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Epoxidised Natural Rubber as a Coupling Agent in in situ *Precipitated Silica–Natural Rubber Composites*

MAYA, K.S.[*,**], RANI JOSEPH[*#], JACOB K. VARKEY[***]
AND BENNY GEORGE[***]

Natural rubber (NR) compounds were prepared with in situ *precipitated silica in the presence of epoxidised natural rubber (ENR) as a coupling agent.* In situ *silica masterbatches were prepared from NR latex along with ENR. For this, NR latex was mixed with a suitable amount of ENR latex and precipitation of silica was carried out using sodium silicate and ammonium chloride. Compounds were prepared with these masterbatches. The mechanical properties of the vulcanisates were compared with two reference compounds prepared from NR and commercially available silica with and without a silane-coupling agent Si-69®. The NR-silica composites prepared with ENR as the coupling agent showed better mechanical properties and improved rubber-filler interaction.*

Key words: epoxidised natural rubber; silica; composites; NR latex; sodium silicate; ammonium choloride; mechanical properties; Si-69®; rubber-filler interaction

Physical properties of rubber vulcanisates are improved by reinforcing with fillers such as carbon black, clay, silica *etc*. For better reinforcement, there must be strong interaction between the polymer matrix and filler which depends on filler surface area, morphology and surface activity[1]. Carbon black is used as the most versatile reinforcing filler for rubber, complimented by silica. The replacement of carbon black by silica gives reduced rolling resistance to tyres and, as a consequence, reduces fuel consumption of the vehicle[2]. This environmental and economical incentive of silica has attracted a great deal of interest. However various contrivances are necessary for silica to compound with the rubber without affecting performance. Silica has a number of hydroxyl groups on the surface which result in strong filler-filler interaction and adsorption of polar materials by the hydrogen bonds[3,4]. Thus silica filled rubber compounds will therefore have poor dispersion of filler and poor cure characteristics.

The well known methods for improvement of the reinforcement effect are the treatment of the silica surface with suitable agents such as silane coupling agents like bis (3-triethoxy

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[*] Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-22, Kerala, India
[**] Department of Chemistry, K.K.T.M. Govt. College, Pullut, Kodungallore, Kerala, India
[***] Rubber Research Institute of India, Kottayam, Kerala, India
[#] Corresponding author (e-mail: rani@cusat.ac.in)

silyl propyl) tetrasulphide (Si-69®). Recent practice involves the *in situ* generation of inorganic scaffolds within the polymer matrix by sol-gel method[5,6]. *In situ* synthesis of silica by sol-gel method requires a large amount of organic solvent and a long reaction time. It has been observed that silica can be incorporated in NR latex by *in situ* precipitation procedure. The vulcanisates prepared by this technique showed superior mechanical properties and rubber-filler interactions compared to those prepared from commercial silicas[7].The principal advantages associated with this technique are it's fairly low temperature requirement, easy route of incorporation and generation of the inorganic component into nano-dimensions.

Epoxidised NR is a modified form of NR with inherent reinforcement with silica. ENR (50 mol%) is found to have high interaction with the silanol groups of silica[8]. It has been reported that by using ENR as a component together with silica, it is possible to achieve significantly improved mechanical properties with respect to similar NR compounds[9]. In the present study we report a method for the preparation of *in situ* precipitated silica based NR compounds with ENR as a coupling agent. Precipitation of silica was done in an NR and ENR latex mix followed by coagulation of the latex. Compounds were prepared and cured up to the optimum cure time and the mechanical properties of the vulcanisates prepared by this technique are compared with those prepared from conventional silica.

EXPERIMENTAL

Materials

NR Latex of 60% dry rubber content (DRC) was supplied by Njavallil Latex, Kochi, India. NR of grade ISNR-5 and ENR 50 mol% latex of DRC 20% was obtained from the Rubber Research Institute of India, Kottayam, India. Sodium silicate 60% concentrate was supplied by Minar Chemicals, Kochi and other chemicals used were of commercial grade.

Preparation of *In situ* Silica Masterbatches

NR latex was filtered and stabilised with non-ionic stabiliser, Vulcastab VL®, mixed with required amount of ENR latex and stirred for 10 min. The required amount of sodium silicate (60%) was added and stirred for 1 h and a saturated solution of ammonium chloride was added drop-wise with constant stirring to precipitate the silica. The latex was coagulated as crumbs by the addition of 2% acetic acid. The crumbs were washed with water until the washings were neutral, pressed to remove water and dried in an air oven at 70ºC for 48 h. Two masterbatches with 20 p.h.r. and 40 p.h.r. silica were prepared with and without ENR. The details of the masterbatches are given in the *Table 1*.

Bound Rubber Content

The fraction of bound rubber in the masterbatches was determined by the following procedure adopted by Yoshikai and co-workers[10]. A specimen of 1mm thickness and 3 mm diameter was cut from the masterbatch and put into a previously weighed cage made of stainless steel wire gauze of 280 mesh. The cage was soaked in toluene at room temperature. The solvent was removed after three days. After seven days the cage was taken out, dried in air for 24 h and subsequently dried to constant weight in an air oven at 100ºC. The bound rubber fraction R_B was calculated from the insoluble rubber fraction using the following equation[6]:

$$R_B = W_{fg} - W\,[m_f / (m_f + m_p)] \,/\, W\,[m_p / (m_f + m_p)] \,{*}100 \qquad \ldots 1$$

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Where,

W_{fg} = Weight of filler and gel
W = Weight of specimen
m_f = Weight of filler in the compound
m_p = Weight of polymer.

Preparation of the Composite

The rubber with *in situ* precipitated silica was kept as the masterbatch and compounds were prepared by mill mixing. Different quantities were added to get the desired concentrations of silica in NR. Mixing was done in a laboratory size (16 cm × 33 cm) two-roll mill at a friction ratio of 1:1.25 as per *ASTM D 3182 (1982)*. The compounding formulation used in the present study is given in *Table 2*. After completion of mixing, the stock was passed six times through the tight nip and finally sheeted out at a fixed nip gap. The samples were kept overnight for maturation. Optimum cure time was determined using Rubber Process Analyser (RPA 2000 – Alpha Technologies). Blanks, cut from unvulcanised sheets were vulcanised at a temperature of 150ºC ± 2ºC and at a pressure of 200 kg cm^{-2} in an electrically heated hydraulic press, to their respective optimum cure times.

Mechanical Properties

Tensile tests. Dumbbell-shaped tensile and angle tear test specimens were punched out from the vulcanised sheets. The measurements were carried out at a crosshead speed of 500 mm per min on a Shimadzu Model AG1 Universal Testing Machine according to ASTM standards, *D 412-68* and *D 624-54*, respectively.

TABLE 1. COMPOSITION OF SILICA MASTER BATCHES (P.H.R.)

Sample name	NR (p.h.r.)	ENR (p.h.r.)	*In situ* silica (p.h.r.)
M-20-1	100	0	19.92
M-20-2	100	4	19.95
M-40-1	100	0	39.81
M-40-2	100	8	39.86

TABLE 2. RECIPE FOR THE PREPARATION OF SILICA-FILLED NR COMPOUNDS (P.H.R.)

Sample code	NR	Masterbatch	COM silica	Si-69®
GUM	100	0	0	0
INS-1	0	120 (M-20-1)	0	0
COM-1	100	0	20	0
CA-1	100	0	20	3
ENR-1	0	124 (M-20-2)	0	0
INS-2	0	140 (M-40-1)	0	0
COM-2	100	0	40	0
CA-2	100	0	40	6
ENR-2	0	148 (M-40-2)	0	0

Base formulation: ZnO–5; Stearic acid–2; DEG–1; Naphthenic oil–3/6; CBS–0.6; TMTD–0.2; Sulphur–2.5.

Abrasion resistance. The abrasion resistance of the samples were studied with a DIN Abrader (*DIN 53516*). Moulded samples of 6 mm ± 0.2 mm diameter and 6 mm thickness were prepared as per *ASTM D 3183* and abrasion loss was measured as per *ASTM D 5963-04*. Abrasion loss was calculated using the equation:

Abrasion loss = (Loss of wt./density) … 2

Hardness. Hardness of the samples was tested using a Zwick 3114 hardness tester. Moulded samples of 6 mm ± 0.2 mm were prepared as per *ASTM D 3183* and hardness was measured as per *ASTM D 2240-05*.

Rebound resilience. Rebound resilience is the energy given up on recovery from deformation to the energy required to produce the deformation. It is expressed as a percentage and measured using falling weight method in a Basore Resilometer as per *ASTM D 2632-01*.

Rubber-filler interaction studies. The strain sweep measurements on unvulcanised samples and vulcanisates were conducted to study the rubber-filler interaction. Filled rubber materials need special instruments for rheometrical testing. Rubber Process Analyzer (RPA 2000 – Alpha Technologies) is a purposely modified commercial dynamic rheometer[11]. The instrument was modified for capturing strain and torque signals, through an appropriate software. Filled rubber materials (vulcanised) exhibit strong non-linear viscoelastic behaviour, the well-known Payne effect, *i.e.* the reduction of elastic modulus with increasing strain amplitude[12]. RPA can do strain sweep tests in which the variation of storage modulus (G'), loss modulus (G'') and complex modulus (G^*) with the change in strain amplitude are measured. With respect to its measuring principle, the RPA cavity must be loaded with a volume excess of test material. In agreement with *ASTM 5289*, the manufacturers recommend to load samples of about 5 g, *i.e.* 4.4 cm^3 for a standard filled rubber compound with a specific gravity of 1.14 g/cc. Samples for RPA testing were consequently prepared by die cutting 46 mm diameter disks out of around 2 mm thick sheets of materials. The testing temperature was selected as 100ºC; a temperature below the curing temperature and the shear strain was varied from 0.5% to 100% keeping the frequency of measurements at 0.5 Hz.

For strain sweep measurements of cured compounds, uncured material is used as the test sample that is cured to its optimum cure time in the RPA cavity and then the strain sweep tests were carried out in a two-stage programme.

Crosslink density. The equilibrium swelling studies of the compounds were carried out in toluene and crosslink densities were calculated. A test sample of approximately 10 mm diameter and 2 mm thickness and 0.2 g weight was punched out from the central portion of the vulcanisates, accurately weighed (test sample *T*), and immersed in toluene in a closed vessel for 24 h. The swollen sample was taken out and weighed (*W*). The sample in vacuum was then kept in air for complete drying (removal of toluene) and weighed to get the dry sample weight (*D*). The volume fraction of the rubber, V_r can be calculated from:

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}} \qquad \dots 3$$

Where,

F = Weight fraction of insoluble components. It is the ratio of the sum of the weights of components like ZnO, fillers *etc.* which are insoluble in the solvent and total weights of all components as per the compounding recipe.

ρ_r = Density of rubber (for NR 0.92 g/cm^3)

ρ_s = Density of the solvent (for toluene 0.886 g/cm^3)

A_0 = Weight of absorbed solvent (W–D)

Knowing the value of V_r, the crosslink density (CLD) can be calculated from the Flory-Rhener equation[13]:

$$CLD = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{2\rho_r V_s (V_r)^{1/3}} \qquad \ldots 4$$

Where,

V_s = Molar volume of the solvent (for tolune it is 106.2 cc/mol)

χ = Interaction parameter of the rubber (for NR 0.42).

RESULTS AND DISCUSSION

In the *in situ* precipitation method, silica is obtained from sodium silicate in the latex medium. The chemistry behind the precipitation of the silica is the reaction between sodium silicate and ammonium chloride as shown below:

$Na_2SiO_3 + 2\,NH_4Cl \rightarrow 2\,NaCl + SiO_2 + {\uparrow}H_2O + NH_3$

The precipitation of silica was conducted after the uniform distribution of sodium silicate in rubber latex giving a fine distribution of silica in rubber latex. The polymer matrix prevents the agglomeration of silica and provides a reduced size for the silica particles. This is clear from the SEM pictures of the silica obtained after the ignition of silica masterbatch. For comparison, the SEM pictures of the *in situ* precipitated silica and commercially available nano silica VN3® are shown in the *Figures 1 (a)* and *1 (b)*.

Figure 2 shows the photographs of the sample containing *in situ* precipitated silica before and after ignition. In the case of the latex precipitated silica, the coagulum after burning the rubber particles away retained the initial shape indicating an improved uniform distribution in the rubber unlike in the case of conventional silica, which crumbled upon ashing.

Bound rubber content assessment is an indirect method to study the elastomer-filler interactions[14]. The bound rubber content depends on characteristics of filler such as surface area, structure or morphology and surface activity. An increased rubber filler interaction increases the bound rubber content.

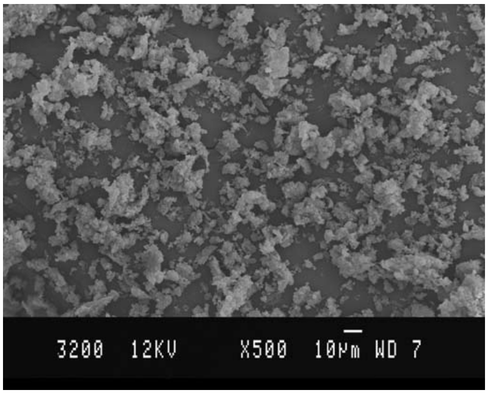


Figure 1(a). Scanning electron micrograph of in situ *precipitated silica.*

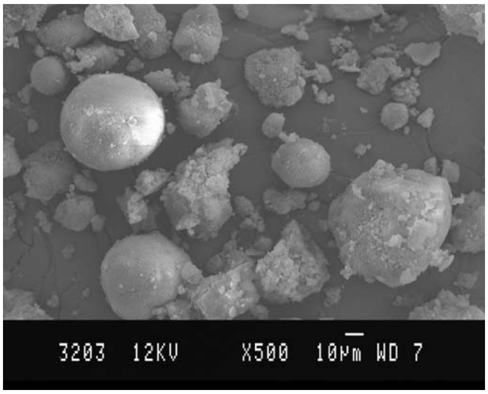


Figure 1(b). Scanning electron micrograph of VN3®.

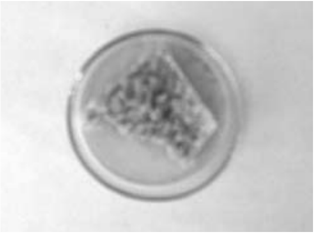


Figure 2(a). Photograph of sample containing in situ *silica before ignition.*

Figure 2(b). Photograph of sample containing in situ *silica after ignition.*

TABLE 3. BOUND RUBBER CONTENT OF SILICA MASTERBATCHES

Sample name	Bound rubber content (%)
M-20-1	80.13
M-20-2	84.92
M-40-1	85.22
M-40-2	87.95

The bound rubber content values of the masterbatches are shown in *Table 3*. The high values show better rubber-filler interaction.

The tensile properties of the composites are shown in *Figures 3* to *6*. *Figure 3* shows the tensile strength of different vulcanisates. It is interesting to note that INS-1 and CA-1 showed almost similar values. Addition of ENR was found to improve the tensile strength. Tensile strength decreased as the filler concentration increased to 40 p.h.r. This effect is well known[15] and can be attributed to poor wetting of the reinforcement particles at filler contents above the optimum composition. *In situ* precipitation gave reinforcement equivalent to that of using Si-69®. *In situ* precipitation in the presence of ENR showed further improvement in the mechanical properties indicating that ENR has a coupling effect on silica as shown in the dry rubber composites. Similarly tear strength values showed the same trend (*Figure 4*). But the tear strength increased with the increase in concentration of filler. *Figure 5* shows the tensile modulus of different composites. With 20 p.h.r. and 40 p.h.r. silica, the tensile modulus was in the order COM < INS < CA < ENR. The presence of a coupling agent increases the tensile modulus. But the *in situ* precipitated silica containing samples showed a little higher value of elongation at break (*Figure 6*). Other technological properties are given in the *Table 4*.

Hardness of the samples was found to be dependent on composition of the filler. They did not vary much with the type of filler, but abrasion loss values varied considerably with the type of filler incorporation. At both concentrations 20 p.h.r. and 40 p.h.r., *in situ* silica with ENR showed remarkably reduced abrasion loss. This is due to the strong adhesion of silica particles on rubber chains.

The coupling effect of ENR can be explained on the basis of the chemical interaction between the epoxy group and silanol groups[16], *i.e.* the polar part of ENR may be coupling with hydroxyl group in the silica. Under acidic

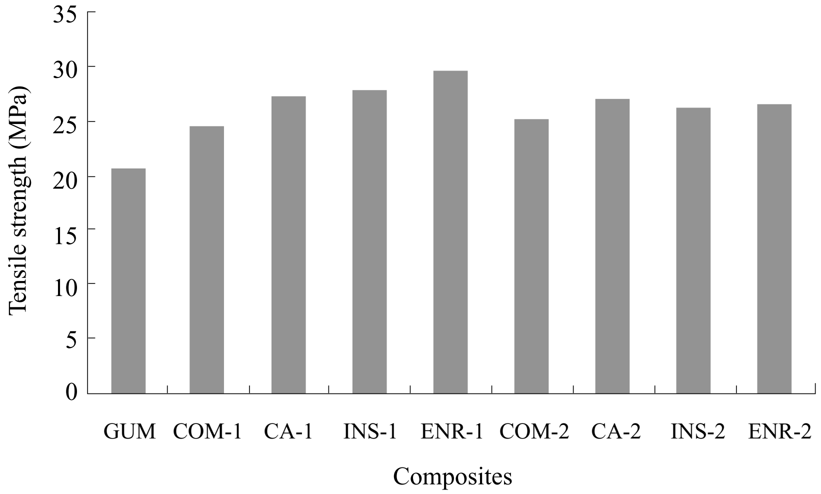


Figure 3. Tensile strength of different composites.

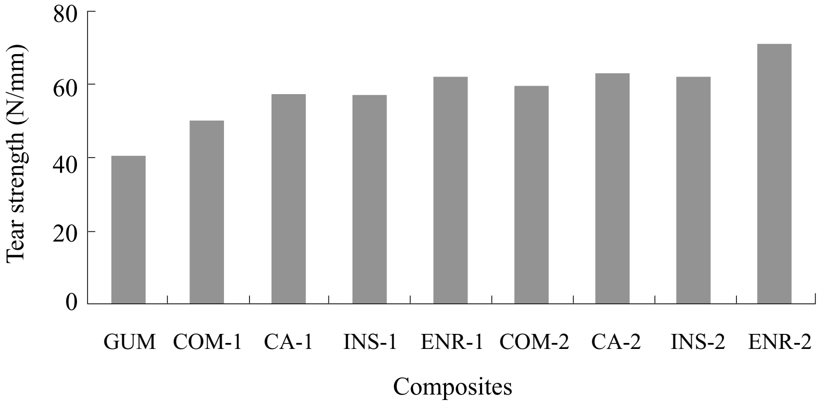


Figure 4. Tear strength of different composites.

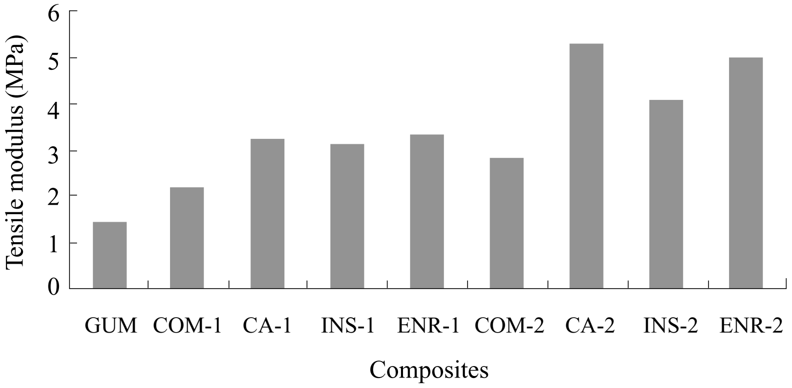


Figure 5. Tensile modulus of different composites.

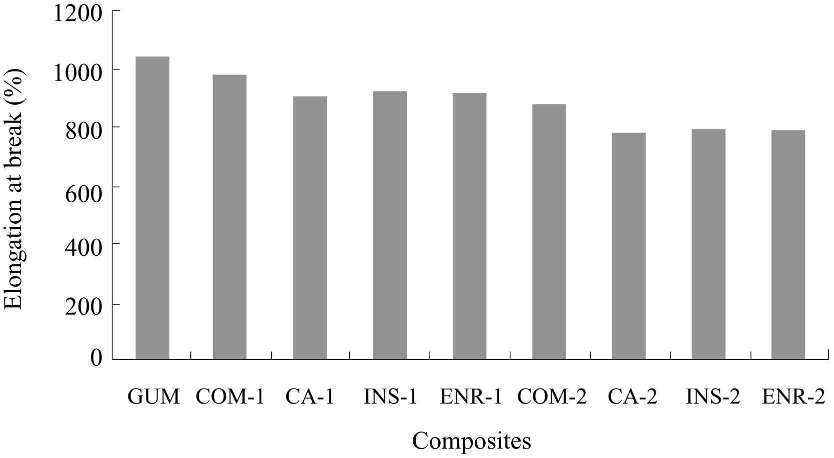


Figure 6. Elongation at break of different composites.

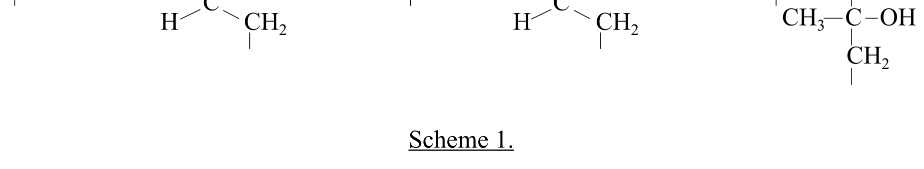
conditions, the epoxy groups are likely to open as a di-ol moiety which can form intermolecular hydrogen bond with the silanol groups of silica (*Scheme 1*).

The Scanning electron microscopic photographs of the tear fracture surfaces of vulcanisates with ENR and Si-69® are shown in *Figures 7 (a)* and *7 (b)*. The tear lines are more visible in the sample with ENR indicating a uniform distribution and improved binding of silica in rubber.

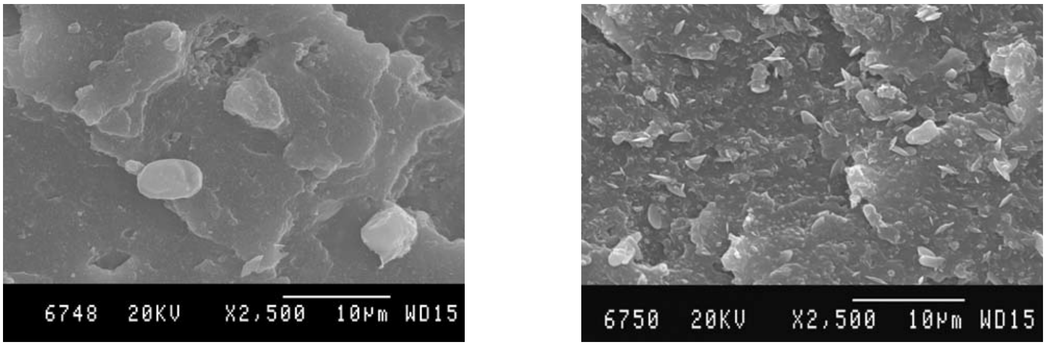
The elastic modulus of a filled rubber is experimentally and strongly dependent on deformation and decreases substantially at higher strains. This phenomenon is known as the Payne effect and is attributed to the presence and breakdown of the filler network during deformation; but investigations performed with both experimental and theoretical approaches showed that the decrease in G^* with the amplitude of deformation (strain) has been attributed to the destruction – reformation of a percolating network of filler[17]. This can also involve polymer bounded to the filler[18] *i.e.* with polymer-filler links too. The complex modulus values at low strains (<15%) are a measure of the filler-polymer interactioin[19,20]. So the variation of complex modulus with strain was studied for all the compounds before and after curing. The values obtained for the uncured compounds are plotted and shown in the *Figures 8* and *9*; *Figures 10* and *11* is for cured compounds. From the graphs it is clear that the compounds with ENR have

TABLE 4. TECHNOLOGICAL PROPERTIES OF THE COMPOUNDS

Sample name	Resilience	Hardness	Abrasion loss	Crosslink density
	(%)	(Shore A)	(mm^3)	($\times 10^{-5}$)
COM-1	65	45	320	4.741
CA-1	60	49	251	5.537
INS-1	58	48	254	6.651
ENR-1	58	48	224	6.852
COM-2	60	58	170	7.439
CA-2	54	60	159	8.212
INS-2	55	59	156	9.224
ENR-2	53	59	152	9.545



Scheme 1.



(a) (b)

Figure 7. SEM pictures of tear fracture surfaces of composites with ENR and with Si-69®.

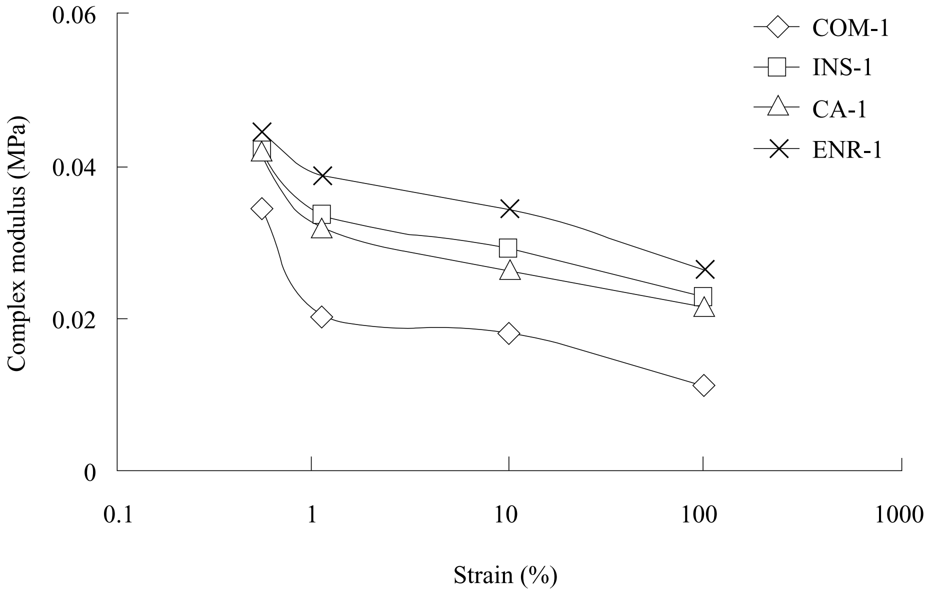


Figure 8. Variation of complex modulus with strain for uncured compounds (20 p.h.r.).

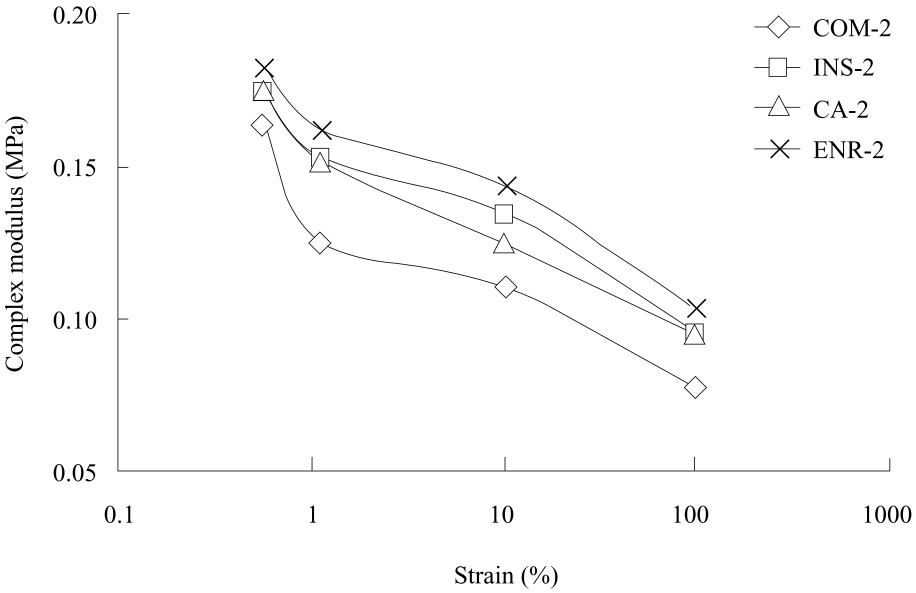


Figure 9. Variation of complex modulus with strain for uncured compounds (40 p.h.r.).

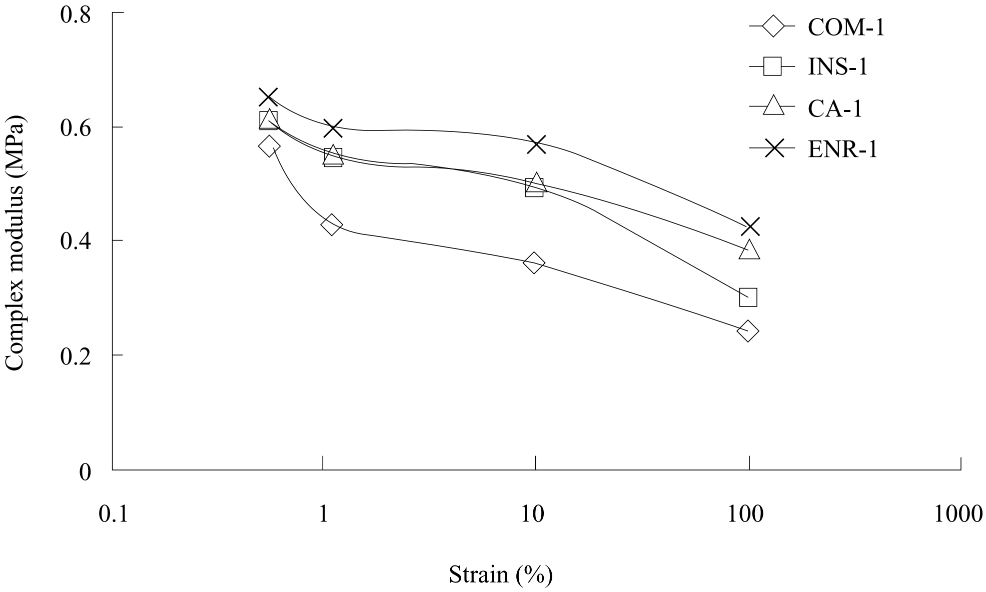


Figure 10. Variation of complex modulus with strain for cured compounds (20 p.h.r.).

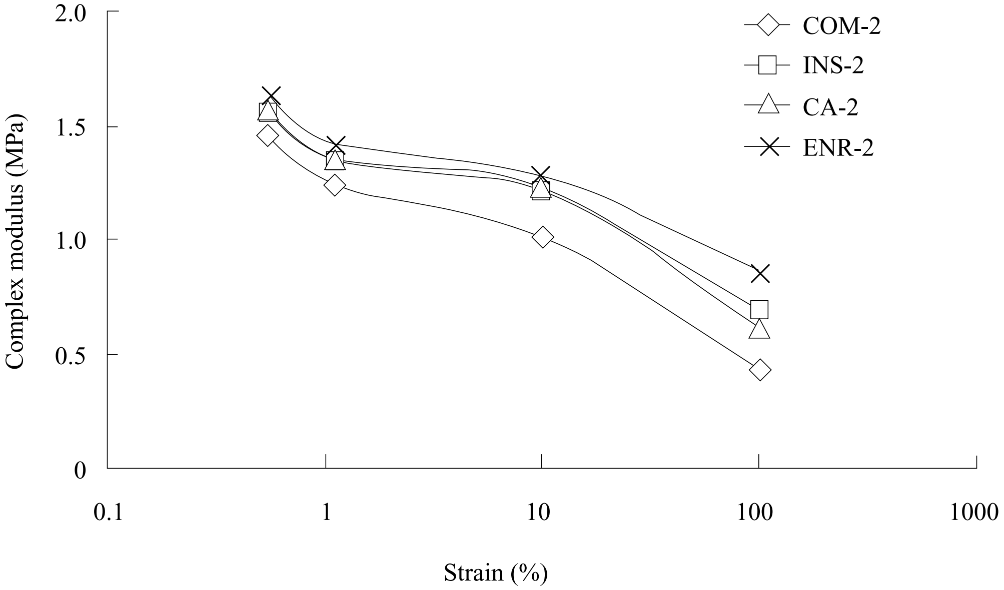


Figure 11. Variation of complex modulus with strain for cured compounds (40 p.h.r.).

comparatively high complex modulus values at low strains for both cured and uncured compounds compared to the compounds with Si-69®. So the high *G** values of composites with ENR may be considered as an indication of rubber-filler interaction, since all composites under comparison have the same filler content *i.e*. with same hydrodynamic effect and same polymer content. The additional crosslinks can also be confirmed by equilibrium swelling studies. *Table 4* shows the crosslink densities of the different compounds. The crosslink density of ENR-1 and ENR-2 are comparatively high, clearly indicating the presence of increased crosslinks.

CONCLUSIONS

ENR was found to act as a coupling agent for *in situ* silica and it yielded improved results when compared with Si-69®. Preparation of masterbatches with *in situ* silica coupled with ENR helped easier in the corporation of silica and gave improved mechanical properties and rubber-filler interactions.

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