Bonding between Epoxidized Natural Rubber and Clay in Presence of Silane Coupling Agent

A. K. MANNA,¹ D. K. TRIPATHY,¹ P. P. DE,¹ S. K. DE,¹ M. K. CHATTERJEE,² D. G. PEIFFER³

¹ Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

² I. C. I. India Ltd., Rishra, Hooghly 712 248, India

³ Exxon Research and Engineering Company, Route 22 East, Clinton Township, Annandale, New Jersey 08801, USA

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ABSTRACT: Based on the results of bound-rubber determination, Monsanto rheometric studies, solvent swelling, measurement of physical properties, and infrared spectroscopic studies, it is revealed that epoxidized natural rubber (ENR) and hard clay interact chemically to form Si–O–C bond during high-temperature (180°C) molding. It is also observed that addition of the silane coupling agent N-3-(N-vinyl benzyl amino)-ethyl- γ -amino propyl trimethoxy silane monohydrogen chloride enhances the extent of the chemical interaction with the formation of coupling bonds of Si–O–Si type between clay and the coupling agent and C–N bonds between ENR and the coupling agent. © 19991999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1895–1903, 1999

Key words: epoxidized natural rubber; clay; silane coupling agent; chemical bonding

INTRODUCTION

Hard clay, also known as Kaolin, containing Si-O and Si-OH groups on its surface, are known to act as low reinforcing fillers in rubbers.^{1–3} The reinforcing ability of clay is poor in comparison to precipitated silica and carbon blacks, although there has been a report on the use of clays in tire compounds.⁴ It has been reported that incorporation of the silane coupling agent N-3-(N-vinyl benzyl amino)ethyl-γ-amino propyl trimethoxy silane monohydrogen chloride causes enhancement in the degree of interaction between rubbers like epoxidised natural rubber and fillers like precipitated silica and carbon blacks.^{5,6} It has also been reported that the reinforcing ability of clay increases on surface modification by silane coupling agents.7-12

Correspondence to: S. K. De. Journal of Applied Polymer Science, Vol. 72, 1895–1903 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/141895-09 The present paper reports the results of studies on the effect of silane coupling agent N-3-(N-vinyl benzyl amino)ethyl- γ -amino propyl trimethoxy silane monohydrogen chloride (Trade name, Z-6032) on the interaction between epoxidized natural rubber (ENR) and clay.

EXPERIMENTAL

Details of the materials used are given in Table I. Formulations of the mixes are given in Tables II and III. Mixing of clay with rubber was done in a Brabender Plasticorder (model PLE 330) fitted with a cam type of rotor for 4 min followed by dropwise addition of the coupling agent and mixing was continued for another 4 min. The rubber compound was then sheeted out in a laboratory size two-roll mixing mill at 25°C.

For the determination of bound rubber, the compounds were conditioned at 25°C for 7 days and then cut into small pieces and immersed in chloroform at 25°C for 72 h. The samples were

Materials	Characteristics	Sources	
Epoxidised Natural Rubber (ENR)	50 mole % of the double bonds are epoxidised; M_w , 4.7 × 10 ⁵ ; M_w/M_n , 3.6; M_L (1 + 4) at 120°C, 42	Kumpulan Guthrie Berhad, Malaysia	
Hard clay	average particle size, 4 μ m	locally available	
Silane coupling agent	pH, 2.0	Dow Corning, USA	
N-3-(N-vinylbezyl amino) ethyl-γ- amino propyl tri-methoxy silane mono-hydrogen chloride (Trade name Z-6032)			
Zinc oxide	Rubber grade	locally available	
Stearic acid	Rubber grade	locally available	
Sulfur	Rubber grade	locally available	
N-Cyclohexyl benzothiazole sulfinamide (CBS)	Rubber grade	ICI India Ltd., Rishra	
Antioxident acenox TQ	Rubber grade	ICI India Ltd., Rishra	

Table I	Details	of Materials	Used
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taken out and vacuum dried to constant weight. The bound-rubber content in the mix was expressed as the percent of insolubilized rubber on the clay surface.

The rheometric studies of the clay-rubber mixes (in the absence of curing agents) were carried out at 180°C in a Monsanto rheometer (MDR-2000) with an arc of oscillation 0.5°. The mixes were then molded at 180°C for 1 h in a laboratory hydraulic press. The mixes containing sulfur and other curatives were molded at 150°C to their optimum cure times as determined by the Monsanto rheometer (Table III).

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

Swelling of the molded samples was carried out by immersing in chloroform at 25°C for 72 h in order to achieve the equilibrium swelling condition. The weight of the samples was taken under swollen condition and the results were expressed

Table IIFormulation of Mixes without CuringAgents

		Mix Designation				
Materials	EZ_5	EC_{100}	$\mathrm{EC}_{100}\mathrm{Z}_{5}$	$EC_{100}Z_{10}$		
ENR	100	100	100	100		
Clay	0	100	100	100		
Coupling agent (Z-6032)	5	0	5	10		

in terms of the swelling index, which is defined as grams of solvent absorbed per gram of rubber vulcanizate.

Thermogravimetric analysis (TGA) of the samples was carried out in DuPont thermal analyzer (model-9000, Wilmington, U.S.A.) in a nitrogen atmosphere at a nitrogen flow rate of 120 mL/min. The temperature range was 50°C to 1000°C and the rate of heating was 20°C/min.

The stress-strain properties and the tension set at 100% elongation were measured as per ASTM D-412-87 in an Instron Universal Testing machine (model 1195, High Wycombe, U.K.). The tear strength was also measured in the same machine according to ASTM-D-624-87.

The presence of functional groups on clay surface was studied by taking the diffused reflec-

Table IIIFormulation of Mixes with CuringAgents

	Mix Designation			
Materials	$EC_{100}S$	$\mathrm{EC_{100}Z_5S}$		
ENR	100	100		
Zinc oxide	5	5		
Stearic acid	2	2		
Clay	100	100		
Coupling agent (Z-6032)	0	5		
Acinox TQ	1.0	1.0		
Sulfur	2.5	2.5		
CBS	1.0	1.0		
Optimum cure time (t_{90}) min at 150°C	38	35		

Parameter	Mix Designation				
	ENR	EZ_5	$\frac{EC_{100}}{(EC_{100}S)^{a}}$	$\frac{EC_{100}Z_{5}}{(EC_{100}Z_{5}S)^{b}}$	$EC_{100}Z_{10}$
Bound rubber (%)	0	0	0 (0)	21 (22)	33
M_{I} (dN.m)	0.17	0.6	0.8 (0.6)	1.1 (0.8)	1.5
$M_{\rm H}^{\rm L}$ (dN.m)	0.25	1.2	1.6 (11.0)	2.5(11.8)	3.4
Δt (dN.m)	0.08	0.6	0.8 (10.4)	1.4 (11.0)	1.9

Table IV Results of Bound-Rubber Determination and Monsanto Rheometric Studies

 $^{\rm a}$ Values in the parentheses are the results of the corresponding sulfur curing system, namely ${\rm EC}_{100}S.$

^b Values in the parentheses are the results of the corresponding sulfur curing system, namely $EC_{100}Z_5S$.

tance infrared Fourier transform spectroscopy (DRIFTS) of powder sample in KBr dispersion using a Shimadzu Fourier Transform Infrared (FTIR) spectrophotometer (model 8101) at a resolution of 4 cm⁻¹. One hundred scans were signal averaged. ATR-FTIR spectra of the samples (molded at 120°C for 2 min and at 180°C for 1 h) were taken in a Shimadzu FTIR spectrophotometer. The spectra were taken using KRS-5 prism placed at an angle of incident of 45° at a resolution of 4 cm⁻¹. One hundred scans were signal averaged for each sample.

RESULTS AND DISCUSSION

Bound Rubber

The results of bound-rubber formation of the mixes are reported in Table IV. It is evident that bound-rubber formation is nil for mixes EC_{100} and EZ_5 . However, incorporation of the silane coupling agent results in the formation of bound rubber in the rubber-filler mixes, and the bound-rubber content increases with the increase in the loading of the silane coupling agent. Expectedly, the presence of the curing agents does not affect the formation of the bound rubber.

Monsanto Rheometric Studies

The Monsanto rheograms of the mixes are shown in Figure 1. The values of maximum torque (M_H) , minimum torque (M_L) and the difference in torque Δt (i.e., $M_H - M_L$) for the mixes without curing agents are shown in Table IV. Although neat ENR does not show any increase in rheometric torque, mix EZ₅ shows a small increase in the torque, indicating low extent of crosslinking of ENR in the presence of the coupling agent. However, addition of clay causes manifold increase in the rheometric torque due to greater extent of crosslinking in the ENR-clay-coupling agent system. It is also observed that the minimum torque is slightly greater in the presence of the coupling agent and it increases with the increase in the loading of the silane coupling agent. The higher minimum torque indicates that the coupling agent promotes hydrogen bonding with —OH groups on the filler surface and ion-molecule interactions,¹³ as discussed later. Δt May be taken as a measure of crosslinking in the rubber phase through rubber-filler chemical bonding,^{14,15} which increases upon increase in the loading of the coupling agent.

Whereas the M_H value is greater in the case of the sulfur-curing system than in the clay-filled





(a)



Figure 2 Scanning electron photomicrographs: (a) $EC_{100}\,(b)\,EC_{100}Z_5.$

system due to higher extent of crosslinking, incorporation of the coupling agent has much less effect on $M_{\rm H}$, which indicates that the coupling agent takes no part in crosslinking at 150°C in the sulfur curing system.

Scanning Electron Microscopy (SEM)

Figure 2 shows the scanning electron photomicrographs of mixes EC_{100} and $EC_{100}Z_5$. It is evident that dispersion of the filler is poor in the case of EC_{100} due to the presence of large agglomerates (average size, 90 μ m) arising out of filler–filler networking. Addition of silane coupling agent improves filler dispersion by lowering the agglomerate size (average size, 20 μ m) due to formation of rubber-filler network at the expense of filler–filler networking.

Solvent Swelling Studies

The results of swelling studies are shown in Table V. It is evident that the swelling index decreases in the presence of the coupling agent. Because the

extent of crossinking is inversely proportional to the swelling index, it can be concluded that addition of the silane coupling agent results in polymer-filler chemical bonding. In the presence of curing agents, addition of the coupling agent has marginal effect on the swelling index. Hence, it is evident that the extent of rubber-filler bonding is greater in the presence of the coupling agent when it is molded at higher temperature (180°C) without curatives, compared to the sulfur curing system molded at 150°C.

Thermogravimetric Analysis

Figure 3 shows the thermogravimetric curves of rubber-filler mixes. It is evident that the mix EC_{100} shows multistep degradation in the temperature range of 350°C to 410°C. In the presence of the coupling agent, degradation starts at 340°C and ends at a higher temperature depending on the concentrations of the coupling agent. It is observed that at 5 and 10 phr loading of the coupling agent, an initial weight loss occurs at 340°C to 370°C, which is due to the degradation of coupling agent, followed by a large weight loss, which is due to the degradation of polymer. It is also evident that in the presence of the coupling agent, 50% degradation of the polymer (T_{50}) occurs at a higher temperature. From the DTG curve (Fig. 3), it is observed that there is a peak in the temperature range of 450°C to 550°C, which may be due to the breakdown of the bonds formed between the coupling agent and clay during molding. The higher thermal stability in the presence of the coupling agent is attributed to the formation of coupling bonds.

Stress-Strain Properties

The stress-strain properties are summarized in Table V. It is observed that in the case of rubberfiller mixes, incorporation of the coupling agent causes enhancement in modulus, tensile strength, elongation at break, and tear strength. The physical properties of the sulfur curing systems are higher than that of the rubber-filler mixes due to greater extent of crosslinking. However, the effect of the coupling agent in the sulfur curing system is less pronounced because the possibility of formation of coupling bonds is less at lower molding temperature (150°C) and time. The marginal enhancement of the physical properties in the sulfur curing system in the presence of the coupling agent may be due to better filler dispersion.

Properties	Mix Designation			
	EZ_5	$\frac{EC_{100}}{(EC_{100}S)^{a}}$	$\frac{EC_{100}Z_5}{(EC_{100}Z_5S)^{b}}$	$EC_{100}Z_{10}$
Tensile strength (MPa)	1.8	2.5(13.5)	4.8 (15.2)	6.7
Modulus at 100% elongation (MPa)	0.5	1.7(3.8)	1.8(3.9)	2.5
Modulus at 200% elongation (MPa)	0.9	1.9 (5.2)	3.5(5.5)	4.7
Modulus at 300% elongation (MPa)	1.2	c (6.7)	4.6 (7.0)	6.3
Elongation at break (%)	360	260 (580)	310 (610)	330
Tear strength (kN/m)	с	12(33)	19 (36)	24
Swelling index	11.4	10.8 (7.1)	8.5 (6.8)	8.0

Table V Physical Properties of the ENR-Clay Mixes Molded at 180°C for 1 h

^a Values in the parentheses are the results of the corresponding sulfur curing system EC₁₀₀S molded at 150°C for 38 min.

^b Values in the parentheses are the results of the corresponding sulfur curing system $EC_{100}^{\circ}Z_5S$ molded at 150°C for 35 min. ^c Results can not be obtained due to weak matrix.

Infrared Spectroscopy

Figure 4 shows the DRIFTS of clay, ATR-FTIR of ENR, and transmission FTIR spectra of the coupling agent. Clay is characterized by broad and strong absorbance at 1150 cm^{-1} to 900 cm^{-1} . The peak at 3696 cm^{-1} is due to the O—H stretching of Si—OH. The other peaks at 1568 cm^{-1} and 1348 cm⁻¹ are characteristic of O—H deformation of H-O-H and Si-OH. The strong absorbances at 1113, 1022, 1003, and 914 cm^{-1} are assigned to Si-O-Si and Al-O-Si asymmetric and symmetric stretching.¹⁶ The weak band at 797 cm⁻¹ is due to Si-O-Si deformation.¹⁶ Infrared spectra of the coupling agent shows strong absorbance at 1085 cm⁻¹ due to Si-O-CH₃ stretching vibration.¹⁷ The absorption band at 1627 cm^{-1} is the characteristic of $-NH_2^+$ rocking vibration.^{17,18} The peak at 1602 cm⁻¹ is due to C=C stretching of vinvl benzene of the coupling agent. In addition, the bands at 715 cm^{-1} and 450 cm^{-1} are typical of an aliphatic amine and C-N-C bending of secondary amine. The most characteristic bands of ENR at 878 $\rm cm^{-1}$ and 840 $\rm cm^{-1}$ are due to the asymmetric and symmetric vibration of epoxy ring.¹⁷ The band at 1650 cm⁻¹ is assigned to C=C stretching. The moderate absorption peaks at 1060 cm^{-1} and 1114 cm^{-1} are due to symmetric and asymmetric stretching of C—O.¹⁷

The ATR-FTIR spectra of mix EZ_5 are presented in Figure 5. It has been observed that with increasing molding time the intensity of the peaks at 874 cm⁻¹, which is due to the epoxy ring vibration, as well as at 3350 cm⁻¹ and 715 cm⁻¹, which are due to stretching and bending vibration of amines,¹⁷ decreases. The difference spectrum shows negative absorbance at these positions. The results clearly indicate that the amine groups of the coupling agent react with the epoxy groups of ENR. In neat coupling agent of $-NH_2^+$ and -NH-, stretching vibrations occur at 3450 cm⁻¹ and 3350 cm⁻¹, but in EZ₅ the two peaks merge



Figure 3 (a) Thermogravimetric analysis of rubberfiller mixes: (---) EC_{100} , (--) $EC_{100}Z_5$, (- · -) $EC_{100}Z_{10}$. (b) Derivative (DTG) curves: (----) EC_{100} , (--) $EC_{100}Z_5$, (- · -) $EC_{100}Z_{10}$.



Figure 4 (a) DRIFTS of clay; (b) ATR-FTIR spectra of ENR; (c) Transmission FTIR spectra of the coupling agent.

and a broad negative peak appears at 3360 cm^{-1} in the difference spectrum due to interaction with the epoxy groups. The positive absorbance at 485 cm⁻¹ and 690 cm⁻¹ are also due to the formation of tertiary amine (deformation) and C—Cl bond deformation, respectively. The negative absorbances at 1650 cm⁻¹ 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 result is also in conformity with the small increase in torque in the rheometric studies.

Figure 6 shows the infrared spectra of EC_{100} . It is evident that molding of clay with ENR mixes leads to broadening and decrease of the peaks at 1113, 1568, and 1348 cm⁻¹, which indicates that there is strong interaction between ENR and clay.

It is also observed that the intensity of the peak at 3696 cm^{-1} , which is due to the Si—OH groups,^{17,18} gradually decreases with increase in molding time, while a decrease in the intensity of the peaks at 870 cm⁻¹ and 840 cm⁻¹, which are characteristics of epoxy groups, is also evident. How-



Figure 5 ATR-FTIR spectra of EZ_5 : (a) after molding for 2 min; (b) after molding for 1 h; (c) the difference spectrum [i.e., (b) - (a)].



Figure 6 ATR-FTIR spectra of EC_{100} : (a) after molding for 2 min; (b) after molding for 1 h; (c) the difference spectrum [i.e., (b) - (a)].

ever, the intensity of the peak at 1650 cm⁻¹, which is due to the C=C stretching of ENR, remains constant. The difference spectra shows the negative absorbance at 3696 cm⁻¹ and 870 cm⁻¹ with a shoulder at 840 cm⁻¹, which signifies that the chemical bonding occurs between the epoxy groups of ENR and the hydroxyl groups on the clay surface during high-temperature molding.

Infrared spectra of the sample $EC_{100}Z_{10}$ are presented in Figure 7. It is observed that the intensity of the peaks at 3696 cm⁻¹ as well as at 870 and 840 cm⁻¹ decrease upon increasing the molding time. The peak at 465 cm⁻¹ slightly decreases and a shoulder at 485 cm⁻¹ arises on molding. The decrease in the intensity of the peak at 3696 cm⁻¹ signifies that —OH of clay surface and —OCH₃ of silane coupling agent react during molding and, simultaneously, the amine groups of the silane react with the epoxy groups to form C—N bonds (tertiary amine). This is also confirmed by the positive absorbance at 485 cm⁻¹ (tertiary amine) and a negative band at 465 cm⁻¹ (secondary amine). The appearance of the new peak at 690 cm⁻¹ indicates formation of C—Cl bond. It is believed that HCl liberated during molding adds to the double bond. The positive absorbance at 690 cm⁻¹ is ascribed to the C—Cl stretching.¹⁷

The reaction between clay and ENR in the absence of coupling agent is depicted in Figure 8 and that in the presence of silane coupling agent in Figure 9.



Figure 7 ATR-FTIR spectra of $EC_{100}Z_{10}$: (a) after molding for 2 min; (b) after molding for 1 h; (c) the difference spectrum [i.e., (b) – (a)].



Figure 8 Proposed mechanism of bonding between ENR and clay.

CONCLUSIONS

Extent of chemical bonding between ENR and clay in the absence of curing agents increases due to addition of the silane coupling agent N-3-(N vinyl benzyl amino)ethyl- γ -amino propyl trimeth-

oxy silane monohydrogen chloride when the rubber-filler mixes are molded at high temperature (180°C). Coupling bond formation between ENR and clay occurs via formation of Si—O—Si and C—N bonds.

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Figure 9 Proposed mechanism of bonding between ENR and clay in the presence of silane coupling agent.

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