Chemical Interaction Between Epoxidized Natural Rubber and Silica: Studies on Cure Characteristics and Low-Temperature Dynamic Mechanical Properties

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SYNOPSIS

The unusual reinforcement mechanism exhibited by silica in epoxidized natural rubber (ENR) may be attributed to the specific chemical interaction or the chemical cross-linking taking place between silica and the epoxy groups while heating the mix. Evidence for the higher interaction is established through rheometric studies conducted at 180°C and changes in the dynamic mechanical characteristics studied over a wide temperature range using a dynamic viscoelastometer for the heated and unheated silica-filled mixes.

INTRODUCTION

Epoxidized natural rubber (ENR) has been introduced to the elastomeric world as a modified form of natural rubber (NR) with high application potential as an oil-resistant, air-impermeable, and highly damping rubber.[1-5] Recent studies conducted by De et al. showed that ENR has potential as a chemically reactive rubber, which can cross-link with other polymers having functional groups such as chloroprene, chlorosulfonated polyethylene, poly(vinyl chloride) carboxylated nitrile rubber, etc.[6-9] Because of the high cross-link densities, when these polymers are reacted, external, conventional curing agents are not required for the curing of these blends. The functionally active epoxy group of ENR is responsible for such interactions. The vulnerability of epoxy groups for such chemical reactions led us to the present investigation to find out the special mechanism responsible for the high reinforcement of silica in ENR. It is known that the active silanol groups can interact with other functional groups containing polymers like carboxylated nitrile rubber. Physical property studies conducted on silica-filled ENR systems showed that there is a marked difference in the interaction mechanism of ENR and silica compared to other fillers.[10] Silica reinforces ENR to an extent similar to the black-filled systems. The interaction or reinforcement mechanism operating in the case of ENR and silica could not be explained properly based on the physical property studies alone. The present study is the result of our experiments on silica-filled ENR systems to find out whether there is any cross-linking between the two, through rheometric studies and low-temperature-to-high-temperature dynamic mechanical property studies in the absence of any conventional curing agents.

Curing agents were avoided to elucidate the interaction mechanism between silica and ENR alone, which may otherwise become complex.

EXPERIMENTAL

Materials and Mixing

A 50 mol % epoxidized NR is used for the study. Formulations and details of materials used are given in Table I. Table II contains conditions followed for the dynamic mechanical analysis. Natural rubber (NR), ISNR-5 grade, is also used in one mix for comparison. Mixing was carried out on a laboratory-size two-roll mixing mill (32.5 × 15 cm). Total mixing time has been kept minimum to avoid sticking of the compound to the mill rolls. Care was taken to see that the mill-roll temperatures are not ex-

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Table I Details of Materials Used

Material	Details
Epoxidized natural rubber (ENR)	50 mol % epoxidized, supplied by Malaysian Rubber Producers' Research Association, Brickendonbury, U.K.
Silica	Ultrasil VN3, supplied by Bayer India Limited, Bombay
Bis(triethoxy silyl propyl) tetrasulfide (Si-69)	Manufactured by Degussa, Germany

ceeding the set temperatures to avoid any crosslinking during mixing.

Sample Preparation and Testing

Cure studies were carried out on a Monsanto Rheometer (model 100S) at 180°C. Samples for dynamic mechanical analysis were prepared in dimensions of 7 × 0.4 × 0.3 cm by compression-molding at 180°C for 1 h. Unheated or uncured mixes were press-molded at 100°C for a limited time to get the proper sample dimensions before testing. One mix was prepared with heated silica. For this, silica was heated in an oven at 120°C for 6 h before it was mixed with the rubber. All the test samples were conditioned at room temperature for a minimum period of 24 h before the tests were carried out.

Dynamic mechanical analysis was done on a dynamic viscoelastometer (Rheovibron, model DDV-III-EP, Orientec Corporation, Japan) at a temperature range of −100°C to +250°C at a heating rate of 1°C/min at 3.5 Hz frequency.

RESULTS AND DISCUSSION

Cure Characteristics

Rheographs of different mixes are given in Table II and are shown in Figure 1. Mix A is pure gum ENR-50. Mix B contains 50 phr unheated silica. It is seen from these two graphs that there is a rise in torque values at 150°C for mix B, whereas mixes containing 50 phr ISAF in ENR-50 (mix H) and 50 phr silica in NR (mix I) did not show any such change in the torque values. Mix A was kept in the rheometer for

Table II Formulations and Conditions Followed

Mix Designations	Ingredients and Conditions Followed
A	ENR-50, 100 phr (gum)
B	ENR-50, 100 phr; silica, 50 phr; unheated
C	ENR-50, 100 phr; silica, 50 phr; Si-69, 2 phr; unheated
D	Mix B heated for 1 h at 180°C
E	Mix C heated for 1 h at 180°C
F	ENR-50, 100 phr; heated silica, 50 phr; heated for 1 h at 180°C
G	ENR-50, 100 phr; silica, 50 phr; Si-69, 2 phr; Na_2SO_4 0.2 phr; heated for 1 h at 180°C
H	ENR-50, 100 phr; C-black (ISAF), 50 phr
I	NR, 100 phr; silica, 50 phr

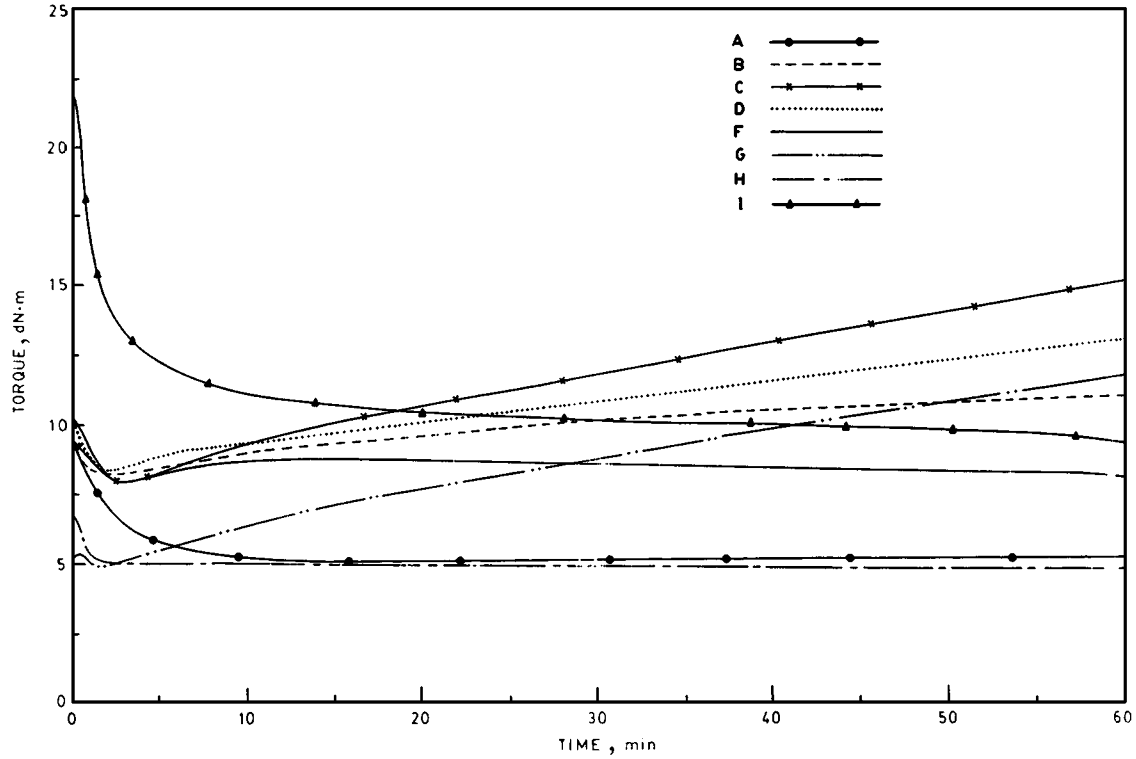

Figure 1 Effect of heating of silica-filled ENR-50 mixes. rheometer curves at 180°C.

1 h at 180°C to determine whether there was any hardening or gelling taking place in the ENR on heating. The resultant plateau curve ruled out any such chances of hardening in ENR at 180°C. This indicates that a chemical reaction is taking place between silica and ENR-50 and that there is slight cross-linking. Generally, the interactions between a filler and a polymer are not high enough so that cross-linking can be detected through a rheometer torque rise. It was expected that a chemical reaction is taking place between the silanol groups and epoxy groups during heating of the mix.

Previous studies on physical properties showed that silica-filled ENR exhibit properties comparable to that of black-filled vulcanizates.[8] This clearly gives evidence for the higher reinforcing ability of silica in ENR. Studies on polymers with functionally active side groups proved that they enter into chemical cross-linking with the silanol groups of silica. Silica filler in epoxy resin is also found to be chemically active. The higher reinforcement observed in the case of silica-filled ENR was presumed to be a similar interaction mechanism to that of black-filled vulcanizates. However, a comparatively good number of cross-links (considerable rise in rheometric torque, nonsticky and transparent vulcanizates) are present in the silica-filled vulcanizates even in the absence of any conventional curing agents.

Here, heating of the mixes should be treated separately from the vulcanization of samples. Usually, vulcanization is done for a much shorter period and at a lower temperature. This indicates that for the cross-linking to take place between the epoxy and silanol groups a higher activation energy is required. Hence, while considering the reinforcement characteristics of conventionally cured silica-filled vulcanizates, it should be taken into account that the chemical interaction under such conditions is comparatively poor.

With 2 phr Si-69 in mix B, the rheometer torque rises further (mix C, Fig. 1). The cross-linking action is further accelerated by the presence of Si-69. Si-69 can cure elastomers because of its chemical structure. Here, also, the observed rise in torque can be attributed to this. Silica generally forms cross-links with elastomers through the silanol groups. To prove this effect, silica was heated in an oven for 6 h at 120°C (percentage weight loss = 6.5) and then mixed with ENR (mix F). Mild heating of silica at 105°C can result in the loss of adsorbed water molecules from its surface and can result in a strained siloxane structure (Figure 2).[11] This may

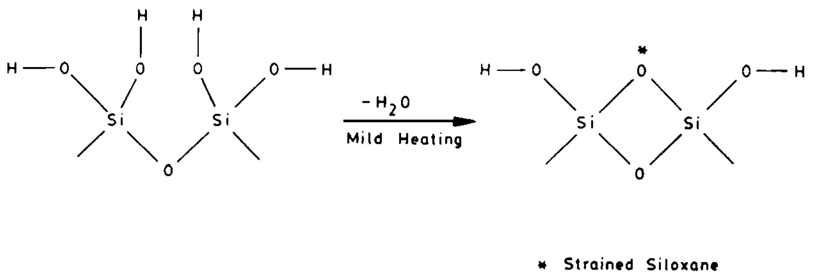

Figure 2 Effect of mild heating on silica-strained siloxane formation.

result in the reduction in the number of geminal silanol groups available on the silica surface that enter into chemical cross-linking with the epoxy groups. Subsequently, there was a retardation effect in the cross-linking rate (curve F, Fig. 1).

Similarly, while cross-linking, some water mol-

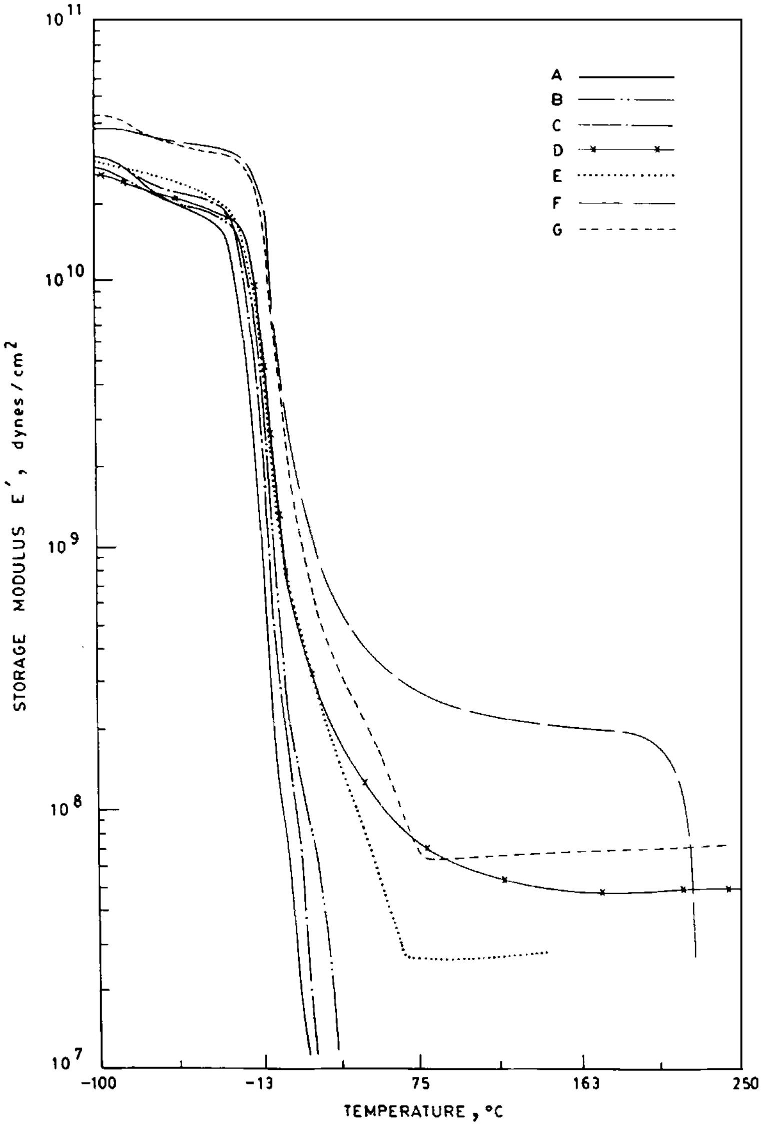

Figure 3 Storage modulus, E' vs. temperature plots at 3.5 Hz. Effect of silica on ENR-50 under conditions given in Table II.

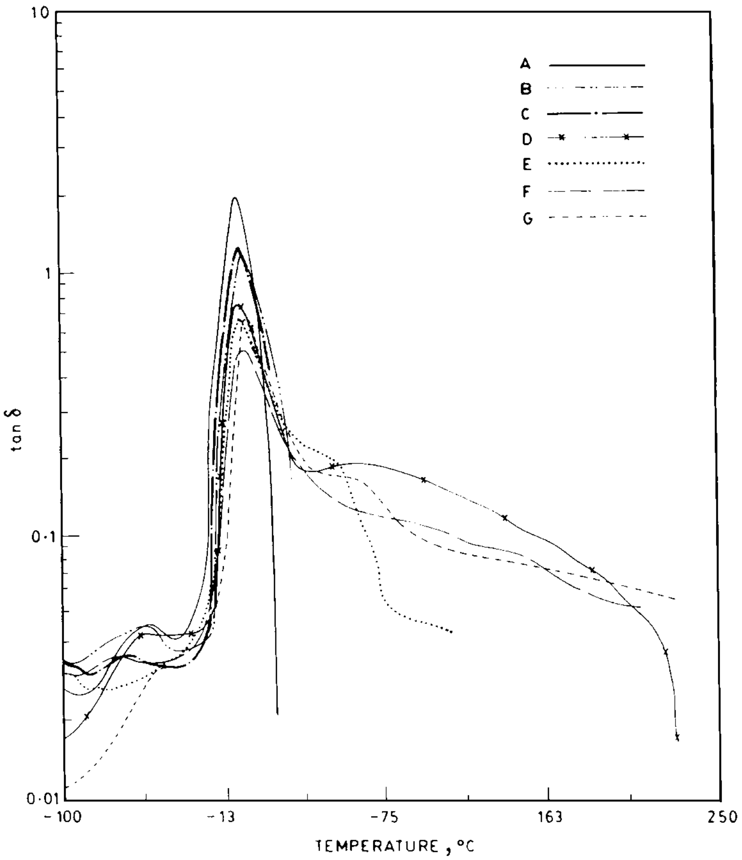

Figure 4 Loss angle tan δ vs. temperature plots at 3.5 Hz. Effect of silica on ENR-50 under conditions shown in Table II.

ecules may be eliminated as a side-reaction product. We have tried to remove these water molecules *in situ* by adding a catalytic amount of anhydrous sodium sulfate into the mixture while mixing. The reaction rate was expected to increase with this. On the contrary, mix G registered a slower cure rate. The reaction mechanism still needs detailed study.

Dynamic Mechanical Properties

Figures 3 and 4 show the effect of silica filler on the dynamic mechanical properties (low temperature to high temperature) of ENR-50. Both heated and unheated samples were analyzed. Studies carried out on carbon black and silica- and clay-filled rubbers showed that there is a striking influence of the interaction parameters of a filler and polymer on the storage modulus values, E', and loss tangent, tan δ, loss tangent peak height, spread, and the glass transition temperature, T_g, etc.[12-15] The effect of varying filler–rubber interaction parameters on E' values is shown in Figure 3. Mixes A, B, and C were unheated, and mixes D, E, F, and G were compression-molded at 180°C for 1 h. Heated samples showed an obvious increase in the spread of the E' curve and the modulus values were higher enough to withstand a higher temperature range, unlike the unheated mixes.

The presence of a stronger network structure is indicated in the case of heated samples due to the cross-linking or strong chemical interaction.[16] The strain applied on the system could easily be dissipated between the cross-link junctions due to the strong interchain linkages, whereas mix E showed a lower heat resistance for the storage modulus values. This may be due to the slight plasticizer action of Si-69.

High temperature E' values were observed in the case of mixes F and G. When the filler is heated, its surface morphology is changed and the surface energy will subsequently show a change. This changed surface structure may result in an increase in the filler modulus alone. Hence, the rise in E' values in the case of mix F is reasonable according to this probability. Addition of sodium sulfate may also be causing changes like this to account for the high-temperature E' values. The influence of filler on the

Table III Glass Transition Temperature and tan δ_{max} Values

Mix Designations	Glass Transition Temperature (°C at 3.5 Hz)	tan δ_{max}
A	−5	1.90
B	−4	1.15
C	−6	1.22
D	−4	0.74
E	−5	0.68
F	−2	0.51
G	−1	0.66

dynamic mechanical properties is negligible in the case of unheated mixes. However, the nature of the E' curves gives strong proof for the existence of a stronger network in the case of heated mixes.

The filler–rubber interaction phenomenon is more clearly explained through the nature of the loss tangent curves (Fig. 4). Tan δ peak height, spread, and location can give a valuable account of the changes occurring in the polymer phase on the addition of filler and cross-links. The α-relaxation peak height gives an indication of the total free volume available in the system. The molecular chain motions become maximum at the glass–rubber transition state. Hence, if any restriction to the free chain mobility is introduced to the polymer phase, it will be reflected in the various aspects of the α-relaxation peak or the loss tangent peak. When the interaction between the rubber and filler increases, either more and more polymer chains will be adsorbed onto the filler surface or changes may occur in the filler structure, so that the occluded or bound rubber amount may change.

Figure 4 shows that the addition of the silica-to-ENR phase reduced the gum polymer α-relaxation peak height. The tan δ_{max} and T_g values are given in Table III. When the interaction rate or cross-linking is further raised as in the case of mix C, tan δ_{max} values reduced further. In the case of mixes D, E, and G, a second hump can be seen above the α-relaxation peak temperature. This shows a higher amount of adsorbed rubber present in the system, which requires a higher energy for the relaxation of the molecular chains when the mixes are heated.[12,15] This gives additional evidence to the fact that heating of silica-filled ENR changes the filler–rubber interaction parameters.

CONCLUSION

Epoxidized natural rubber, 50 mol %, is found to have high interaction with the silanol groups of silica filler. The interaction rate increases with the addition of a silane coupling agent as evidenced through rheometric and dynamic mechanical analysis. Dynamic mechanical analysis of heated and unheated mixes gave additional proof to the nature of interaction between ENR and silica in the absence of any conventional vulcanization agents.

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