

Dynamic Mechanical Properties and Hysteresis Loss of Epoxidized Natural Rubber Chemically Bonded to the Silica Surface

AJAY K. MANNA, P. P. DE, D. K. TRIPATHY

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

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ABSTRACT: High-temperature (180°C) molding of epoxidized natural rubber (ENR) filled with precipitated silica leads to chemical bond formation between epoxy groups of ENR and silanol groups of silica. The extent of chemical bond formation is further enhanced in the presence of the silane coupling agent *N*-3-*N*-(vinyl benzyl amino)ethyl- γ -amino-propyl trimethoxy silane mono hydrogen chloride (trade name Z-6032). The results of hysteresis loss measurements show that hysteresis loss increases with increase in coupling agent loading as a result of the higher modulus of the compounds compared to that of the ENR–silica mix. The dynamic mechanical property measurements show that the addition of coupling agent increases the glass-transition temperature. Whereas strain-dependent dynamic mechanical properties show that filler structure breakdown increases with increasing loading of coupling agent. Sulfur-cured systems show higher filler structure breakdown compared to that of nonsulfur systems. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2171–2177, 2002

Key words: epoxidized natural rubber; silica; hysteresis loss; dynamic mechanical properties

INTRODUCTION

It was previously reported that high-temperature molding of a mixture of epoxidized natural rubber (ENR) and precipitated silica results in the formation of chemical bonds between ENR and silica. The extent of chemical bond formation is further enhanced by the presence of the silane coupling agent *N*-3-*N*-(butyl benzyl amino)ethyl- γ -amino-propyl trimethoxy silane mono hydrogen chloride (trade name Z-6032).¹ There are several reports on the strain-dependent dynamic mechanical properties of sulfur-cured elastomers, which concluded that the Payne effect increases with increasing filler–filler networking (η) factor,

whereas polymer–filler interaction reduces the same.^{2–5} The modulus of unfilled compound does not change significantly upon increasing strain amplitude over the range of DSA tested; rather, it decreases for filled rubber, showing a nonlinear behavior, which is generally termed the *Payne effect*. Formation of coupling bonds between polymer and filler enhances the polymer–filler interaction parameter (*I*).^{6,7} Wolff et al.⁸ reported that addition of a silane coupling agent in the silica-filled rubber compounds leads to lower rolling resistance of tire, the wet traction remained unchanged, and the tread wear index decreased. It is also found that incorporation of hexamethylene diamine (HMDA) into the ENR compounds improves the mechanical properties of the ENR compounds: the elastic modulus was enhanced and $\tan \delta$ at 70°C was remarkably reduced, whereas $\tan \delta$ at low temperature remained unchanged.

Correspondence to: D. K. Tripathy.

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Table I Details of Materials Used

Material	Characteristic	Source
Epoxidized natural rubber, Kumpulan (ENR-50)	50 mol % of the double bond are epoxidized M_w/M_n , 4.7×10^5 Mooney viscosity, ML(1+4) @ 120°C, 42	Guthrie Berhad, Malaysia
Precipitated silica (trade name, Hi-Sil 223)	Particle size, 22 μm N_2SA , ^a 150 m ² /g	PPG Industries, USA
Silane coupling agent, <i>N</i> -3(<i>N</i> -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 procured
Stearic acid	Rubber grade	Locally procured
Sulfur	Rubber grade	Locally procured
Antioxidant (Acenox-TQ)	Rubber grade	ICI (India) Ltd., Rishra, W.B., India
Cyclohexyl benzothiazole sulfenamide (CBS)	Rubber grade	ICI (India) Ltd., Rishra, W.B., India

^a N_2SA is the nitrogen surface area.

The improvements mean that ENR/HMDA compounds reveal good rolling resistance and wet traction as tread of a full economic tire. The improvement was achieved by the increase in the crosslinking density attributed to the reaction between ENR and HMDA.⁹ With a coupling agent, the silica network is substantially depressed and the dynamic properties are improved. Although the Payne effect is drastically reduced, which is even smaller than its carbon black counterpart, the dynamic hysteresis is greatly improved.⁸ Recently, Wang reviewed the effect of polymer–filler and filler–filler interactions on the dynamic mechanical properties of filled vulcanizate.¹⁰ In this report the effect of rubber–filler coupling bonds on the hysteresis and dynamic mechanical properties was studied with ENR–silica systems both in the absence and the presence of sulfur-curing agents.

EXPERIMENTAL

The details of the materials are given in Table I and the formulation of the mixes is given in Tables II and III.

Mixing

Prior to mixing, silica was dried in an oven at 120°C for 12 h and cooled to room temperature (25°C) in a desiccator. Then silica was mixed in a

Brabender Plasticorder (Germany) with a rotor speed of 60 rpm. To ensure homogeneous mixing of silica and elastomer, mixing was carried out in two stages. In the first stage, silica was allowed to mix with the elastomer for 5 min and discharged. In the second stage, the mixes were fed back to the Brabender after passing two to three times in a two-roll mixing mill at room temperature. The coupling agent was added dropwise in the Brabender in the first stage of mixing. The final mixing was carried out for another 5 min in the Brabender Plasticorder. The curatives (where necessary) were added to the rubber–filler mixes in the open mill at room temperature and the mixing time was kept constant to 5 min for all the cases.

Cure Characteristics

The cure characteristics of the filled rubber compounds were analyzed by using a Monsanto mov-

Table II Formulation of Rubber-Filler Mixes

Material	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.

Table III Formulation of Mixes Containing Sulfur-Curing System

Material	Mix Designation	
	EHS ^a	EHZ ₅ S ^a
ENR-50	100	100
Hi-Sil 223	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 EHZ₅S, 19.

^b Antioxidant, amine based.

^c Accelerator.

ing die rheometer (model MDR-2000; St. Louis, MO) with an arc of oscillation of 0.50. The rheometric studies were carried out at 180°C for silica-filled samples in the absence of curing agents for 60 min. For the samples containing curatives, the optimum cure time (t_{90}) was determined by rheometer (MDR-2000) at 150°C. The rheometric data are presented in Table IV.

Molding

The samples containing no curatives were molded at 180°C in an electrically heated hydraulic press, for 60 min under a pressure of 15 MPa and the samples containing sulfur-curing agents were molded at 150°C to their optimum cure time (t_{90}).

Dynamic Mechanical Thermal Analysis (DMTA)

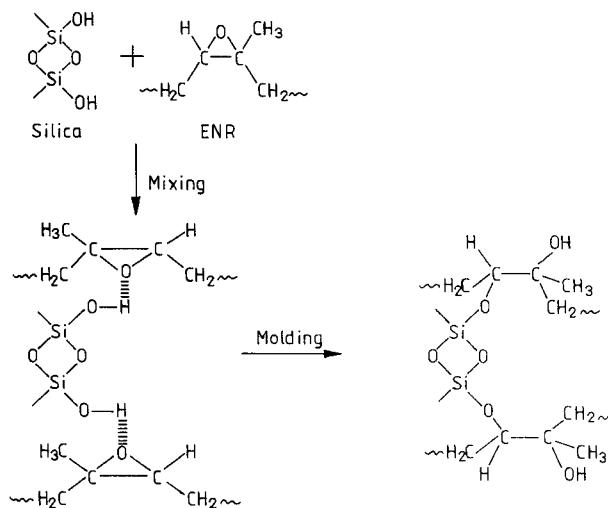
Dynamic mechanical properties were studied by using a Rheovibron (model DDV-111-EP; Orientec Corp., Japan) at a frequency of 3.5 Hz, and a

Table IV Rheometric Data of the Mixes

Parameter	Mix Designation				
	EZ ₅	EH	EHZ ₂	EHZ ₅	EHZ ₁₀
M_H (dN · m) ^a	0.6	10.8	16.0	20.8	20.1
M_L (dN · m) ^b	0.4	5.3	7.5	8.7	8.1
$M_H - M_L$	0.2	5.5	8.5	12.2	11.9

^a Maximum rheometric torque.

^b Minimum rheometric torque.

**Figure 1** Proposed reaction mechanism between ENR and silica.

double strain amplitude of 0.116% in tension mode. The temperature scan was made from -100 to 200°C with a linear rise of temperature of 2°C/min.

Strain-Dependent Dynamic Mechanical Analysis

The strain-dependent dynamic mechanical properties were also measured using a Rheovibron (model DDY-111-EP) at room temperature (25°C) at a constant frequency of 3.5 Hz. The variation of percentage double strain amplitude (%DSA) was in the range of 0.083 to 5.0%, given by the following equation:

$$\% \text{DSA} = (2A/L) \times 100$$

where A is the amplitude of vibration and L is the length of the sample.

Hysteresis Measurements

The hysteresis measurements were carried out with a dumbbell-shaped test specimen as per ASTM-D-412-80 in a Zwick Universal Testing Machine (Germany) (model 1445), at 100% elongation and at a strain rate of 500 mm/min.

RESULTS AND DISCUSSION

On high-temperature molding (180°C) epoxy groups of ENR react with the surface silanol

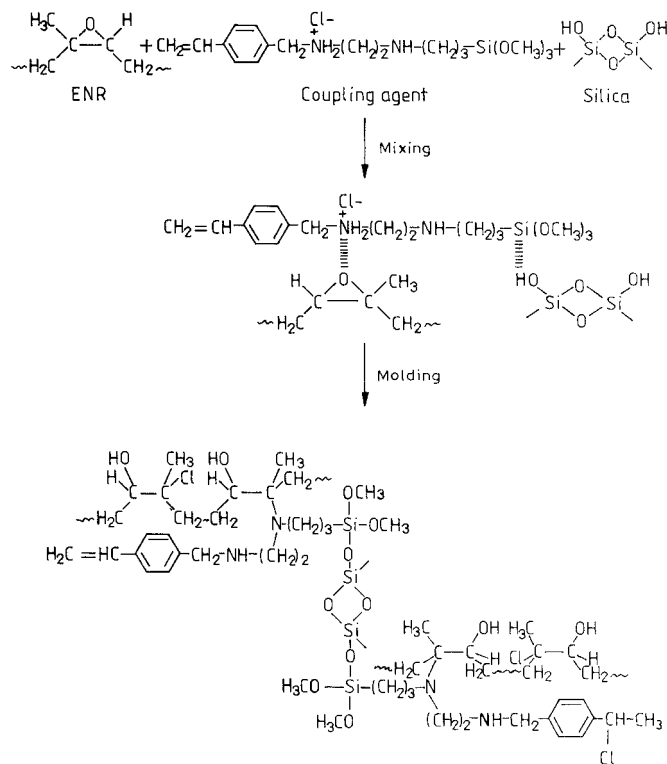


Figure 2 Proposed reaction mechanism between ENR and silica in the presence of a silane coupling agent.

groups of silica. FTIR spectroscopic studies show that ENR is bonded to the silica surface through Si—O—C linkages as shown in Figure 1.¹ In the presence of the coupling agent the extent of coupling bond formation increases. The amine groups of the silane coupling agent react with the epoxy groups of ENR to form C—N bonds between ENR and the coupling agent, whereas the trimethoxy silane functionality reacts with the silanol groups on the silica surface, leading to silyl ether linkages between silica and the coupling agent, as shown in Figure 2.¹

Low-Temperature Dynamic Mechanical Properties

Figure 3 shows the low-temperature dynamic mechanical properties of typical rubber–filler mixes. The glass-transition temperature (T_g) and storage modulus at 30°C are summarized in Table V. It has been observed that T_g of the mix EH (after 2-min molding) occurs at -3.1°C , whereas with increasing molding time to 60 min it shifts to the higher temperature -1.2°C . The shifting of T_g to higher temperature signifies that some of the polymer chains are chemically bonded to the sil-

ica surface, which restricts the movement of polymer chains and increases the T_g .⁸ On addition of the coupling agent (5 phr) T_g is further shifted to the higher temperature (i.e., 0.7°C). The results indicate that the extent of polymer–filler coupling bond formation increases in the presence of a coupling agent. However, with further addition of the coupling agent (10 phr), T_g shifts to a lower temperature (i.e., -1.4°C), which is attributed to the plasticizing effect of the unreacted coupling agent. From Table V it is evident that the storage modulus E' at 25°C increases on increasing the molding time and with the addition of the coupling agent (5 phr). However, at higher doses of coupling agent (10 phr) E' decreases because of the plasticizing effect of unreacted coupling agent.

Strain-Dependent Dynamic Mechanical Properties

Polymer–filler chemical interaction is also substantiated from the strain-dependent dynamic mechanical properties of the rubber–filler mixes. Figure 4 shows the variation of storage modulus E' with %DSA for the typical rubber–filler mixes,

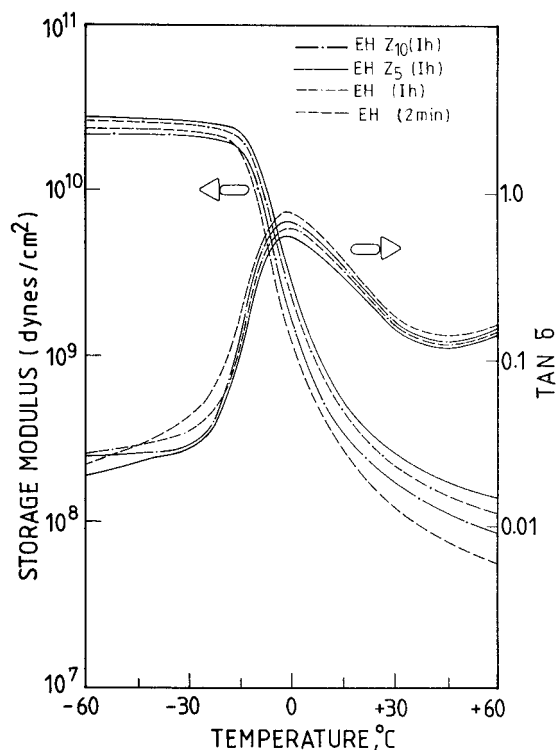


Figure 3 Plots of storage modulus E' and $\tan \delta$ versus temperature for different rubber–filler mixes: ---, EH (after 2-min molding); - · - · -, EH (after 60-min molding); —, EHZ₅; — · —, EHZ₁₀.

the results of which are summarized in Table VI. It has been observed that with increasing molding time and loading of the coupling agent (up to 5 phr) storage modulus at low %DSA (0.083%) increases, whereas at 10 phr coupling agent loading the E' value is slightly lower because of the plasticizing effect of the unreacted coupling agent, as discussed earlier. The storage modulus at high %DSA (5.0%) also shows a similar trend. The $\Delta E'$ (i.e., $E_0 - E_\infty$), which is a measure of filler structure breakdown, increases on increasing molding time as well as with increasing loading of the coupling agent up to 5 phr, beyond which (i.e., at 10 phr loading of coupling agent) $\Delta E'$ decreases.

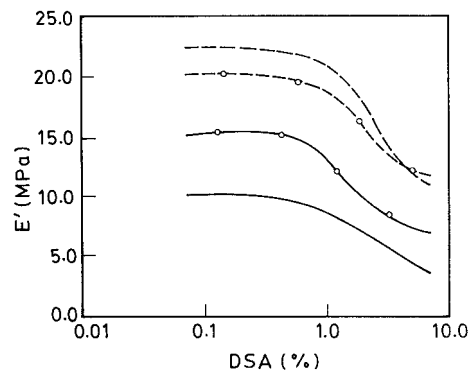


Figure 4 Variation of storage modulus E' as a function of %DSA: —, EH; —○—, EHZ₂; ---, EHZ₅; --○--, EHZ₁₀.

The $\Delta E'$ values of the sulfur-cured systems (i.e., the mixes EHS and EHZ₅S) are very close to each other, which shows the coupling agent has no significant effect in the case of sulfur-curing systems.

Networking Factor and Interaction Parameter

Ayala et al.¹¹ proposed a rubber–filler interaction parameter, which is defined as

$$I = \sigma/\eta$$

where σ is the slope of the stress–strain curve in the relatively linear region of low elongation and η is the filler–filler networking factor, calculated from the ratio of storage modulus at low and high strain.

Figure 5(a) shows variation of the networking factor η as a function of coupling agent loading. It is evident that η decreases on increasing the loading of coupling agent. It is interesting to note that, since η is the ratio of E' at low %DSA to E' at high %DSA, it is controlled by the E' at high %DSA. In the present case though, structure breakdown is higher at intermediate (2–5 phr) coupling agent loading, and η decreases gradually

Table V Values of T_g , $\tan \delta$ at T_g , and Storage Modulus (E') at 30°C of Typical Rubber-Filler Mixes

Mix Designation	T_g (°C)	$\tan \delta$ at T_g	E' at 25°C (dyn/cm ²)
EH (2-min molding)	-3.1	0.712	1.21×10^8
EH (60-min molding)	-1.2	0.656	2.07×10^8
EHZ ₅ (60-min molding)	+0.7	0.583	2.65×10^8
EHZ ₁₀ (60-min molding)	-1.4	0.678	1.81×10^8

Table VI Results of Storage Modulus (E') at Minimum (0.083%) and Maximum (5.0%) DSA and $\Delta E'$ at 25°C

Mix Designation	E' at 0.083% DSA (MPa)	E' at 5.0% DSA (MPa)	$\Delta E'$ (MPa)
EH	9.4	3.6	5.8
EHZ ₂	15.2	6.9	8.3
EHZ ₅	23.7	12.3	11.4
EHZ ₁₀	20.1	12.8	7.3
EHS	30.0	6.1	23.9
EHZ ₅ S	28.5	6.0	22.7

with increasing coupling agent loading. The sulfur-curing systems show very close values of networking factors η (4.91 for the mix EHS and 4.75 for the mix EHZ₅S), which indicate that the coupling agent has no significant effect because the

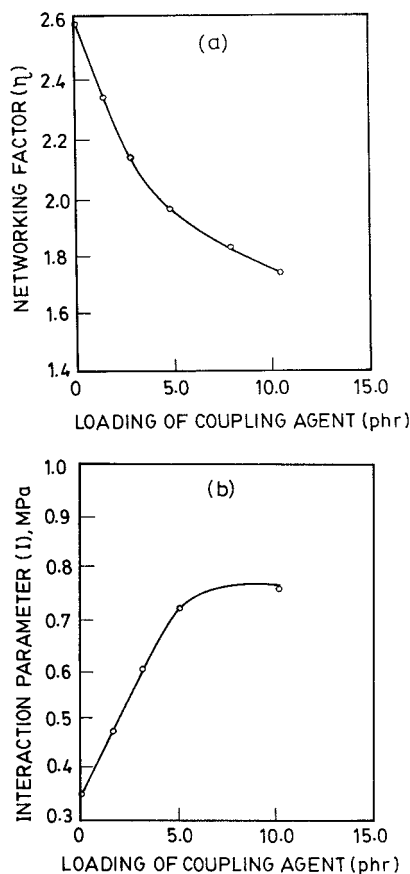


Figure 5 (a) Variation of networking factor η as a function of coupling agent loading (phr). (b) Variation of interaction parameter I as a function of coupling agent loading (phr).

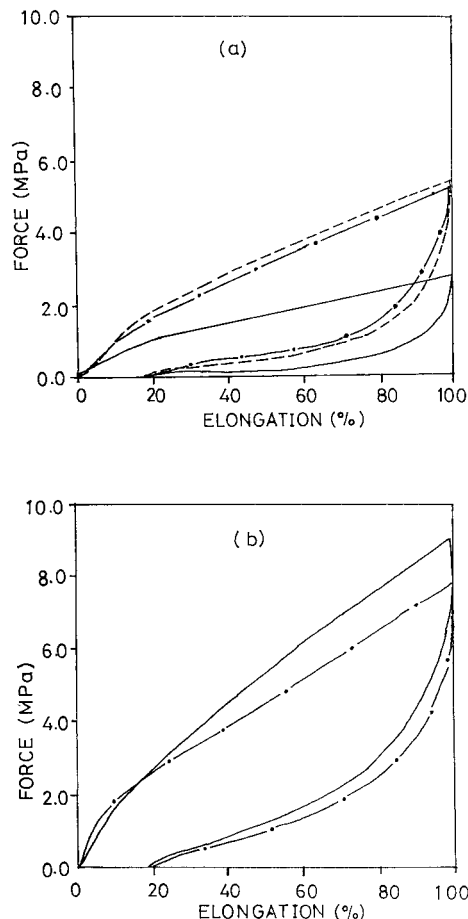


Figure 6 (a) Hysteresis loss of ENR-silica-coupling agent systems in the absence of sulfur-curing agents: —, EH; ---, EHZ₅; - · -, EHZ₁₀. (b) Hysteresis loss of ENR-silica-coupling agent systems in the presence of sulfur-curing agents: —, EHS; - · -, EHZ₅S.

samples were molded at low temperature (150°C) for a shorter time (t_{90}).

Figure 5(b) shows the variation of polymer-filler interaction parameter I as a function of the coupling agent loading. It is observed that I increases with increasing loading of coupling agent and attains a plateau value at 10 phr loading of the coupling agent. In the case of sulfur-curing systems values of I are very close (i.e., 0.16 MPa for EHS and 0.15 MPa for EHZ₅S) as a result of the plasticizing effect of unreacted coupling agent for the mix EHZ₅S.

Hysteresis Loss

Figure 6(a) shows the hysteresis loss of rubber-filler mixes molded at 150°C for 60 min and the numerical values are reported in Table VII. It is

Table VII Results of Hysteresis Loss of Different Rubber Compounds

Mix Designation	Hysteresis Loss (J/m ²)
EH	0.058
EHZ ₅	0.107
EHZ ₁₀	0.095
EHS	0.152
EHZ ₅ S	0.137

evident that hysteresis loss increases with increasing loading of coupling agent and the highest hysteresis loss is obtained in the case of 5 phr coupling agent loaded sample (mix EHZ₅S). Similar data were also obtained in the case of silica-filled sulfur-cured SBR in the presence of marcaposilane. The results are consistent with the proposed reaction mechanisms (Figs. 1 and 2). Because silica formed a "shell" of rubber, the stiffness of the rubber shell is insufficient to contribute to reinforcement in the absence of coupling agent. If this is strongly attached to the filler surface, it exerts its effect on molecular motion of rubber chains more distant from that surface. The increased modulus and larger stress softening obtained with silica in the presence of a coupling agent means a tighter network and a larger strain amplification, respectively.¹³ The coupling agent promotes the chemical bonding between ENR and silica, which increases the modulus and stress softening of the compounds. This is reflected from the increase hysteresis loss, 0.058 to 0.107 J/m², but it decreases with 10 phr loading of coupling agent (Table VII). At 10 phr loading of coupling agent, however, hysteresis loss is less because of lower modulus and almost similar strain recovery in the return cycle.

Figure 6(b) shows the hysteresis loss of sulfur-cured systems. It is apparent that hysteresis loss is much higher in the case of sulfur-cured systems because of the higher modulus and higher stress softening of the sulfur-cured compounds. Upon addition of the silane coupling agent in the sulfur-

cured system, hysteresis loss is reduced because of lower modulus attributed to the plasticizing effect of the unreacted coupling agent, decreasing from 0.152 to 0.137 J/m² (Table VII).

CONCLUSIONS

Polymer-filler coupling bonds shifts the glass-transition temperature (T_g) toward higher temperature and the enhancement of the modulus also occurs, as in the case of network bonds. Breakdown of the filler structure is higher in the case of sulfur-cured systems compared to that of nonsulfur systems. Consequently, hysteresis loss is also higher in the case of sulfur-cured systems compared to that of nonsulfur systems, although in both cases the coupling agent shows a plasticizing effect after 5 phr loading.

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