Bonding Between Precipitated Silica and Epoxidized Natural Rubber in the Presence of Silane Coupling Agent

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ABSTRACT: Results of Monsanto rheometic studies and measurements of physical properties reveal that precipitated silica interacts chemically with epoxidized natural rubber (ENR) during high temperature (180°C) molding and the extent of chemical interaction increases in the presence of silane coupling agent, namely N-3(N-vinyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrogen chloride. Fourier transform infrared spectroscopic studies show that silica is bonded to ENR through formation of Si—O—C bond, whereas in the presence of silane coupling agent, silica is bonded to the coupling agent through Si—O—Si bond, and ENR is bonded to the coupling agent through C—N—C bond formation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 389–398, 1999

INTRODUCTION

Reinforcement of rubber by precipitated silica is adversely affected due to lack of strong polymer-filler bonding.[1–4] Recently it has been reported that the surface energy of filler plays an important role in the reinforcement of rubbers and has a profound influence on the performance of rubber products.[5,6] Functionalized polymers interact strongly with surface silanol groups of precipitated silica.[7,8] Coupling agents are used to reduce the specific component of surface energy (that is, the polar component). Use of silane coupling agents in silica filled rubber compounds causes improvements in modulus, compression set, heat build-up, and abrasion resistance.[9–15] The degree of improvement is generally dependent on the type of elastomers. For example, highly unsaturated rubbers seem to respond more favorably toward reinforcement than those with less unsaturation.[16,17] The silane coupling agents are capable of reacting with both silica filler and rubber. Hertl[15,16] showed that methoxy silanes were reactive with anhydrous silica in the temperature range of 90–220°C. It has also been reported that trifunctional groups on the silane coupling agent have greater reactivity than di- or mono-functional ones.[17] The hydrolysis of triethoxy silane depends on the silanol/water ratio and becomes maximum when this ratio is approximately unity.[18] It has also been reported that addition of silane coupling agents to silica and carbon black filled rubbers increase the crosslink density[19] and the epoxy groups react with amines though the rate of the reaction is slow.[20] McManus et al.[20] showed that salt of amino silane coupling agent can easily open up epoxy ring forming bonds.

The present article reports the results of studies on the role of N-3(N-vinyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrogen chloride in the bonding between precipitated silica and epoxidized natural rubber (ENR). Studies include bound rubber determination, Monsanto rheometry, thermogravimetry, solvent swelling studies, stress-strain properties, and infrared spectroscopy. For comparison, a sulfur vulcaniz-

Table I Details of Materials Used

Material	Characteristic	Source
Epoxidized natural rubber abbreviated as ENR-50	50 mol % of the double bond are epoxidized; $\bar{M}_w/\bar{M}_n$, 4.7×10^5 Mooney Viscosity, ML (1 + 4) @ 120°C, 42	Kumpulan Guthrie, Berhad, Malaysia
Precipitated silica, (trade name, Hi-Sil223)	Particle size, 22 μm; N_2SA,[a] 150 m²/g	PPG Industries Ltd., USA
Silane Coupling Agent, N-3(-N-vinyl benzyl amino) ethyl-γ-amino propyl trimethoxy silane monohydrogen chloride (trade name Z-6032)	pH, 2.0	Dow Corning, USA
Zinc oxide	Rubber grade	Locally available
Stearic acid	Rubber grade	Locally available
Sulfur	Rubber grade	Locally available
Antioxidant	Rubber grade	ICI (India) Ltd., Rishra, W.B., India
Cyclohexyl benzothiazole sulfenamide abbreviated as CBS	Rubber grade	ICI (India) Ltd., Rishra, W.B., India

[a] N_2SA is the nitrogen surface area.

ing system for ENR has been included in the studies.

EXPERIMENTAL

The details of the materials used are given in Table I and the formulations of different mixes are given in Table II. Before mixing, silica was dried in an oven at 120°C for 6 h. The mixing was carried out in a Brabender Plasticorder (PLE-330; Duisburg, Germany) at 25°C for 8 min at a rotor speed of 60 rpm. Mixing was done in two stages: in the first stage, silica was mixed with rubber for 4 min, then coupling agent was added in drops and mixing was continued for a further 4 min. The mixture was then taken out from the Brabender Plasticorder and sheeted out in a two-roll mill. Next, this mixture was put again in the Brabender Plasticorder and mixed for an additional 2 min and then sheeted out in the two-roll mixing mill. The maximum temperature rise during mixing in the Brabender Plasticorder was 60°C.

For the bound rubber measurement, the mixes were conditioned at room temperature (25°C) for 7 days, and then cut into small pieces. Approximately 0.5 gm accurately weighted of each sample in a constant weight wire net case (150 mesh) was immersed in 300 ml of chloroform for 72 h. The

Table II Formulation of Rubber-Filler Mixes

Materials	Mix Designation				
	EZ_5	EH	EHZ_2	EHZ_5	EHZ_{10}
ENR-50	100	100	100	100	100
Hi-Sil 223	0	60	60	60	60
Z-6032[a]	5	0	2	5	10

[a] Silane coupling agent.

samples were then taken out and vacuum dried to constant weight at 60°C. The bound rubber content was expressed as the weight percent of the insolubilized rubber on the silica surface.

The cure characteristics of the ENR-silica mixes were studied in a Monsanto rheometer (MDR-2000; Akron, OH) at 180°C at 0.5° arc of oscillation. The molding of the rubber-filler mixes were carried out at 180°C for 1 h under a pressure of 10 MPa in an electrically heated hydraulic press. The samples were then cooled to room temperature (25°C) under pressure by circulating cold water through the platens of the press. Compounds containing curing agents were molded at 150°C to their optimum cure times (t_{90}) as recorded from MDR-2000 at 150°C.

Thermogravimetric analyses (TGA) of the samples were carried out in a Du Pont Thermal Analyzer (9000 series; Wilmington, DE) in nitrogen environment at a flow rate 120 ml/min, in the temperature range 50 to 1000°C. The activation energy of thermal decomposition of polymer was determined from the TG and its derivative (DTG) thermograms by the method of Freemann and Carroll.[21]

Swelling of the molded samples was done in chloroform at 25°C for 72 h and then the weight of the samples was taken in the swollen condition. The results of the swelling studies were expressed as percent volume swell.

Scanning electron microscopic studies of the samples were carried out on cryo-fractured samples after gold coating in a Hitachi Microscope (model S-415A; Tokyo, Japan) at a magnification of 250×.

The physical properties were measured in a Zwick Universal Testing Machine (model 1445; Ulm, Germany). Stress-strain properties of the molded samples were determined according to the ASTM D-412 (1986), method-A at a crosshead speed of 500 mm/min. Tear strength of the samples was measured using a 90° nick cut crescent samples following the method ASTM D624(1986). The tension set at 100% elongation was measured using the tensile specimen, following ASTM D-412(1986) with a cross head speed of 500 mm/min. The samples were stretched for 10 min and then relaxed for 10 min.

Diffuse reflectance infrared fourier transformed spectroscopy (DRIFTS) of silica sample was carried out by using a KBr dispersion in a Shimadzu DRS-arrangement (model 8101; Tokyo, Japan). The spectrum was taken at a resolution of 2.0 cm^{-1} and 400 scans were signal averaged. The

Table III   Formulation of the Mixes Containing Sulfur Curing System

Materials	Mix Designation	
	EHS[a]	EHZ$_5$S[a]
ENR-50	100	100
Hi-Sil223	60	60
Zinc oxide	5	5
Stearic acid	2	2
Z-6032	0	5
Acenox-TQ[b]	1	1
CBS[c]	1.5	1.5
Sulfur	2.5	2.5

[a] Optimum cure time (t_{90}) at 150°C (min), for mix EHS, 22; mix EHZ$_5$S, 19.
[b] Antioxidant, amine based.
[c] Accelerator.

ATR-FTIR spectra of the rubber samples were carried out using a KRS-5 crystal at an angle of 45°, in a Shimadzu (Model 8101) spectrophotometer. The resolution was kept at 2.0 cm^{-1} and 40 scans were signal averaged for each sample. Thin films (thickness ~0.2 mm) for ATR-FTIR spectra were prepared for the mixes EH, EHZ$_5$ by molding the samples at a pressure of 10 MPa under Teflon sheets at 180°C for different times (that is, 2 min and 60 min).

RESULTS AND DISCUSSION

Bound Rubber

The results of bound rubber determination are shown in Table IV. Bound rubber formation is nil in the case of neat ENR and mix EZ$_5$. However, an ENR-silica mix forms a definite amount of bound rubber. It is also evident that incorporation of coupling agent increases the bound rubber. The coupling agent is capable of forming ion-molecule interaction with the oxygen atom of epoxy group of ENR through its —NH$_2^+$-functionality as well as it can interact with O—H groups of silica through its —Si(OCH$_3$)$_3$ functionality, by hydrogen bonding as discussed later (Fig. 9) leading to enhancement of bound rubber formation.[22] Expectedly, bound rubber formation does not change in the sulfur curing systems.

Monsanto Rheometric Studies

The results of rheometric studies are shown in Figure 1 and Table IV. Neat ENR does not show

Figure 1 Rheometric studies of different mixes at 180°C: (— ~ —) ENR; (- - -) EZ_5; (- - - - -) EH; (——) EHZ_2; (— · · —) EHZ_5; (— · —) EHZ_{10}.

any increase in torque, but small torque rise in the presence of silane coupling agent (mix EZ_5) indicates that ENR gets crosslinked lightly by the coupling agent. Moreover, in the presence of silica the torque rise increases as compared with mix EZ_5. Again, the torque rise, as measured by Δt (that is, the difference between the maximum torque and the minimum torque), increases when both silica and coupling agent are present in the system during high temperature (180°C) rheometric studies. It is also evident that the minimum torque (M_L) increases with increase in the coupling agent loading and passes through a maximum at 5 phr loading of the coupling agent. It has been reported earlier that M_L corresponds to filler-filler interagglomeration.[23] Since incorporation of the silane coupling agent into the silica filled rubber reduces the filler-filler networking factor, high M_L values in the present case is believed to be due to the strong polymer-filler interaction through ion molecule interaction and hydrogen bonding (Fig. 9), as discussed later. The higher M_L values are also observed in the case of polychloroprene rubber which is specially reactive toward mercaptosilane.[24] The Δt value attained maximum at 5 phr loading of the coupling agent and reaches plateau at 10 phr of coupling agent loading. While the M_H value is greater in the case of sulfur curing systems due to higher extent of crosslinking, incorporation of the coupling agent has little effect on the M_H and M_L

values, indicating that the coupling agent takes no part in crosslinking at 150°C in the case of the sulfur curing system. Although addition of silane coupling agent in the ENR-silica system at 180°C causes increase in Δt, it remains unchanged in the case of sulfur curing system at 150°C.

Thermogravimetric Analysis

Figure 2 shows the effect of silane coupling agent on the thermogravimetric plots of the rubber-filler mixes molded at 180°C. It is evident that addition of the silane coupling agent increases the thermal stability. The higher thermal stability signifies that incorporation of the coupling agent causes higher extent of chemical bonding between silica and ENR. It is also evident that the thermal degradation occurs in two steps, and the corresponding activation energy values are reported in

Figure 2 Thermogravimetric analysis of rubber-filler mixes: (a) TG thermograms; (——) ENR, (- - -) EH, (- · -) EHZ_5, (— · —) EHZ_{10}; (b) derivative plots (DTG) designation same as in (a).

Table IV   Results of Bound Rubber Determination and Monsanto Rheometric Studies

Parameter	Mix Designation					
	ENR	EZ$_5$	EH (EHS)[a]	EHZ$_2$	EHZ$_5$ (EHZ$_5$S)[b]	EHZ$_{10}$
Bound rubber (%)	0.0	0.0	95 (96)	106	122 (125)	136
M_H (dNm)[c]	0.25	0.6	10.8 (27.1)	16.0	20.8 (29.0)	20.1
M_L (dNm)[d]	0.17	0.4	5.3 (5.2)	7.5	8.7 (5.6)	8.1
M_H–M_L	0.08	0.2	5.5 (21.9)	8.5	12.2 (23.40)	11.9

[a] Values in the parentheses are the results of the corresponding sulfur cure system, namely mix EHS.
[b] Values in the parentheses are the results of the corresponding sulfur cure system, namely mix EHZ$_5$S.
[c] Maximum rheometric torque.
[d] Minimum rheometric torque.

Table V. Expectedly, addition of coupling agent increases the activation energy of thermal degradation from 23 kJ/mol to 31 kJ/mol in the first step of degradation. It is also apparent that at 10 phr loading of coupling agent, the additional peak in the temperature range of 350 to 375°C indicates presence of unreacted coupling agent which evaporates at a lower temperature before the occurrence of two-step thermal degradation. In the case of neat ENR and EH, initial decomposition peak is very sharp (DTG curve, Fig. 2), whereas in the case of EHZ$_5$, the peak is broad and shifted to the higher temperature, indicating that the coupling agent forms more stable bonds.

Scanning Electron Microscopy (SEM)

Figure 3 shows the SEM photomicrographs of the brittle fracture surface of EH, EHZ$_5$. It is evident that dispersion is poor in the case of EH, due to the presence of large agglomerates (average size, 120 μm) arising out of filler-filler networking. Addition of silane coupling agent improves the filler dispersion by lowering the agglomerate size (average size, 30 μm), due to formation of rubber-filler networking at the expense of filler-filler networking. Similar results have been reported by Bandyopadhyay et al.[9] in the case of silica-filled

carboxylated nitrile rubber in the presence of 3-amino propyl triethoxy silane.

Physical Properties

The physical properties are summarized in Table VI. It is apparent that both tensile strength and

(a)

(b)

Figure 3   SEM photomicrographs of cryo-fractured silic-filled ENR: (a) EH; (b) EHZ$_5$.

Table V   Activation Energy of Thermal Degradation

Mix Designation	Activation Energy, (E_a) kJ/mol	
	Step I	Step II
EH	23	41
EHZ$_5$	31	45

Table VI Physical Properties of Rubber-Filler Mixtures Molded at 180°C for 60 Min

Properties	Mix Designation						
	EZ_5	EH (EHS)[a]		EHZ_2	EHZ_5 (EHZ_5S)[b]		EHZ_{10}
Tensile strength (MPa)	1.8	8.0 (16.0)		12.5	15.2 (18.1)		14.0
Modulus at 100% elongation (MPa)	0.9	5.2 (8.2)		6.5	7.7 (8.6)		6.2
Elongation at break (%)	265	250	(220)	240	250	(240)	290
Tear strength (kN/m)	c	29	(46)	30	38	(49)	35
Volume swell (%)	1140	580	(430)	500	420	(410)	410
Tension set (%)	28	20	(16)	15	12	(12)	13

[a] Values in the parentheses are the results of the corresponding sulfur curing system, namely mix EHS, molded for 22 min at 150°C (Table III).

[b] Values in the parentheses are the results of the corresponding sulfur curing system, namely mix EHZ_5S, molded for 19 min at 150°C (Table III).

[c] Cannot be measured; the matrix is weak.

modulus at 100% elongation increase in the presence of the coupling agent. Since there is no curing agent present in the rubber-filler mixes, the increase in tensile strength and modulus is due to the formation of coupling bonds, which is also responsible for the increase in the tear strength and decrease in the percent volume swell and tension set. It is evident that the physical properties of the sulfur curing system molded at 150°C are greater than the rubber-filler mixes molded at 180°C, due to the higher degree of crosslinking in the former. Although the effect of the coupling agent on the physical properties of the molded rubber-filler mixes is remarkable due to participation of the coupling agent in bonding between rubber and the filler, the coupling agent has little effect on the properties of the sulfur curing system.

Infrared Spectroscopic Studies

Figure 4 shows the results of FTIR spectroscopic studies on silica and silane coupling agent and ENR. The spectrum of silica is characterized by the strong absorbance at 1096 cm^{-1} which is due to Si—O—Si asymmetric stretching. The other characteristic peaks at 3760, 960, and 798 cm^{-1} are due to —OH stretching of Si—OH, Si—O stretching of Si—OH, and Si—OH deformation,[25] while the peak at 470 cm^{-1} is due to Si—O—Si symmetric stretching. IR spectra of the coupling agent shows strong absorbance at 1085 cm^{-1} due to Si—O—CH$_3$ stretching vibration.[26] The absorption band at 1627 cm^{-1} is characteristic of —NH$_2^+$-rocking vibration.[25] The peak at 1602 cm^{-1} is due to C=C stretching of vinyl benzene of the coupling agent. In addition, the bands at 715

and 450 cm^{-1} are typical of aliphatic amine and C—N—C bending of secondary amines.[26] The most characteristic peak of ENR at 878 and 840 cm^{-1} is due to asymmetric and symmetric vibration of the epoxy ring.[26] The band at 1650 cm^{-1} is assigned to C=C stretching. The moderate absorption peaks at 1060 and 1114 cm^{-1} are due to asymmetric and symmetric stretching of the C—O bond.[25]

The ATR-FTIR spectra of mix EZ_5 are presented in Figure 5. It is evident that in the case of neat ENR epoxy ring vibration occurs at 878 cm^{-1} which is shifted to 874 cm^{-1} in the presence of silane coupling agent, which is due to ion-molecule interaction between epoxy groups of ENR and —NH$_2^+$-groups of coupling agent (Fig. 9). It has also been observed that with increasing molding time, the intensity of the peaks at 874 cm^{-1}, which is due to the epoxy ring vibration, and at 3350 cm^{-1} and 715 cm^{-1}, which are due to stretching and bending vibrations of amines[25] decreases. The difference spectrum shows negative absorbance at these positions. In neat coupling agent, —NH$_2^+$- and —NH-stretching vibration occurs at 3350 and 3450 cm^{-1}, but in EZ_5 the two peaks merge and a broad negative peak appears at 3360 cm^{-1}, due to the interaction between the amine groups and the epoxy groups. The positive absorbances at 485 and 690 cm^{-1} are due to the formation of tertiary amine (deformation) and C—Cl bond deformation, respectively. The negative absorbances at 1650 and 1602 cm^{-1} are due to the reaction of both C=C bond of ENR and vinyl benzene groups of the coupling agent, with the HCl liberated from the coupling agent. This

also evident that on molding, the intensity of the peaks at 876 and 3700 cm^{-1} decreases while a new peak at 3650 cm^{-1} arises. The difference spectra (that is, the spectrum of the specimen molded for 60 min minus spectrum of the speci-

Figure 4 (a) DRIFTS of silica; (b) ATR-FTIR spectra of ENR; (c) transmission FTIR spectra of silane coupling agent.

result is also in conformity with the observed small increase in the rheometric torque, as reported earlier.

Figure 6 shows ATR-FTIR spectra of mix EH molded for 2 min and 60 min. In neat silica, Si—OH stretching occurs at 3720 cm^{-1} which is shifted to 3700 cm^{-1} (broad), indicating the presence of hydrogen bonding between O—H of silica and epoxy groups of ENR (Fig. 8). It is observed that in mix EH, the Si—O—Si stretching peak is shifted toward lower frequency (1078 cm^{-1}) by 18 cm^{-1} and becomes more broadened. This spectral feature indicates that there is strong interaction between silica and ENR. The peaks at 876, 1647, and 1377 cm^{-1} are assigned to the epoxy groups, C=C and C—CH$_3$ stretching, respectively. It is

Figure 5 ATR-FTIR spectra of mix EZ$_5$: (a) sample molded for 60 min; (b) sample molded for 2 min; (c) the difference spectrum, (b-a).

Figure 6 ATR-FTIR spectra of mix EH: (a) sample molded for 60 min; (b) sample molded for 2 min; (c) the difference spectrum, (a-b).

men molded for 2 min) shows negative absorbance at 876 and 3700 cm^{-1} which can be ascribed to the chemical reaction between epoxy groups of ENR and Si—OH groups of silica. The positive absorbance at 3650 and 1062 cm^{-1} results due to the formation of C—OH (tertiary) and Si—O—C bonds, respectively. The peak (positive) at 1280 cm^{-1} (in the plane —O—H deformation of tertiary alcohol) confirms the formation of tertiary alcohol during molding.

Figure 7 shows ATR-FTIR spectra of the mix EHZ$_5$ at different molding times. From the difference spectrum (that is, the spectra of 60 min molded sample minus the spectra of 2 min molded sample) it is evident that the peaks at 876 and

3700 cm^{-1} show negative absorbance. The results signify that a portion of the epoxy groups react during molding [Fig. 7(c)]. The new peak at 485 cm^{-1} is the characteristic of C—N—C (tertiary amine) deformation, whereas the positive absorbance at 1078, 1011, and 796 cm^{-1} are the characteristics of Si—O—Si (asymmetric stretching), —Si(OCH$_3$)$_2$ deformation, respectively.[25] These results indicate that the epoxy groups of ENR react with the amine functionality to form C—N bonds as well as trimethoxy silane functionality reacts with silica to form Si—O—Si bonds. The negative peak at 1647 cm^{-1} confirms that C=C bond reacts with HCl, liberated from the coupling agent during high temperature molding and saturates double bonds. The positive absorbance at 2963 cm^{-1} (C—H stretching of saturated hydro-

Figure 7 ATR-FTIR spectra of mix EHZ$_5$: (a) sample molded for 60 min; (b) sample molded for 2 min; (c) the difference spectrum, (a-b).

Figure 8 The probable mechanism of bonding between ENR and precipitated silica.

carbon) also confirms the occurrence of the above reaction while the positive absorbance at 704 cm^{-1} confirms the formation of C—Cl bonds during high temperature molding, the positive absorbance at 1260 cm^{-1} indicates the formation of secondary alcohols.

The probable mechanism of rubber-filler bonding in the absence of coupling agent is shown in Figure 8. In the presence of the coupling agent coupling bonds are formed through the reactive functional groups (amine and methoxy), in addition to silyl ether linkage as shown in Figure 9.

CONCLUSIONS

Silanol groups on silica interact strongly with ENR through formation of Si—O—C bond, and

Figure 9 The probable mechanism of bonding between ENR and precipitated silica in the presence of the silane coupling agent.

the extent of the chemical interaction depends on the molding time. Addition of the silane coupling agent namely, N-3(N-vinyl benzyl amino) ethyl-γ-aminopropyl trimethoxy silane monohydrogen chloride enhances the chemical interaction through formation of coupling bonds. It is believed that HCl (present as salt in the coupling agent) is liberated during molding and opens up the epoxy groups of ENR and thus facilitates the reaction between the amino groups of the coupling agent and the epoxy groups of ENR. Formation of coupling bonds causes increase in the mechanical properties of the molded rubber-filler mixes, even in the absence of curing agents.

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