intensity at 957 cm^{-1} is changed in different sets of vulcanizates. In SBR/RR = 70/30 blend for CVs both in presence and absence of TESPT show lower intensity of Si—OH group. The higher amount of RR in this composition with reactive groups can react with more amount of functional group of Si (which is 4-coordinated species). For the appearance of this band, one coordinating site must be free i.e. free —OH group. If this —OH react with rubber network, then gradually the peak intensity should be decreased.

In SBR/RR = 80/20, composition peak intensity is maximum due to two reasons (1) lower amount of RR and (2) absence of TESPT. As a result of which, availability of free silica is increased consequently Si—OH bond intensity increases.
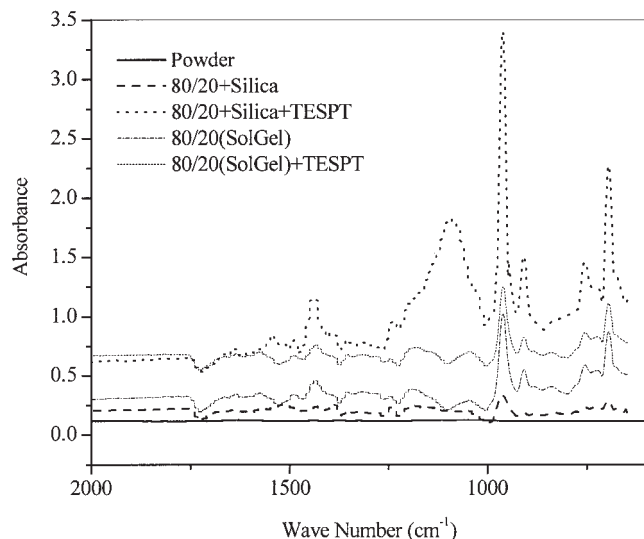
Figure 4   ATR of SBR/RR (80/20) SGVs and CVs.

In pure SBR gum rubber, there are two characteristic peaks at 914 and 700 cm^{-1} due to the presence of *trans*-1,4-hydrogen in butadiene back bone and γH with respect to the benzene ring of styrene.

From FTIR spectrum, it was observed that peak at 955–960 cm^{-1} is due to the presence of free silanol group in the compounded rubber, which is completely absent in GRT. From the comparative study of conventional SBR/RR (80/20) and SBR/RR (40/60) vulcanizates, it was confirmed that in 80/20 blend system the maximum absorption is due to the presence of silanol group (Fig. 4). However, in 40/60 blend system the intensity of this peak is very low due to the presence of high amount of RR (Fig. 5). The lowering in absorption intensity for this particular peak position definitely indicates that there is some rubber silica interaction.
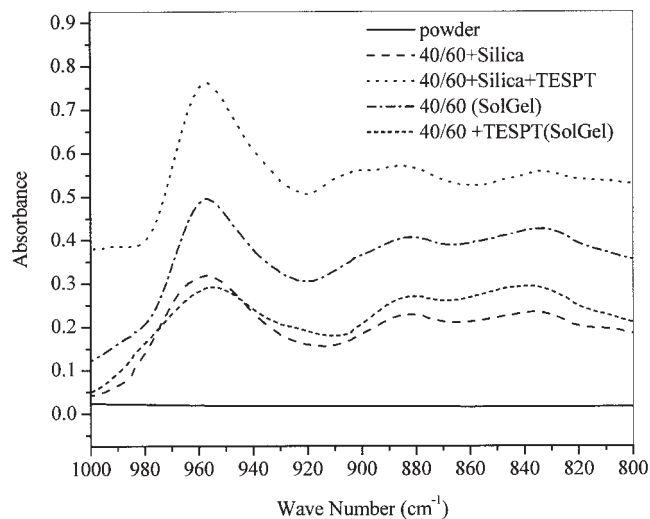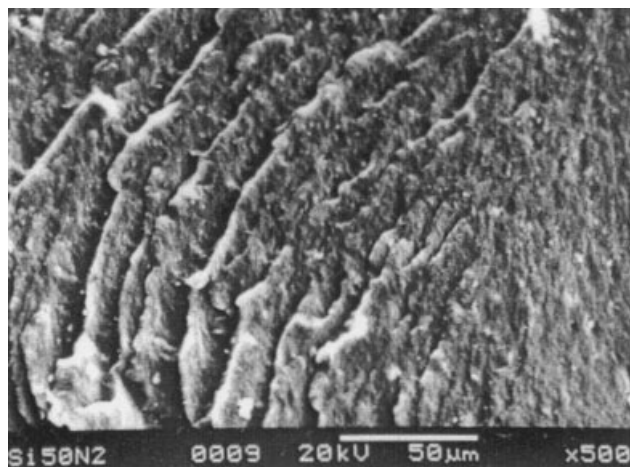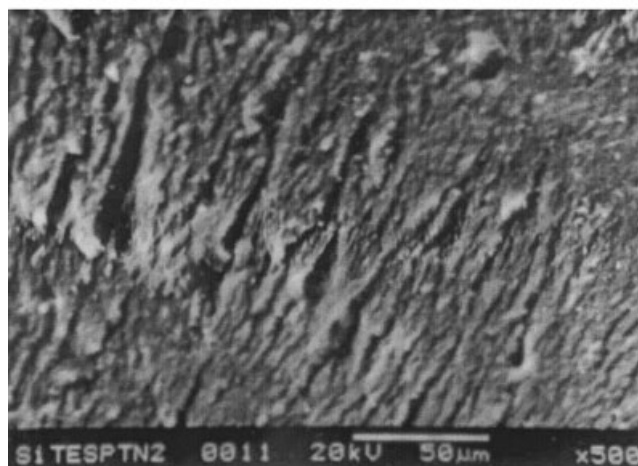

Figure 6   Phase morphology of cryogenically fractured conventional SBR/RR vulcanizate (a) without TESPT (b) with TESPT.

The same trend was also observed for conventional SBR/RR 80/20 and 40/60 blend system in presence of TESPT. But the absorption intensity of CVs with TESPT is higher than CVs without TESPT. This is due to the fact that added TESPT already react with reactive functionality of RR, and consequently, the external silica faces lower number of reactive group to react with. Therefore, more amount of unreacted silica shows the greater number of silanol linkages. So, these types of vulcanizates gives intense absorption peak at 955–960 cm^{-1} compared to that of only silica-based vulcanizates.

In case of SGVs 80/20 mix shows maximum absorption compared to that of the 40/60 mix because of the same reason discussed earlier. TESPT-modified SGVs also shows the low absorption intensity.
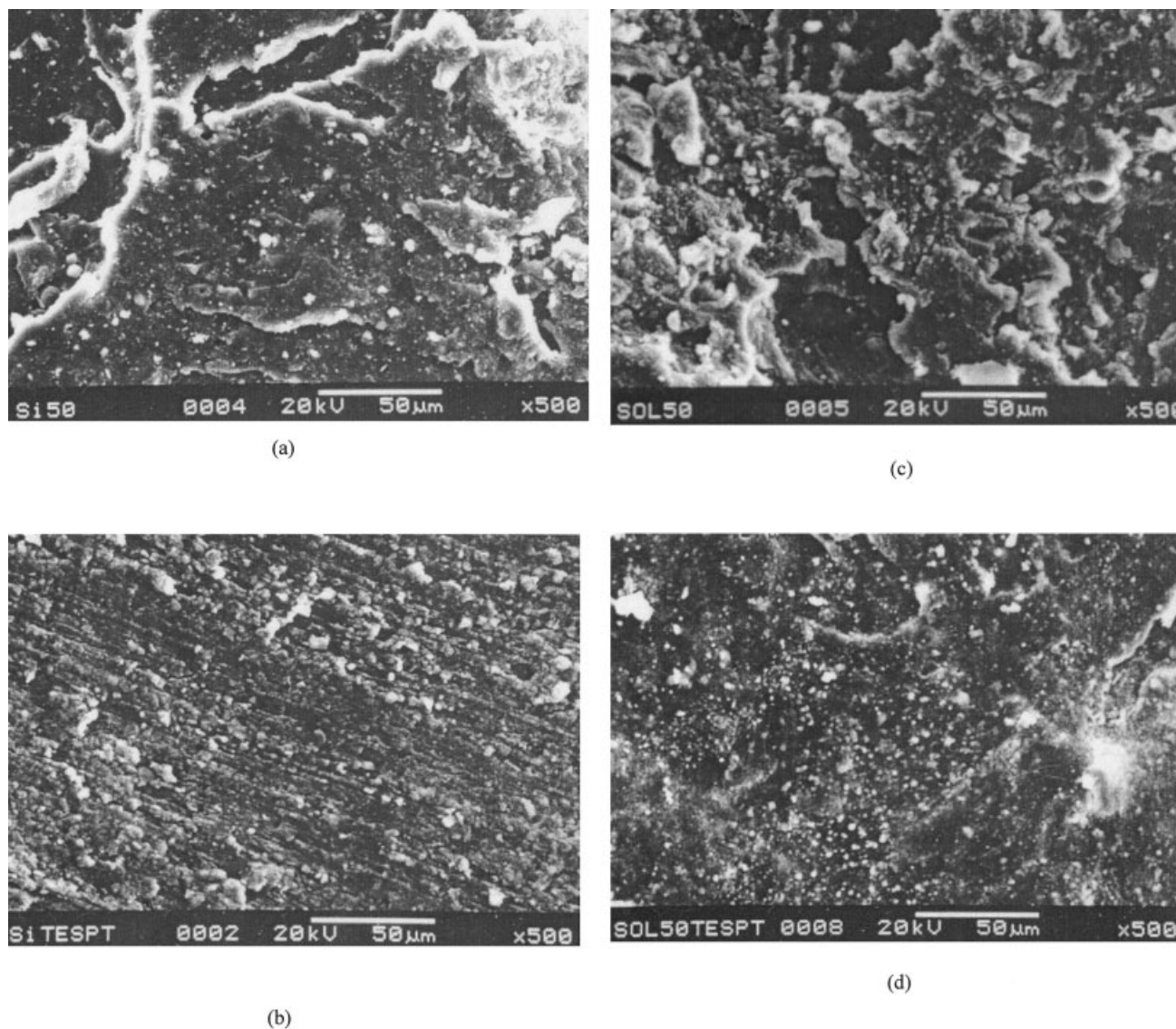

Figure 5   ATR of SBR/RR (40/60) SGVs and CVs.

Figure 7 Failure surface morphology of CVs and SGVs (a) CV without TESPT, (b) CV with TESPT, (c) SGV without TESPT, and (d) SGV with TESPT.

Scanning electron microscopy

Phase morphology

To get clear idea of the silica distribution in SBR/RR CVs, both in absence and presence of TESPT, the cured samples was cryogenically fractured and morphology was studied [Figs. 6(a,b)]. Two phases could be seen so that silica is dispersed in SBR/RR matrix. In both the vulcanizates, the silica particles are well dispersed. Absence of vacuoles in both the vulcanizates indicates high level of interaction between silica and rubber, from which an improved strength for the conventional SBR/RR vulcanizate can be predicted.

Failure surface morphology

The morphology of tensile fractured SBR/RR, SGV, and CV is shown in Figures 7(a–d). It is evident from

SEM picture that silica particles are dispersed more homogeneously in CV compared to that of the SGV in absence of TESPT [compare 7(a) and 7(c)]. The well-dispersed silica in the CV is ascribed to the lower concentration of silanol group on the surface of silica particles compared to the SGV, which is also proved from ATR. For the SGV [Fig. 7(c)], the large aggregates of silica particles were confirmed and the presence of pseudonetwork structure in the SGV was suggested by SEM observation. The homogeneous dispersion of silica in CV and SGV with TESPT is comparable [Figs. 7(b) and 7(d)].

CONCLUSIONS

This work was devoted to screening the potential application of RR for reinforcement of silica when combined with virgin rubbers to produce new rubber

products with useful properties. From the experiments, following conclusions can be drawn.

- TESPT containing vulcanizates had longer optimum cure time (t_{90}) and significantly higher extent of cure as compared with TESPT less system.
- The mechanical properties of the CVs are superior to that of the SGVs in absence of TESPT. But in presence of TESPT the reverse trend is observed.
- With increase in the proportion of RR in the vulcanizate, penetration of TEOS into the rubber matrix is decreased; therefore, silica incorporation by sol–gel technique is diminished.
- For the case of TESPT less systems, crosslinking value of SGVs are much higher than that of the CVs, which is further increased with TESPT.
- ATR study indicates that the RR enhances the rubber filler interactions.
- Study of phase morphology reveals the high level of interaction between silica and rubber.

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