Use of Epoxidized Rubber Seed Oil as a Coupling Agent and a Plasticizer in Silica-Filled Natural Rubber Compounds

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ABSTRACT: To obtain good reinforcement by silica filler in nonpolar rubbers, it is almost essential to use coupling agents, such as bis(triethoxy silyl propyl) tetrasulfane (TESPT). Chemicals that can interact with the silanol groups on the silica particles and reduce their network formation are also expected to enhance reinforcement. We made a comparative evaluation of TESPT, epoxidized rubber seed oil (ERSO), and their combination as a coupling agent and a plasticizer in silica-filled natural rubber compounds. The results indicate that compounds containing ERSO showed physical and mechanical properties between that of TESPT and naphthenic oil. The action of ERSO in the improvement of the properties was expected to be bifunctional and similar to that of TESPT; that is, it caused the hydrophobation of silica, which increased its degree of dispersion and the formation of chemical bonds with the rubber, thereby ensuring strong polymer–filler interactions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3531–3536, 2004

**Key words:** rubber; fillers; crosslinking; elastomer; silica

INTRODUCTION

The rubber tree (*Hevea brasiliensis*) is widely used as a source of natural rubber (NR), and its seed has been found to be rich in oil.[1–3] Rubber seed is an important byproduct of the rubber tree. Fresh seed contains about 65% kernel and 35% shell.[4] Although there is variation in the oil content of seeds from different clones, the average oil yield is about 42 wt % of the dried kernel.[5–7] The composition and characteristics of rubber seed oil (RSO) vary with planting location and clone.[8] RSO is a light yellow, semidrying oil, and it is extracted by expulsion. The oil contains about 18–22% saturated and 78–82% unsaturated higher fatty acids.

There are various industrial applications for RSO. The oil is used for the production of factice.[9] Vijayagopalan and Gopalakrishnan[10] reported the epoxidation of RSO with hydrogen peroxide and acetic acid. Epoxidized rubber seed oil (ERSO) is used in formulations for anticorrosive coatings and adhesives.[11] RSO is also suitable for the production of low-quality soap.[12] The properties of RSO resemble those of linseed oil. It was, therefore, conceived as having strong potential to replace linseed oil, partially in alkyd production.[13] RSO is suitable for the production of fat liquor for the leather industry[14] and in the preparation of grease.[15] RSO has been evaluated as an alternative to diesel fuel.[16] Aigbodion et al.[17] reported the use of RSO and ERSO in NR compounds for the improvement of processability characteristics and physicomechanical properties. RSO can be used as a multipurpose ingredient for NR and styrene–butadiene rubber (SBR).[18] It imparts excellent mechanical properties to NR and SBR vulcanizates when it is substituted for conventional plasticizer. It also improves aging resistance, reduces cure time, increases abrasion resistance and flex resistance, and reduces blooming. It would probably be suitable for the preparation of hydrogenated or hardened oil for edible purposes. According to Okieimen and Ebhoaye, RSO, ERSO, and their lead and barium salts can be used as heat stabilizers for PVC.[19–21] Hydrogenation of the fatty acid from RSO yields about 80% (w/w) stearic acid.[22] In aerial spraying, RSO could be mixed with spray oil in the ratio 1:3 (RSO/spray oil).[23]

Precipitated or fumed silica, with a very low particle size, has been used in white and colored rubber compounds because of its high reinforcing effect, which is similar to that of carbon black. Because of the presence of functional groups, such as the —OH attached to the silica particle, it forms strong agglomerates through hydrogen bonding. The highly polar nature and high structure of silica make it very difficult to mix with nonpolar rubbers.[24] Additionally, fine-particle silica has a tendency to adsorb the accelerators, which causes an increase in the cure time of a compound. Because of these difficulties, the use of silica in rubber compounds is limited to certain products, including shoe soles, hot-water bottles, and rice polisher brake/

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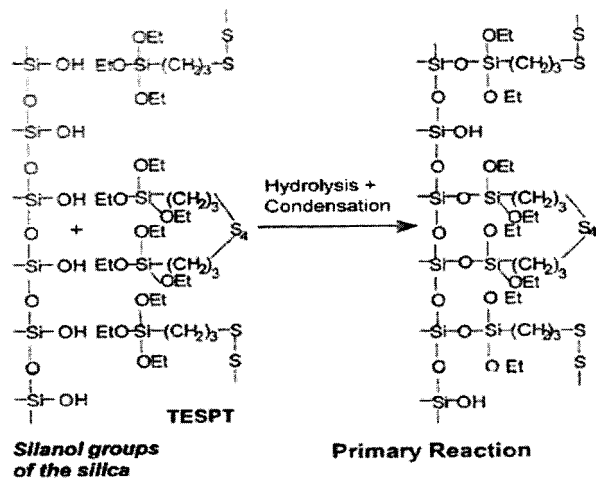
Scheme 1 Mechanism of the silanization primary reaction.

rolls. The modification of the silica surface with bifunctional organosilanes has been helpful in overcoming many of the above problems. Such modified silica can be easily dispersed in rubber and has shown the maximum reinforcement effect.[25,26] Subsequently, several organosilanes have been developed and evaluated in rubber compounding along with silica.[27] Among these, bis(triethoxy silyl propyl) tetrasulfane (TESPT) has become the most widely used. It has been reported that bifunctional organosilanes such as TESPT (Si-69) function as a coupling agent in silica-filled nonpolar rubbers in the following way.[28]

During mixing, one of the ethoxy silyl group of the coupling agent reacts with the silanol group of the silica (Scheme 1). This is followed by a condensation reaction between pairs of neighboring silane molecules (Scheme 2). At a higher temperature during vulcanization, a third reaction between the coupling agent and the rubber takes place through added sulfur
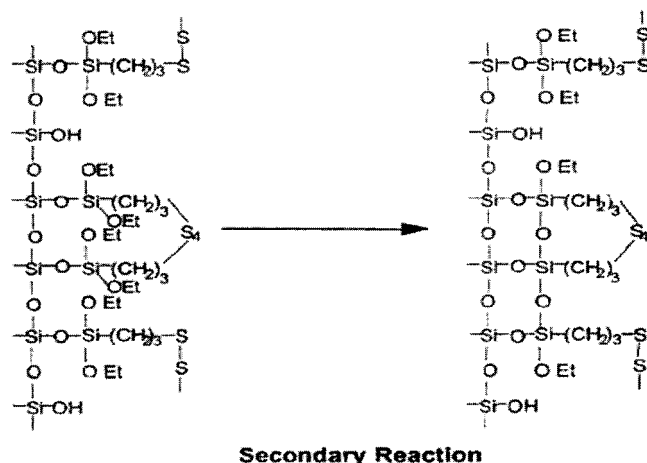
Scheme 2 Mechanism of the silanization secondary reaction.

TABLE I
Fatty Acid Composition of RSO

Fatty acid	Content (%)
Palmitic acid	10.8
Stearic acid	10.0
Oleic acid	23.5
Linoleic acid	38.5
Linolenic acid	16.2
Unidentified	1.0

in the compound or that generated by disproportionation of TESPT. Thus, during mixing, hydrophobation of the silica surface takes place, which reduces the silica–silica network and makes the polar silica more compatible with the nonpolar rubber. The reaction between the silane and rubber that takes place during vulcanization completes the silica–silane–rubber coupling and leads to better polymer–filler interactions, which results in maximum reinforcement without effects on processing safety.[29] Silica-filled compounds prepared with organosilane coupling agents showed improvement in properties such as tensile and tear strength, heat build-up, rolling resistance, and wet skid resistance. The observation that compounds with low rolling resistances, better wet traction, and improved wear resistances was developed through a combination of carbon black and silica along with organosilane coupling agents, generated renewed interest in the use of silica in tire-tread compounds.[30]

Vegetable oils such as RSO are composed of triglycerides of saturated and unsaturated higher fatty acids. The unsaturated acids may be monounsaturated (e.g., oleic), diunsaturated (e.g., linoleic), or triunsaturated (e.g., linolenic) carboxylic acids. They can be easily epoxidized by reaction with performic acid.[31] ERSO is expect to act as a bifunctional coupling agent for silica reinforcement because the epoxy group can react with the silanol group of the silica, and the double bond of the higher fatty acid can be used to link it with the rubber hydrocarbon by reaction with sulfur added in the compound during vulcanization. In this article, we report the results of experiments conducted with this objective.

EXPERIMENTAL

NR used for this study was ISNR 5 grade, obtained from Pilot Block Rubber Factory of the Rubber Board (Kerala, India). RSO, which was prepared by the expulsion process of the dried kernel, was obtained from Virudhunagar (Tamilnadu, India). Tables I and II give the composition and properties of the RSO used in this study. ERSO was prepared from RSO with formic acid and hydrogen peroxide as epoxidizing agents at 58–60°C. The epoxidation level was determined by the

TABLE II
Physical Properties of the RSO Used in This Study

Parameter	Value
Acid value	36
Saponification value	191
Iodine value	132
Hydroxyl value	31
Unsaponifiables (%)	0.80
Refractive index	1.47
Specific gravity (30°C)	0.92
Titre (°C)	28

acidimetric method[16] and was further confirmed by Fourier transform infrared analysis. ERSO with a 5% oxirane oxygen content was used in this study. All of the other ingredients used in this study were rubber chemical grade. The formulations of the prepared compounds are given in Table III.

The rubber compounds were prepared with a 300 × 150-mm laboratory two-roll mixing mill at a friction ratio of 1:1.25. The cure characteristics at 150°C were determined with Monsanto R-100 rheometer (Missouri). Mooney scorch time (t_5) at 120°C was determined with a Mooney viscometer (SMV-202; Shimadzu, Singapore). The compounds were vulcanized with the optimum cure time at 150°C in an electrically heated hydraulic press. Dumbbell-shaped test pieces were punched out from the vulcanized sheet along the direction of grain and tested for tensile properties per ASTM D 412–80, with a Zwick 1474 universal testing machine (Ulm, Germany). Tests such as hardness (ASTM D 2240-97), abrasion loss (DIN 53516-77), compression set (ASTM D 395-98), and resilience (ASTM D 1054-91) were also performed. The aging resistance of the vulcanizate was determined by examination of the tensile properties of the samples before and after ag-

ing at 70°C for 7 days in a hot-air circulating oven. We determined the extent of crosslinking of the vulcanizates through swelling studies by keeping the samples in toluene for 48 h at 25°C per the method reported by Ellis and Welding,[32] which takes into account the correction of the swelling increment with duration of immersion after the equilibrium is attained. The volume fraction of rubber (V_r) in the swollen sample was calculated with the equation

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where T is the weight of test specimen; D is its deswollen weight; F is the weight fraction of the insoluble component; A_0 is the weight of the absorbed solvent, corrected for the swelling increment; and ρ_r and ρ_s are the densities of the rubber and solvent, respectively [ρ_r (NR) = 0.92 g cm^{-3} and ρ_s (toluene) = 0.86 g cm^{-3}]. The value of V_r could be taken as a measure of crosslink density.

A modified preswelling procedure, which was designed to chemically break polymer–filler bonds, was also used to determine the effect of polymer–filler attachment on the effective number of network chains. We swelled the sample for 48 h in uncapped bottles in toluene in an ammoniacal atmosphere (in a dessicator, the bottom of which contained concentrated ammonia). V_r' was calculated with the previous equation, and the difference between V_r and V_r' gave us an account of the rubber–filler attachment.[33]

RESULTS AND DISCUSSION

Cure characteristics

The rheographs of compounds S1–S3 are shown in Figure 1, and the details of the cure parameters are

TABLE III
Formulation of Mixes

Ingredient	S1	S2	S3	S4	S5	S6
NR	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Ultrasil VN3	30	30	30	50	50	50
Si-69 (TESPT)	3	—	—	6	3	3
Naphthenic oil	—	3	—	—	3	—
ERSO	—	—	3	—	—	3
HSL	1	1	1	1	1	1
MBTS	1	1	1	1	1	1
DPG	0.75	0.75	0.75	0.75	0.75	0.75
DEG	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

S1 = 30 VN3 + 3 Si-69; S2 = 30 VN3 + 3 naphthenic oil; S3 = 30 VN3 + 3 ERSO S4 = 50 VN3 + 6 Si-69; S5 = 50 VN3 + 3 naphthenic oil + 3 Si-69; S6 = 50 VN3 + 3 ERSO + 3 Si-69; HSL = 2, 2,4-trimethyl-1,2-dihydroquinoline; MBTS = dibenzthiazyl disulfide; DPG = diphenyl guanidine; DEG = diethylene glycol.
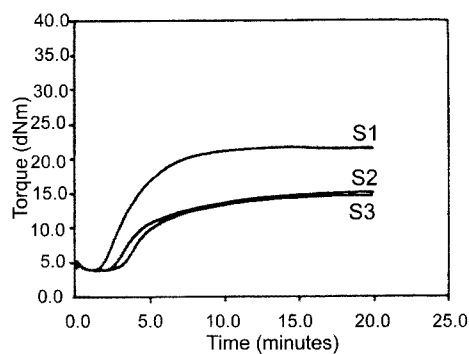
Figure 1 Rheographs of compounds S1, S2, and S3 at 150°C.

given in Table IV. As shown in the rheographs, compound S1, which contained TESPT, had the maximum rheometric torque (M_H) value compared to S2 and S3, which contained naphthenic oil and ERSO, respectively. Compound S1 had a lower cure time and scorch times compared to S2 and S3. Between S2 and S3, the latter showed a slightly lower increase in rheometric torque ($M_H - M_L$, where M_L is the minimum rheometric torque) and a slightly higher scorch time. The reduced cure time and t_5 of compound S1 resulted from the fact that TESPT can also act as an accelerator[34] and a curing agent[25,34] in addition to its role as a coupling agent. This was evident from the fast cure rate (Fig. 1) and higher V_r value (Table V) of compound S1 compared to S2 and S3. The lower $M_H - M_L$ value and higher scorch time of compound S3 compared to S2 may have been due to utilization of part of the sulfur by the unsaturated fatty acids (ca. 76%) present in ERSO. This argument was supported by the lower V_r value of S3 compared to S2 and S1. However, in the case of compounds S4, S5, and S6 (Fig. 2), which contained higher dosages (50 phr) of silica, compound S5 showed higher M_L, M_H, and $M_H - M_L$ values and a reduced cure time. At a higher loading of silica (50 phr), the chance for the formation of a silica–silica network structure through hydrogen bonding of the silanol groups is higher. In the presence of a higher dosage (6 phr) of TESPT, the silanol groups of silica react with ethoxy silyl groups of the TESPT,[28] resulting in the hydrophobation of silica, which prevents the formation of a silica–silica network structure. This leads to better dispersion of silica and a reduction in viscosity.[35,36] The observed lower M_L, M_H, and $M_H - M_L$ values of S4 compared to those of S5 were due to this reason because S5 contained 3 phr naphthenic oil and 3 phr TESPT in place of 6 phr TESPT in S4. Compound S4 showed a lower scorch time and a higher V_r value (Table V), indicating the participation of TESPT in the vulcanization process. Compound S6 contained 3 phr ERSO and 3 phr TESPT, and it showed lower M_L, M_H, and $M_H - M_L$ values compared to S5,

indicating the involvement of ERSO in the hydrophobation of silica through the reaction between the epoxy group and the silanol group of silica.[37,38] Among the three, compound S6 showed the longest scorch and cure times. This was due to the competition by the unsaturated fatty acids for sulfur during vulcanization, as evidenced by a lower V_r value for S6.

Physical and mechanical properties

It has been established that TESPT enhances the reinforcement activity of silica in nonpolar rubbers through the hydrophobation of silica by reaction of the silanol group of silica with the ethoxysilyl group of silane during mixing and also by the formation of a crosslink with the rubber hydrocarbon during vulcanization.[39,40] It has also been proven that depending on the availability of sulfur in the compound, TESPT can act as a sulfur donor and increase the crosslink density of the matrix.[41] The net result of these reactions is a high improvement in physical properties when such compounds are mixed and vulcanized under suitable conditions. The results presented in Table V are in line with these findings.

Among S1–S3 and S4–S6, the compounds that contained TESPT (S1 and S4) showed higher tensile strengths and moduli and lower elongations at break. These two compounds also showed higher V_r values, indicating higher levels of crosslinking. Between the compounds that contained naphthenic oil and ERSO (i.e., S2, S3, S5, and S6), compounds S3 and S6 showed higher tensile strengths, lower moduli, and higher elongations compared to S2 and S5, respectively. The lower moduli and higher elongations may have been the result of better hydrophobation of silica by the epoxy group of the ERSO and the lower crosslinking density of the rubber matrix, respectively, in S3 and S6. The higher tensile strength of compounds S3 and S6 over S2 and S5 might have been the result of the better dispersion of silica achieved through hydrophobation. It is possible that zinc soap formed by the reaction of zinc oxide and the higher fatty acids present in ERSO might also have helped in the achievement of a better dispersion of silica in these

TABLE IV
Cure Characteristics of the Compounds

No.	Rheometric torque (dNm)			Cure time (min) at 150°C	t_5 (min) at 120°C
	M_L	M_H	$M_H - M_L$		
S1	3.6	21.4	17.8	7.0	11.4
S2	3.7	14.7	11.0	9.5	13.2
S3	3.7	14.2	10.5	9.7	13.8
S4	8.7	32.0	23.3	16.0	20.8
S5	11.2	36.2	25.0	15.0	31.6
S6	10.8	30.9	20.1	18.0	39.8

TABLE V
Physical and Mechanical Properties of the Vulcanizates

Parameter	S1	S2	S3	S4	S5	S6
Hardness (Shore A)	57	57	56	73	73	72
Tear strength (kN/m^{-1})	89.8	61.6	71.2	111.9	98.7	102.3
Compression set (%)	33.1	36.0	36.5	36.0	39.0	39.0
Heat build-up (°C)	11	14	15	23	24	24
Dynamic set (%)	.088	2.20	1.72	1.12	2.39	1.65
Rebound resilience (%)	60.0	60.0	60.0	55.0	55.0	56.0
Din abrasion loss (mm^3)	123.6	154.0	153.9	126.9	135.6	136.0
M_{100} (MPa)	2.30	2.00	1.80	4.30	3.49	3.30
M_{300} (MPa)	6.70	4.50	4.30	11.99	8.99	8.80
Tensile strength (MPa)	35.5	27.2	29.5	28.3	26.4	28.0
AA*	24.5	26.5	27.9	25.1	25.1	26.6
Elongation at break (%)	705	713	768	568	619	642
AA*	505	631	719	458	538	546
M_{300}/M_{100}	2.91	2.25	2.39	2.79	2.57	2.67
V_r	0.2229	0.1820	0.1778	0.2854	0.2696	0.2669
$V_r - V_r$	0.0808	0.0590	0.0638	0.1261	0.1144	0.1164

AA* = value after ageing at 70°C for 96 h.

compounds. It has been reported that the ratio of 300% modulus (M_{300}) to 100% modulus (M_{100}) is a good indication of reinforcement by filler in a vulcanizate.[42] The M_{300}/M_{100} values given in Table V clearly show that the TESPT–ERSO combination was helpful for the achievement of better reinforcement by silica than the TESPT–naphthenic oil combination. This was further supported by the higher $V_r - V_r'$ values for S3 and S6 compared to S2 and S5, respectively. However, compounds that contained TESPT alone were superior to those containing ERSO or a combination of ERSO and TESPT. The reason for this could have been the lower level of matrix crosslinking achieved in vulcanizates containing ERSO and could be corrected by extra sulfur addition.

The hardness of the vulcanizates containing ERSO was lower compared to that of the other vulcanizates, which may have been due to lower levels of crosslink density, as indicated by the V_r values. However, the tear strengths of the vulcanizates that contained TESPT–ERSO or a combination of ERSO and TESPT were much better than those of the vulcanizates con-

taining naphthenic oil or naphthenic oil–TESPT. This was, again, the result of the better dispersion of silica achieved in the former compounds through the hydrophobation of silica by TESPT or an ERSO–TESPT combination.

The compression set of the vulcanizate depended on crosslink density and reinforcement levels. Whereas higher level of reinforcement increased the set, a reverse trend was true with an increase in crosslink density. Compounds S1 and S4 showed lower set values in the respective groups, even though the levels of reinforcement in these were higher. This was because of the higher levels of crosslink density of these vulcanizates, as indicated by the higher V_r values, compared with that of the other vulcanizates. The compression set values of S2 and S3 and those of S5 and S6 were comparable. This observation could have been the net result of a combination of effects due to levels of hydrophobation and dispersion of silica and the level of crosslinking in the matrix. As in the case of compression set, a lower heat build-up was recorded for the vulcanizates containing TESPT alone compared to the other vulcanizates. Among S1, S2, and S3, the compound containing the ERSO–TESPT combination showed a higher heat build-up, probably because of a lower level of crosslinking of the matrix. However, at higher silica loading, the difference was less noticeable. The reduction in filler–filler interaction through the hydrophobation of silica by TESPT and the combination of ERSO and TESPT became evident when the dynamic set values of the compounds were compared. The vulcanizates S2 and S5, which contained naphthenic oil and a combination of naphthenic oil and TESPT, respectively, showed much higher dynamic set values compared with the vulcanizates that contained TESPT alone (S1 and S4) or a
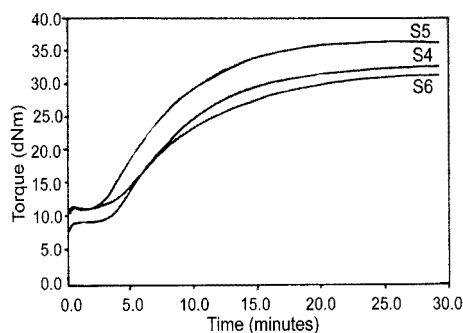

Figure 2 Rheographs of compounds S4, S5, and S6 at 150°C.

combination of ERSO and TESPT (S3 and S6). This observation was not in line with the trend seen in compression set of the vulcanizates, which may have been due to the differences in mode and extent of deformation occurring in these two types of tests. In the dynamic set measurement, the sample was subjected to high-frequency cyclic loading, and thereby, the broken agglomerates/networks of silica did not get enough time to recombine, which resulted in a higher permanent set. Because the possibility of the existence of silica network was higher in compounds containing naphthenic oil compared with those containing TESPT or ERSO, compounds S2 and S5 underwent higher sets under cyclic loading. Because the deformation level in the rebound resilience test was low, no wide difference in the resilience of vulcanizates S1, S2, and S3 and that of S4, S5, and S6 was observed.

The abrasion resistance of the compounds S1 and S4, which contained TESPT, was excellent compared to the other compounds. There was no appreciable difference in the abrasion resistance of vulcanizates that contained naphthenic oil and ERSO. The tensile strength and elongation at break values of the vulcanizates after aging at 70°C for 7 days indicated a lower retention of these properties for vulcanizates S1 and S4, which contained TESPT, compared to the other compounds. This could have been due to a total higher amount of sulfur (added sulfur plus that liberated from TESPT) in these compounds, which could have produced preferentially polysulfidic crosslinks of poor thermal stability. No appreciable difference was noted in the aging resistance of compounds that contained naphthenic oil and ERSO.

CONCLUSIONS

The evaluation of TESPT, naphthenic oil, and ERSO in silica-filled NR compounds showed a very good improvement in physical properties of the vulcanizates containing TESPT and ERSO compared to those containing naphthenic oil. The action of ERSO in the enhancement of properties was expected to be bifunctional and similar to that of TESPT, that is, through the hydrophobation of silica, which increased its degree of dispersion and through the formation of a chemical bond with the rubber, thereby ensuring strong polymer–filler interactions.

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