Effect of Vulcanization Technique on the Physical Properties of Silica-Filled EPDM Rubber

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ABSTRACT: The present study aims to enhance EPDM rubber–silica interaction by employing a special technique called Two-Stage Vulcanization, with the help of a multifunctional rubber additive, bis diisopropyl thiophosphoryl disulfide (DIPDIS). In this process EPDM rubber was heated along with rubber additives up to the time just before the commencement of cure and then filler was incorporated to the preheated rubber to get the final mix. The efficiency of this novel technique is evaluated by the enhancement of physical properties of the silica-filled vulcanizates. This novel technique is also employed to investigate the effect of a silane-coupling agent, viz., bis (3-triethoxy silyl propyl) tetrasulphide (TESPT), in addition to DIPDIS, on the rubber–filler interaction. The positive role of this technique in enhancing the rubber–filler interaction is evidenced by the dynamic mechanical analysis and scanning electron microscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1132–1139, 2006

INTRODUCTION

The properties of rubber compounds (e.g., tensile strength, wear resistance, resilience, and flex resistance) could be improved by loading the compounds with selective fillers. Different grades of carbon black has been used as fillers in the past.[1] But progressively more attention is being paid to the use of mineral fillers such as silica and clay instead of costlier carbon black fillers.[2–7] In addition silica offers several advantages over carbon black. In tire tread, comparable wear resistance and better wet-grip in combination with a lower rolling resistance were obtained by using silica rather than carbon black.[8–9] But reinforcement by silica filler has not been achieved to the desired level because of the lack of strong silica–rubber bonding. However, in most applications filler–rubber bonding could be introduced by using specific coupling agents. Bifunctional organosilanes are commonly used to modify the surface of silica to improve its interaction with hydrocarbon rubber. This approach makes it possible to fabricate rubber compounds using silica, which meet the performance requirements traditionally obtained by the use of carbon black.

The presence of saturated backbone makes EPDM more resistant to oxygen, ozone, UV, and heat than low-cost diene elastomers such as NR, BR, and SBR etc. These inherent properties make EPDM the most preferred elastomer for outdoor applications such as automotive sealing systems, building profiles and roof sheeting, and under-the-hood application.

In our previous work,[10] we found that bis diisopropyl thiophosphoryl disulphide (DIPDIS), a multifunctional rubber additive, is capable of providing a fair degree of rubber–filler interactions in the two-stage vulcanization process of carbon black-filled EPDM rubber. In the present study efforts have been made to enhance EPDM rubber–silica interactions by modifying the EPDM rubber with the help of two-stage vulcanization technique in the presence of DIPDIS. Bis (3-triethoxy silyl propyl) tetrasulphide (TESPT), a well-known silica-coupling agent, having structural similarity with DIPDIS, has been employed to obtain a clear understanding about the effectiveness of this novel process.

EXPERIMENTAL

Materials

EPDM (Herlene-521, Herdillia Unimers, India; ENB content, 5%; E/P ratio, 52 : 48; ML (1 + 4) at 100°C, 45; total ash content, 0.15%; specific gravity, 0.86) was used in the present investigation. Zinc oxide (SD Fine Chemicals, India), stearic acid (Merck, India), Sulfur (Merck, India; mp, 118°C), and precipitated silica (MFIL-200, HDS, Madhu Silica, India) were used as received. Bis (diisopropyl) thiophosphoryl disulphide (DIPDIS) was synthesized and purified in the laboratory.[11] TESPT was obtained from Degussa, Germany.

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Iso-octane (SD Fine Chemicals, India) and toluene (SD Fine Chemicals, India), were used as solvent in the present investigation.

Compounding of rubber

One-stage vulcanization

Compounding of rubber formulations was carried out in a laboratory size two-roll mixing mill of roll size 203×102 mm^2 (Berstorff, Germany), with friction ratio 1.2 as per ASTM D15–54 T (1994). EPDM rubber was first masticated to from a smooth band in the front roll of the mill and the compounding ingredients were sequentially added in the order zinc oxide, stearic acid, and silica. Finally curatives (DIPDIS and sulfur) were added to the mix after cooling the mill. The stocks were cured under pressure at 160°C up to optimum cure time (t_{90}). For TESPT-containing compound, TESPT was mixed during the addition of silica.

Two-stage vulcanization

In this process EPDM rubber was masticated and the compounding ingredients such as zinc oxide, stearic acid, DIPDIS and sulfur were gradually incorporated into the rubber matrix. The time (t) required for commencement of curing of the compound thus obtained was calculated from rheograph at 160°C in a Monsanto Oscillating Disk Rheometer (R-100). The compounded EPDM mix was then heated at 160°C in the hydraulic press for the predetermined time (t) to get the modified EPDM. Filler was then incorporated into the modified EPDM to get the filled, modified EPDM compound. Then the compounded rubber stocks were cured after 24 h of resting under pressure at 160°C temperature for the respective optimum cure time ($t = t_{90}$). After curing, the vulcanized sheet was taken out from the mold and immediately cooled under tap water to restrict further curing.

Measurement of physical properties

Modulus at 200 and 300% elongation, tensile strength, and percentage elongation at break were measured by following ASTM D 412–51T. The hardness values were determined by the procedure stated in ASTM D 2240–85, using a Shore A Durometer. The tensile strength specimens were aged in a circulating air-aging oven at (100 ± 2)°C. After aging for 72 h, modulus at 200 and 300% elongation, tensile strength, percentage elongation at break, and hardness were measured. The crosslinking values were determined according to the procedure described elsewhere.[12]

Toluene and n-hexane were used for bound rubber determination.[13] All uncured compounds (compounds obtained after final mixing) were stored at room temperature for 1 week before extraction. Weighed amount of compound ($\sim$0.2 g) was cut into small pieces and placed into a stainless steel wire cage of known weight. The cage was then immersed in 25 mL of toluene for 7 days at room temperature and the solvent was renewed after 3 days. Finally the sample was kept in n-hexane for another day. After extraction, the compound and the wire cage were dried for 1 day in air at room temperature and then for 24 h in an oven at 105°C. The percent (%) bound rubber of the polymer, R_B, were then calculated according to the following equation [8].

$$R_B = \frac{W_{fg} - W[m_f(m_f + m_p)]}{W[m_p/(m_f + m_p)]} \times 100$$

where W_{fg} is the weight of gel containing filler after extraction, m_f is the weight of the filler in the compound, and m_p is the weight of polymer in the compound

Dynamic mechanical analysis

Tg of silica-filled EPDM rubber was determined using Dynamic Mechanical Analyzer (DMA; Model Q 800, TA Instrument, New Castle, DE). The test temperature range was from -100°C to 60°C with a heating rate of 5°C min^{-1}, the test amplitude and frequency being 20 μm and 1 Hz, respectively. The results were presented in terms of loss tangent (tanδ) and temperature.

Scanning electron microscopy studies

Scanning electron microscopy (SEM) studies were carried out on the fractured surfaces of specimens derived from tensile testing. These specimens were stored in a desiccator and then sputter-coated with gold onto the fractured surface within 24 h of testing. The SEM observations were made using JSM 5200 Scanning Electron Microscope.

RESULTS AND DISCUSSION

During vulcanization of silica-filled rubber, the curatives are adsorbed on the polar surface of silica particle, leading to vulcanizates with poor mechanical properties because of the lack of proper vulcanization. Our objective is to form sulfidic pendent groups derived from DIPDIS on to the unsaturated side chain of EPDM rubber prior to the addition of silica so that the probability for total adsorption of curatives by silica will be restricted. In this regard vulcanization was
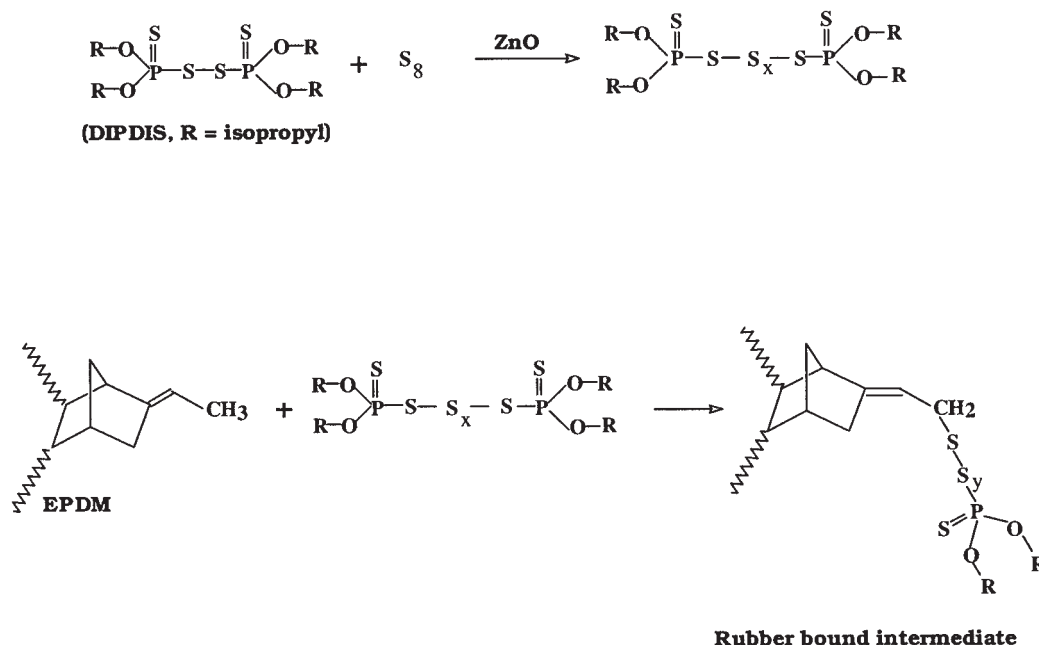
Scheme 1 Reactions of DIPDIS with EPDM in presence of ZnO and sulfur.

carried out by one-stage and two-stage process both in the presence and absence of TESPT.

One-stage vulcanization

Datta et al.[14,15] reported that the bis (diisopropyl) thiophosphoryl disulfide (DIPDIS), having structural similarity with bis (3 triethoxy silyl propyl) tetrasulfide, plays an important role (as coupling agent) in rubber–silica interaction (Scheme 1). Reinforcing silica is incorporated in various proportions into EPDM rubber matrix both in the presence and absence of silane-coupling agent. Table I shows the formulations of the mixes and the cure characteristics of one-stage vulcanization at 160°C. From Table I it can be inferred that with the increase in the proportion of silica filler (mixes 1–5) the maximum rheometric torque (R_∞) decreases. This is due to the fact that the adsorption of polar curatives on silica surface occurs and such tendency increases with increase in the proportion of silica. But this deleterious effect is very less in mixes

containing TESPT. The R_∞ values of the mixes containing TESPT (mixes 6–10) remain almost unchanged for different amounts of filler loading. This observation indicates that the adsorption of curatives on silica surface becomes less in the presence of TESPT. The absolute values for scorch time (t_2) is higher in mixes containing TESPT when compared to those of the mixes without TESPT. From this result it is evident that the processing of TESPT-containing vulcanizates are easier than that of vulcanizates without TESPT. However, the t_2 values for mixes containing TESPT are decreased as the filler proportion increased. In the same manner optimum cure time (t_{90}) is also decreased with the increase in the filler loading both in the presence and absence of TESPT. Physical properties of one-stage vulcanizates are shown in Figure 1. It is evident from Figure 1(a) that the values of 100% modulus are increased with the increase of silica loading both in the presence and absence of TESPT. But for the modulus at 300% elongation [Fig. 1(b)] the optimum value was obtained at 30 phr silica in the ab-

TABLE I
Formulation and the Cure Characteristics of One-stage Silica-Filled EPDM Vulcanizates at 160°C

Mix[a]	1	2	3	4	5	6	7	8	9	10
Silica	20	25	30	35	40	20	25	30	35	40
TESPT[b]	–	–	–	–	–	1	125	1.5	1.75	2
Maximum rheometric torque, R_∞ (Nm)	4.3	4.2	4.1	2.8	2.3	5.6	5.55	5.5	5.3	5.3
Scorch time, t_2 (min)	3.5	3	3	2.5	2.25	4.5	3.5	3	2.5	2.5
Optimum cure time, t_{90} (min)	13	10.5	10	6	5.25	16.5	15.5	14.5	12.5	11.75

[a] All the mixes contain 100 g EPDM, 5 phr ZnO, 2 phr stearic acid, 3.834 phr DIPDIS (9 mmol), and 0.5 phr sulfur. TESPT was taken 5% by weight with respect to silica.
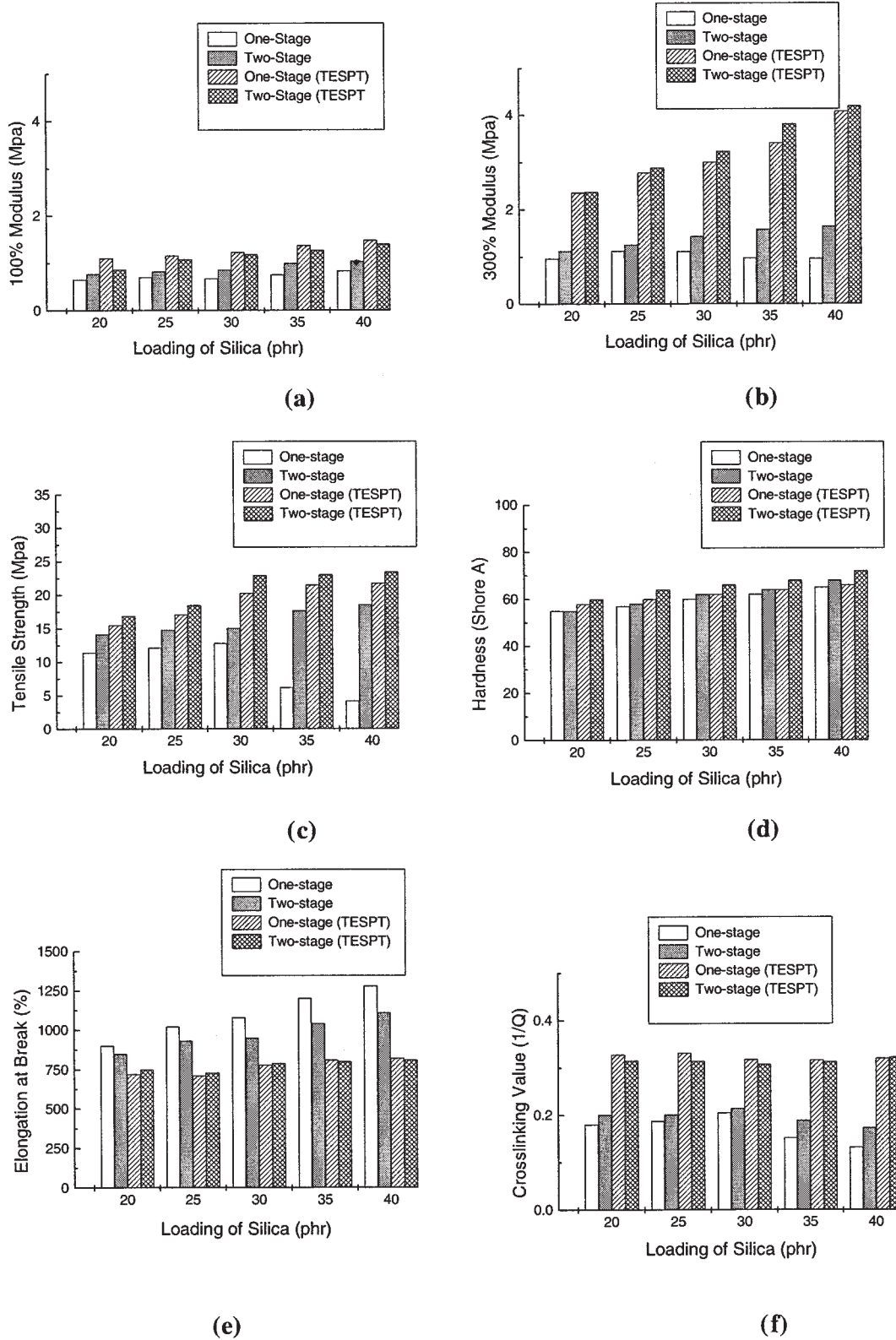
Figure 1 The comparison of (a) 100% Modulus; (b) 300% Modulus; (c) Tensile Strength; (d) Hardness; (e) Elongation at Break, and (f) Crosslinking Value versus silica loading of EPDM rubber derived from one-stage and two-stage process both in the presence and absence of TESPT.

sence of TESPT. However, in the presence of TESPT, 300% modulus follows the same trend as for 100% modulus. Maximum tensile strength was observed for

the vulcanizates containing 30 phr silica [Fig. 1(c)] but in presence of TESPT the values are increasing with the increase of silica loading. The values of hardness

|	Mix	1'	2'	3'	4'	5'	6'	7'	8'	9'	10'
First stage	EPDM	100	100	100	100	100	100	100	100	100	100
	ZnO	5	5	5	5	5	5	5	5	5	5
	Stearicacid	2	2	2	2	2	2	2	2	2	2
	S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	DIPDIS[a]	3.834	3.834	3.834	3.834	3.834	3.834	3.834	3.834	3.834	3.834
	Preheating time	10	10	10	10	10	10	10	10	10	10
Second stage (after preheating compounded EPDM at first stage)	Silica	20	25	30	35	40	20	25	30	35	40
	TESPT	–	–	–	–	–	1	1.25	1.50	1.75	2
Maximum rheometric Torque, R_∞, (Nm)		4.3	4.2	4.2	3.45	3.02	5.45	5.35	5.1	4.9	5.05
Scorch time, t_2 (min)		2.5	2.25	1.75	1.25	1.5	2.5	2	2	2	2
Optimum cure time, t_{90} (min)		11.25	7.5	6.5	5.25	4.5	14	13	12.5	12	12

[a] Weight corresponds to 9 mmol DIPDIS.

are also increased with the filler loading [Fig. 1(d)]. High elongation is the characteristics of silica-filled rubber vulcanizates. It is also reflected in the experimental results, and the elongation at break is increased as the loading of filler is increased [Fig. 1(e)]. It is observed from Figure 1(e) that presence of TESPT decreases the elongation at break in a considerable extent. Here it is important to note that the extent of increase of elongation at break is greater for the vulcanizates without TESPT. But in presence of TESPT the values remain almost constant. The crosslinking value (1/Q) derived from swelling experiment is maximum at 30 phr loading but there is no such optimization level for TESPT containing vulcanizate [Fig. 1(f)]. This indicates that the crosslinking density does not depend upon the filler loading (in between 20 and 40 phr loading) in the presence of TESPT. This may be due to the fact at 5% (w/w) TESPT concentration with respect to filler, maximum rubber–rubber and rubber–filler interactions are taking place.
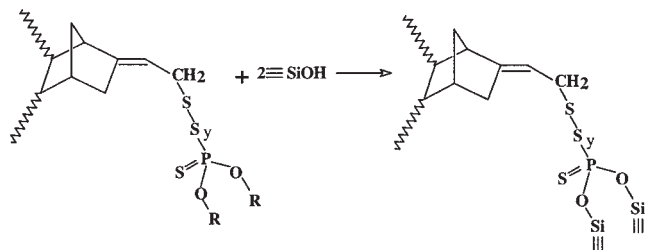
Two-stage vulcanization

The composition and curing characteristics of the mixes (1'–10') are given in Table II. For all the mixes the t_2 and t_{90} values are diminished further with respect to corresponding one-stage vulcanizates. This means that much reactive pendant DIPDIS fragments boost up the vulcanization process. Comparison of maximum rheometric torque values for one-stage and two-stage technique indicates that considerable increment occurs for the mixes containing 35 and 40 phr silica (compare mixes 4 and 5 with 4' and 5'). But in the presence of TESPT there are no significant change of R_∞ values between one-stage and two-stage vulcanizates. In the case of high loading of silica under consideration, the polar hydroxyl groups of silica adsorb the curatives, resulting in scarcity of curatives in the rubber matrix. But when two-stage vulcanization

process was carried out then at the first step of the two-stage process, the DIPDIS molecules got anchored to the EPDM rubber backbone (Scheme 1); hence the silica could not take the opportunity to adsorb curatives at once (Scheme 2).

The physical properties are presented in Figure 1(a–d). It is evident from these figures that the modulus at 100 and 300% elongation are increased for two-stage vulcanizates without TESPT when compared to those for one-stage vulcanizates without TESPT. This means that the rubber-filler interactions are enhanced for the mixes without TESPT in the two-stage vulcanization process. In the presence of TESPT the enhancement of 100% modulus with loading of silica is negligible for two-stage vulcanizates. But 300% modulus for higher loading of silica (35 and 40 phr) are increased to some extent. For higher loading of silica the adsorption of curatives is greater for one-stage vulcanization process, but in the two-stage process the curative adsorption is minimized by preheating the curatives with EPDM rubber. For all the cases tensile strength increases for two-stage vulcanizates when compared with the vulcanizates derived from one-stage process. However, the beneficial effect of two-stage vulcanization is very much pronounced for the TESPT-less system at higher loading of silica. Here at 35 and 40 phr of silica remarkable enhancement of tensile strength has been observed. It has been thought that the pendent thiophosphoryl moiety, connected to the EPDM rubber backbone, formed in the first step of the two-
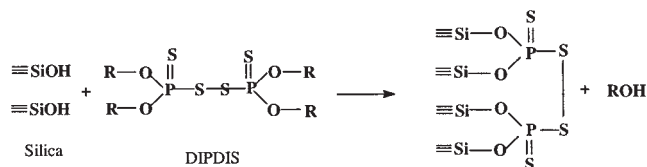
Scheme 2 Reactions between silica and DIPDIS.

Scheme 3 Reaction of silica with pendant DIPDIS fragments.

Figure 2 Effect of vulcanization technique on bound rubber (%) of silica-filled EPDM compounds both in the presence and absence of TESPT.

stage process is polysulfidic in nature[16] and this polysulfidic bond (Scheme 3) is likely responsible for the ultimate tensile properties. Hardness values of the two-stage vulcanizates are also increased to some extent. The two-stage vulcanization method decreases the elongation at break for TESPT-less systems, but this technique effects little on the elongation at break for TESPT-containing system. This is due to the fact that more rubber–filler interaction produces vulcanizates with lower elongation at break. From swelling experiment the crosslinking values were derived and presented in Figure 1(f). It is evident from this figure that the crosslinking values do not depend upon the vulcanization process for TESPT-containing vulcanizates but an increment of crosslinking value is observed for TESPT-less system. In all cases $1/Q$ values were increased and the values are increased to a greater extent for 35 and 40 phr silica loading when compared with corresponding one-stage vulcanizates.

Bound rubber

Bound rubber is the rubber portion that can no longer be separated from the filler when the rubber mix is extracted in a good rubber-solvent. It is an important parameter to determine rubber–filler interactions, and it is the percentage of polymer adsorbed on the filler surface in gel form after solvent treatment. The enhanced rubber–filler interaction provides high value of bound rubber and good mechanical properties. Figure 2 shows the bound rubber content of one-stage and two-stage silica-filled EPDM compounds. For all the cases bound rubber content are higher for two-stage compound when compared to the corresponding one-stage compound. But for TESPT-containing compounds, the increment is not so high as shown by the TESPT-less system. It seems that additional physicomechanical interactions and hydrogen bonding might have been occurred between the alkoxy groups of the pendant DIPDIS fragments attached onto the EPDM backbone (introduced in the first stage of the two-stage vulcanization) with polar hydroxyl groups present on the silica surface. This additional interac-
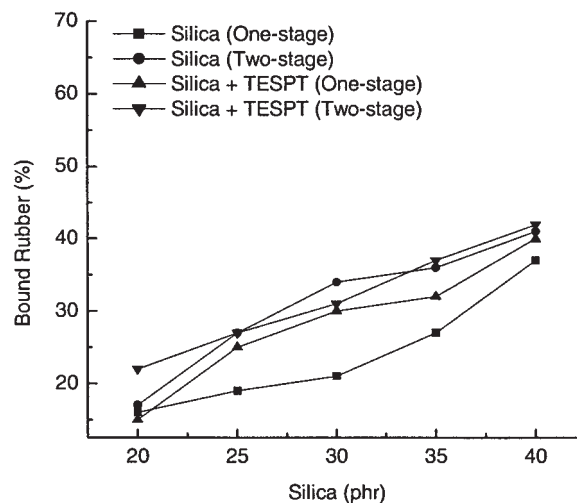
tion is responsible for higher bound rubber content of the two-stage compounds.

Dynamic mechanical analysis

The results obtained from Dynamic mechanical analysis were in agreement with those of the physical properties of the silica-filled vulcanizates. In Figure 3, the dotted curve stands for one-stage vulcanizate and the solid-line curve stands for two-stage vulcanizates containing 40 phr silica. The height of tanδ peak decreased and the peak position is shifted to a high temperature for the two-stage vulcanizates. Generally, the T_g of the filled rubber is shifted to a high temper-
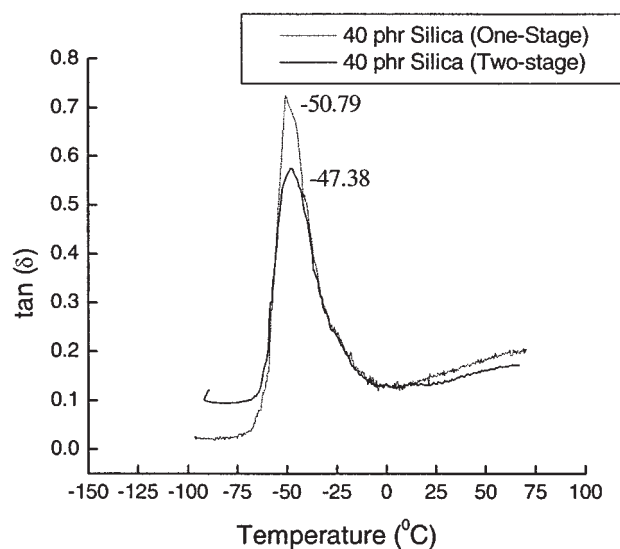

Figure 3 Loss tangent versus temperature for silica-filled (40 phr) EPDM compounds: One-stage (—); Two-stage (—).
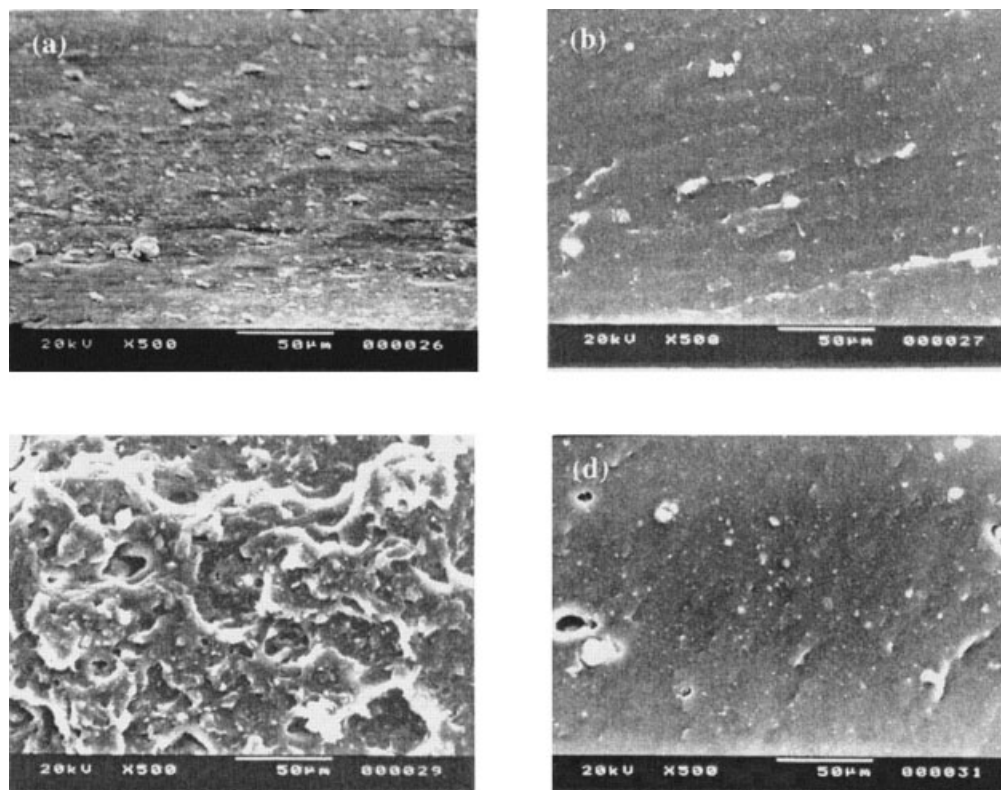
Figure 4 SEM micrographs of tensile-fractured surfaces of the silica-filled (40 phr) EPDM rubber vulcanizates: (a) one-stage with TESPT; (b) two-stage with TESPT; (c) one-stage without TESPT; (d) two-stage without TESPT.

ature region and the height of tanδ peak becomes lower when the interactions between the rubber and the fillers is strong enough.[17] Thus, the enhanced physical properties for the two-stage vulcanizates arise because of efficient rubber–filler interactions by the help of pendant DIPDIS moieties formed in the first stage of the two-stage vulcanizates.

SEM studies

To investigate the influence of vulcanization technique on the dispersion of silica, scanning electron microscopy analysis was done. Figure 4(a–d) shows the SEM photographs of the tensile-fractured surfaces of the silica-filled EPDM at 40 phr filler loading with TESPT (mix 10 and mix 10′) and without TESPT (mix 5 and mix 5′). It is evident from Figure 4(a,b), that there is no significant change in the micrographs for the mixes containing TESPT. However, silica particles are little bit more homogeneously dispersed in the EPDM matrix for the two-stage vulcanizates than for the corresponding one-stage vulcanizates. But in absence of TESPT, the micrograph [Fig. 4(c)] obtained from one-stage vulcanizate shows an uneven and inhomogeneous surface with full of vacuoles. But in the micrographs [Fig. 4(d)] of the two-stage vulcanizates with similar composition, a smooth homogeneous surface

was observed. This is due to the fact that in the two-stage process the hydrophilicity of the rubber matrix is increased through organografting of the curatives, as a result the rubber-filler interactions are enhanced.

Aging characteristics

Thiophosphoryl disulfide has been shown to yield substantial amount of zinc dithio phosphate in situ, which play active role of effective antioxidant.[11,18] Moreover, EPDM is a class of elastomer having saturated backbone. So, it may be reasonably expected that vulcanizates made of EPDM and thiophosphoryl disulfide could offer excellent age resistance property. It is evident from Table III that aged property with regard to tensile strength is decreased in most of the cases. However, the vulcanizates derived from two-stage process are much better resistant to prolonged oxidative degradation. On the contrary interesting results were found for mix 4 and mix 5 containing 35 and 45 phr silica, respectively. Here the tensile strength of the aged vulcanizates is increased. The increment of tensile strength is much more pronounced for one-stage vulcanizates. This may be due to the fact that at one-stage process the curatives, adsorbed on silica surface, are responsible for postcuring of the vulcanizates in the aging condition. As far as

TABLE III
Change in Physical Properties after Air Aging at (100 ± 2)°C during 72 h

MIX*	1	2	3	4	5	6	7	8	9	10
ATS (%)	51 (61)	59 (70)	75 (89)	248 (105)	310 (120)	48 (52)	56 (58)	53 (62)	70 (79)	78 (96)
ΔM 100% (%)	143 (135)	170 (142)	191 (144)	169 (138)	149 (142)	144 (120)	161 (131)	154 (142)	177 (155)	187 (161)
ΔM 300% (%)	207 (184)	204 (202)	211 (183)	216 (204)	212 (180)	232 (227)	244 (229)	244 (231)	266 (208)	247 (208)
ΔEB (%)	59 (62)	53 (61)	50 (64)	63 (66)	71 (71)	44 (48)	44 (48)	41 (48)	47 (59)	47 (60)
Change in hardness (points)	+6 (+5)	+6 (+7)	+5 (+7)	+5 (+5)	+4 (4–6)	+3 (+5)	+5 (+3)	+6 (+3)	+6 (+4)	+8 (+3)

[a] Values in parentheses are aged values of the corresponding two-stage vulcanizates.

the modulus values are concerned, the increment of the values was observed. However, this increment is greater for one-stage vulcanizates. The elongation at break values is severely affected for all the cases. Hardness values show the same trend as that of modulus.

CONCLUSIONS

Modification of EPDM rubber by two-stage vulcanization technique with the help of DIPDIS enhances the interaction between the EPDM rubber and silica. As a result the mechanical properties for two-stage vulcanizates are considerably improved when compared with those for one-stage vulcanizates. However, in presence of TESPT the effect of vulcanization technique is not pronounced. Shifting of T_g peak towards high temperature region for two-stage vulcanizates clearly indicates enhanced rubber–filler interaction in the vulcanizates.

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