

polymer communications

Effect of silane coupling agent on the chemorheological behaviour of epoxidised natural rubber filled with precipitated silica

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Results of measurements of physical properties and solvent swelling of the extrudates indicate that epoxidised natural rubber (ENR) interacts chemically with precipitated silica when the mix of the two was extruded at 150–170°C in a Monsanto Processability Tester (MPT). The extent of interaction between the rubber and the filler depends on the extrusion time, the volume fraction of the filler, the shear rate and the addition of the silane coupling agent, namely *N*-3-(*N*-vinyl benzyl amino) ethyl- γ -aminopropyl trimethoxy silane monohydrochloride. The activation energy of the chemical interaction between ENR and silica decreases on the addition of the silane coupling agent. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

It has been reported that during molding of the rubber–filler mixes at high temperature (170°C), precipitated silica chemically reacts with epoxidised natural rubber (ENR) and the effect is more prominent in the presence of silane coupling agent, namely *N*-3-(*N*-vinyl benzyl amino) ethyl- γ -aminopropyl trimethoxy silane monohydrochloride¹.

The rheological behaviour of carbon black filled systems has been studied by several workers^{2–7}. The effect of the state of cure on the rheological behaviour of thermosets have also been reported^{8–14}. Rivin and True pointed out that the long range filler–polymer and filler–filler interactions decrease at high shear rate and consequently the viscosity of the rubber compounds depends mainly on the filler loading and not on the structure of filler¹⁵. Mallick *et al.* studied the effect of carbon black on the chemorheological behaviour of the blends of polyacrylic acid (PAA) and epoxidised natural rubber in a Monsanto Processability Tester (MPT)¹⁶. The rheological behaviour of SBR compounds affected by vulcanisation kinetics was studied by Isayev and Wan^{17,18}. Recently Bandyopadhyay *et al.* studied the effect of silane coupling agent, namely (3-aminopropyl) triethoxy silane on the chemorheological behaviour of a mixture of carboxylated nitrile rubber (XNBR) and surface oxidised ISAF carbon black¹⁹.

The present paper reports results of studies on the effect of volume fraction of precipitated silica on the chemorheological behaviour of ENR, with special reference to the effect of silane coupling agent, namely *N*-3-(*N*-vinyl benzyl amino) ethyl- γ -aminopropyl trimethoxy silane monohydrochloride.

Experimental

The details of the materials used are given in Table 1 and the formulations of the mixes are given in Table 2, where all the ingredients are added in terms of phr, which is defined as

parts per hundred parts of rubber by weight. In the mix designation E, S and Z stand for ENR, silica and coupling agent (Z-6032), respectively. The mixing of the rubber, filler and silane coupling agent was carried out in a Brabender Plasticorder (PLE 330) at room temperature (250°C) at a rotor speed of 60 rpm. First silica was mixed with ENR for 4 min, then silane coupling agent was added drop-wise and the mixing was further contained for 4 min. The mixes were then taken out from the Brabender Plasticorder and final sheeting was done in a two-roll mill.

The flow properties of the rubber–filler mixes were measured in a Monsanto Processability Tester (MPT, model 83077) which is a constant flow rate capillary rheometer that can be operated manually or in a programmed way. The barrel, piston and capillary are electrically heated with a microprocessor-based temperature controller system. The capillary used for extrusion of the rubber compounds has *L/D* ratio of 30:1, with compound entrance angles of 45° and 60°. The barrel and capillary diameters were 19.06 and 1.00 mm, respectively. The preheating time for all the samples was 5 min and the change in shear rates was achieved by changing the plunger speed. During extrusion the plot of the capillary pressure against time was automatically recorded in a graph by a plotter. Extrusion of the mixes were carried out at the temperatures 150–170°C. The effect of shear rates on the chemical interaction between rubber and silica was studied at 160°C with a silica loading of 60°C with a silica loading of 60 phr and silane coupling agent loading of 8 phr. For the calculation of activation energy of the rubber–filler interaction, extrusion of the mixes ES₆ and ES₆Z₈ were carried out at three different temperatures, 150°, 160° and 170°C.

The solvent swelling of the extrudates was done in chloroform for 72 h at 25°C and the final weight was taken under swollen condition. The results are expressed as percentage volume swell. The physical properties of the extrudates were determined in a Zwick Universal Testing Machine (UTM), model-1435 at room temperature (25°C), the rate of grip separation being 500 mm/min. The area of cross section of the extrudates were calculated from the average diameter of the extrudates.

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Table 1 Details of materials used

Materials	Characteristics	Source
Epoxidised natural rubber (ENR)	50 mole percent of the double bonds are epoxidised	Kumpulan Guthrie, Berhad, Malaysia
Silica (Hi-Sil 223)	Particle size 22 μm , N_2SA^a , 150 m^2/g	PPG Industries Ltd, USA
Silane coupling agent <i>N</i> -3-(<i>N</i> vinyl benzyl amino) ethyl- γ -amino propyl tri-methoxy silane mono-hydrochloride (Trade name, Z-6032)	Specific gravity 0.9 at 25°C; pH 2.0	Dow Corning, USA

^aNitrogen surface area**Table 2** Formulations of mixes

Materials (phr) ^a	Mix designation ^b						
	ES ₄	ES ₅	ES ₆	ES ₆ Z ₂	ES ₆ Z ₄	ES ₆ Z ₆	ES ₆ Z ₈
ENR	100	100	100	100	100	100	100
Silica	40	50	60	60	60	60	60
Coupling agent (Z-6032)	0	0	0	2	4	6	8

^aphr = parts per hundred rubber^bE stands for ENR

S stands for silica

Z stands for silane coupling agent

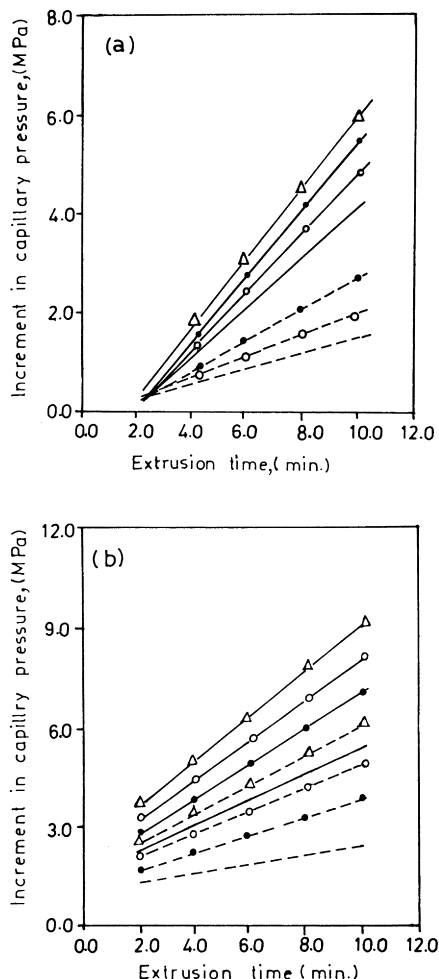


Figure 1 (a) Plots of increment in the capillary pressure with extrusion time for ENR-silica and ENR-silica-coupling agent mixes at 160°C and at a shear rate of 49.2 s^{-1} ; (---) ES₄, (-○-○-) ES₅, (-·-·-) ES₆, (—) ES₆Z₂, (-○—) ES₆Z₄, (-·—) ES₆Z₆, (-△—) ES₆Z₈. (b) Plots of increment in the capillary pressure with extrusion time for different rubber filler mixes 160°C at different shear rates; (---) ES₆, (—) ES₆Z₈, 12.2 s^{-1} ; (-·-·-) ES₆, (-·—) ES₆Z₈, 24.3 s^{-1} ; (-○-○-) ES₆, (-○—) ES₆Z₈, 49.2 s^{-1} ; (-△-△-) ES₆, (-△—) ES₆Z₈, 98.3 s^{-1}

Results and discussion

Plots of the increment in the capillary pressure (ΔP) versus extrusion time (t) for various ENR-silica mixes are shown in *Figure 1*. It is evident that ΔP increases with increase in extrusion time and the rate of increase in ΔP is higher at higher loading of silica. Furthermore, the effect is more pronounced in the presence of silane coupling agent. Neat ENR, however, does not show any such increment in ΔP with extrusion time, indicating that the increment in the capillary pressure with extrusion time in the case of rubber-silica mixture is due to the chemical bonding between the surface silanol groups of the filler and the epoxy groups of the rubber¹. It is also evident that the extent of the chemical interaction increases with increase in the loading of the coupling agent. The $-\text{NH}_2^+$ groups of the coupling agent reacts with epoxy groups of ENR forming C-N bonds between the coupling agent and ENR. With increase in the loading of the coupling agent the concentration of $-\text{NH}_2^+$ groups increases and consequently the rate of the chemical reaction increases.

The effect of shear rate on the increment of capillary pressure (ΔP) is also shown in *Figure 1*. The results clearly indicate that the rate of the chemical interaction increases with increase in shear rate and the effect is more prominent in the presence of the silane coupling agent. Increase in the shear rate leads to a greater number of collisions between the active sites of the polymer, filler and the coupling agent and consequently, the rate of the chemical interaction increases.

Tables 3 and *4* summarise the results on the effects of the extrusion time, shear rate and coupling agent loading on the mechanical properties and solvent swelling of the extrudates. It is observed that tensile strength and modulus of the extrudates increase with increase in the extrusion time and the shear rate, while the elongation at break decreases. It is also evident that addition of the silane coupling agent causes increase in the tensile strength, modulus and elongation at break. It is also observed that the volume swell decreases with increase in shear rate and the effect is more pronounced in the presence of the coupling agent. The results indicate

Table 3 Effect of extrusion time on the mechanical properties of extrudates^a

Mix designation	ES ₆			ES ₆ Z ₈		
	4	8	12	4	8	12
Extrusion time (min)						
Modulus at 100% elongation (MPa)	3.5	3.8	4.0	3.8	4.0	4.3
Modulus at 200% elongation (MPa)	5.3	3.9	6.5	5.9	6.7	6.9
Tensile strength (MPa)	6.9	7.0	7.5	8.2	8.9	9.5
Elongation at break (%)	249	39	230	314	294	272

^aExtrusion temperature 160°C; shear rate 49.2 s⁻¹**Table 4** Effect of shear rate on the mechanical properties and solvent swelling of extrudates

Mix designation	ES ₆				ES ₆ Z ₈			
	12.2	24.3	49.2	98.3	12.2	24.3	49.2	98.3
Shear rate (s ⁻¹)								
Modulus at 100% elongation (MPa)	3.5	4.2	4.4	5.0	4.0	4.5	4.7	5.0
Modulus at 200% elongation (MPa)	5.4	6.0	6.2	7.2	6.8	7.1	7.5	7.8
Tensile strength (MPa)	6.2	7.0	7.4	8.1	8.7	9.0	9.5	10.0
Elongation at break (%)	265	242	230	215	284	275	247	238
Volume swell (%)	1380	1250	1160	1020	1120	1040	980	840

^aExtrusion done at 160°C and extrudates collected after 10 min

that the extent of coupling bond formation increases with increase in the extrusion time, shear rate and coupling agent loading.

The chemorheology of a mix is influenced by the reaction of kinetics of the system^{11,12}. The linear rise in the capillary pressure with extrusion time, as shown in *Figure 1*, can be expressed as

$$d(\Delta P)/dt = m \quad (1)$$

where ΔP is the increment in the capillary pressure at any time t and m is a constant for a particular formulation at a particular temperature and obtained from the slope in *Figure 1*. Since the increment in the capillary pressure is due to enhanced viscosity through rubber–filler interaction, therefore following Lodge²⁰, it can be stated that

$$\Delta P = C_{\alpha}RT \quad (2)$$

where C_{α} is the extent of the interaction, R is the universal gas constant and T is the absolute temperature. From equations (1) and (2) it can be written

$$dC_{\alpha}/dt = m/RT \quad (3)$$

where, dC_{α}/dt is the rate of the interaction. As the concentration of the functional groups in the rubber is sufficiently high and taken as constant, the rate of the interaction is dependent only on the concentration of the silanol groups on the silica surface for mixes not containing silane coupling agent or on the loading of the coupling agent at a fixed filler loading, as the case may be. Hence the process follows the pseudo-unimolecular rate equation which in the present case is defined as:

$$m/RT = kC \quad (4)$$

where C is either the concentration of the active sites on the silica surface or the coupling agent and k is the specific reaction rate constant.

Figure 2 shows the variation of the rate of the rubber–filler interaction with volume fraction of filler at constant temperature and shear rate. It is observed that the rate of interaction increases with increase in the volume fraction of the filler. *Figure 2* also shows the variation of the rate of the

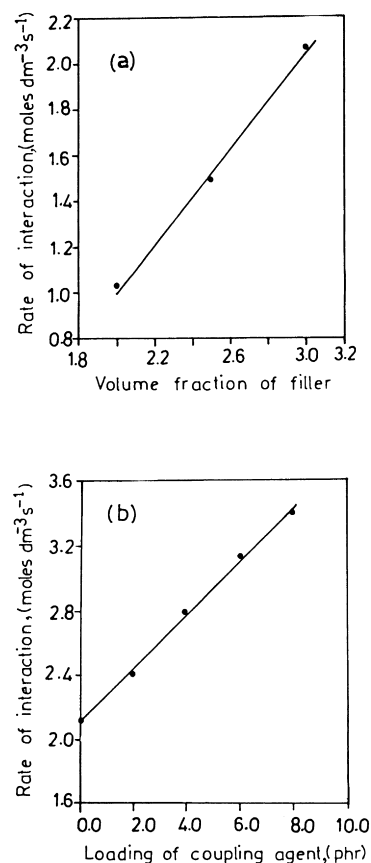


Figure 2 (a) Variation of the rate of interaction with the volume fraction of silica filler at 160°C and at a shear rate of 49.2 s⁻¹. (b) Variation of the rate of interaction with coupling agent loading at 160°C and at a shear rate of 49.2 s⁻¹

interaction as a function of coupling agent loading at a constant filler loading. It is evident that the rate of the chemical interaction increases with increase in the coupling agent loading. The higher rate of interaction in the presence of the silane coupling agent is presumably due to the greater extent of polymer–filler coupling bond formation as the

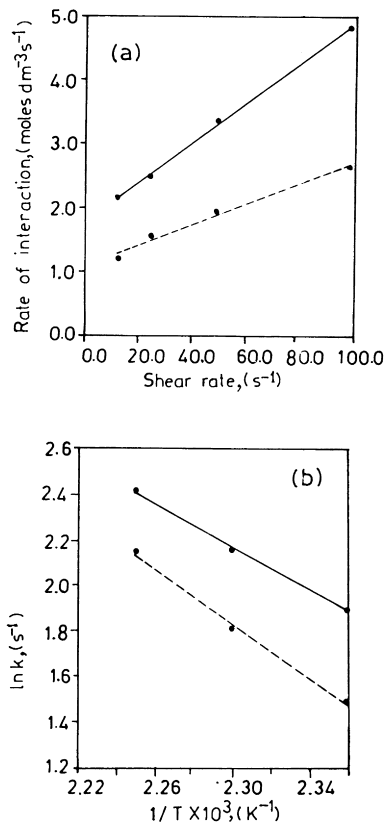


Figure 3 (a) Variation of the rate of interaction with shear rate at 160°C; (---) ES₆, (—) ES₆Z₈. (b) Plots of ln *k* versus 1/*T* (---) for ES₆, (—) ES₆Z₈, at a shear rate of 49.2 s⁻¹

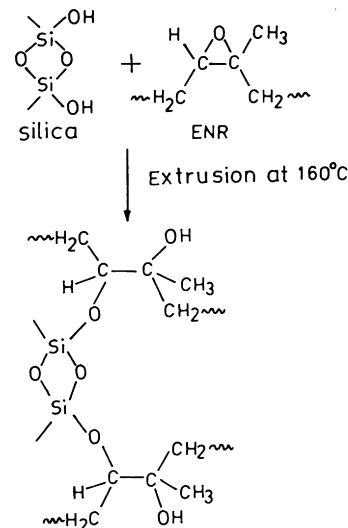


Figure 4 Proposed mechanism of the reaction between ENR and silica

coupling agent is capable to activate and open up the epoxy groups of ENR through its $-\text{NH}_2^+$ groups¹.

Figure 3 shows the effect of shear rate on the rate of rubber–filler interaction. It is observed that the rate of interaction increases with increase in the shear rate²¹ and the effect is more prominent in the presence of the silane coupling agent.

The activation energy of the chemical interaction between the rubber and filler in the presence of the coupling agent has been calculated from the Arrhenius equation

$$k = A_0 e^{-E_a/RT} \quad (5)$$

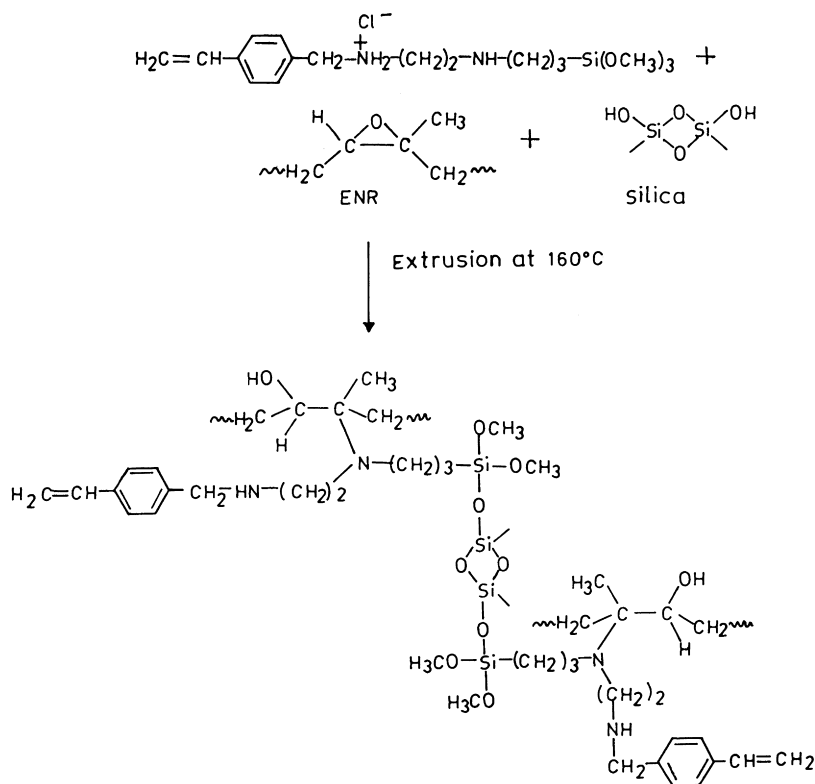


Figure 5 Proposed mechanism of the reaction between ENR and silica in the presence of silane coupling agent

where A_0 is the frequency factor and E_a is the activation energy, obtained from the plot of $\ln k$ versus $1/T$ (Figure 3). It is found that the activation energy of the rubber–filler interaction decreases in the presence of the silane coupling agent (mix ES₆, 67.3 kJ/mol versus mix ES₆Z₈, 44.1 kJ/mol). The decrease in the activation energy signifies that the epoxy ring opening is facilitated in the presence of the silane coupling agent.

Figures 4 and 5 suggest a probable mechanism of the chemical interaction between ENR and silica, illustrating the role of coupling agent in the chemical interaction. It has been proposed earlier that during high temperature molding of the rubber–filler mixture the silanol groups (-OH) on silica filler surface react with the -OCH₃ group of the coupling agent, while -NH₂⁺ reacts with the epoxy groups of ENR leading to the coupling bond formation¹.

Conclusions

ENR and silica chemically interact with each other when the mixture of the two is extruded in a Monsanto Processability Tester at high temperature (170°C). The extent of the interaction increases with increase in the volume fraction of the filler, increase in shear rate and addition of the silane coupling agent, namely *N*-3-(*N*-vinyl benzyl amino) ethyl- γ -aminopropyl trimethoxy silane monohydrochloride.

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