Epoxidized Natural Rubber as a Reinforcement Modifier for Silica-Filled Nitrile Rubber

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ABSTRACT: Hydrated silicas impart better physical properties to polar rubbers, compared to those of hydrocarbon rubbers. However, to achieve optimum properties silane coupling agents are crucial in such formulations. Epoxidized natural rubber (ENR) in small proportions is used as a reinforcement modifier for silica-filled nitrile rubber (NBR). Two systems of cure were used: N-cyclohexyl-2-benzthiazyl sulfenamide (CBS) alone and in combination with diphenyl guanidine (DPG). In the CBS accelerated system, incorporation of an optimum concentration of about 15% of ENR on total rubber was found to improve technological properties. Addition of a secondary accelerator further improves these properties. Comparable results are obtained with those containing coupling agent and NBR–ISAF. High bound rubber and volume fraction values indicate a high polymer–filler interaction and gel content resulting from the NBR–ENR interaction. Results of this study reveal that ENR could be used as a reinforcement modifier for the NBR–silica system. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 292–306, 2002

Key words: epoxidized natural rubber; nitrile rubber; silica; reinforcement modifier

INTRODUCTION

Carbon blacks are known to be fillers that impart optimum reinforcing potential to rubber products. However, precipitated silica is also rated as a filler that imparts high tear strength, low heat buildup, and better compound adhesion characteristics.[1] Further, it is obtained from a regenerating source, unlike carbon blacks, which are manufactured from fossil feeds through highly energy demanding operations.[2] Hence reinforcement of rubbers with silica may be favored over carbon black on economic grounds. There is continuing interest to provide improved properties to non–black-filled rubber goods. Nitrile rubber (NBR), which remains amorphous under all con-

ditions, including stretching, requires reinforcing fillers in the manufacture of products. Hydrated silica imparts better physical properties to polar synthetic rubbers like NBR than it does to nonpolar rubbers like natural rubber (NR), styrene–butadiene rubber (SBR), and the like, and is used to produce colored articles that require high strength properties and also transparent and translucent products. Nitrile rubber reinforced with silica is used in the manufacture of rice dehusking rollers, which require nontoxicity, high performance, and resistance to abrasion, heat, and oil.

In contrast to carbon black, the surface characteristics of hydrated precipitated silica cause a number of difficulties in its use as a reinforcing filler, particularly in hydrocarbon elastomers. Thus a silane coupling agent is used to bind the polymer to silica, which takes place during vulcanization of the product, thus increasing the level

Table I Formulation of Compounds (CBS Cure)

Ingredient	1	2	3	4	5	6	7	8	9	10
Nitrile rubber	100	97.5	95	90	85	80	75	100	100	100
ENR-50	—	2.5	5.0	10	15	20	25	—	—	—
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ultrasil VN$_3$	50	50	50	50	50	50	50	50	50	—
DOP[a]	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
CBS[b]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Si-69	—	—	—	—	—	—	—	1.0	4.0	—
ISAF	—	—	—	—	—	—	—	—	—	50

[a] Dioctyl phthalate.
[b] N-Cyclohexyl-2-benzthiazyl sulfenamide.

of reinforcement.[1] However, the high cost of such chemicals is a limiting factor for its widespread use. Recent studies by Varkey et al.[3] indicated that, in small proportions, epoxidized natural rubber (ENR) can be used as an interface modifier for NR–silica systems. NBR and ENR can form blends with good compatibility.[4] The objective of the present study is to examine the possibility of using ENR as a reinforcement modifier for silica-filled nitrile rubber, substituting a silane coupling agent. These systems were compared with nitrile rubber reinforced with carbon black.

EXPERIMENTAL

Materials

Nitrile rubber: Aparene N 423-NS, manufactured by Gujarat Apar Polymers (India), having an acrylonitrile content of 33%.

ENR-50: Epoxidized natural rubber (50 mol %), prepared by epoxidizing NR latex using performic acid generated in situ.[5]

Hydrated silica: Ultrasil VN$_3$, manufactured by Degussa AG (Germany).

Coupling agent: Si-69 [bis(3-triethoxy propyl)-silyl tetrasulfide], manufactured by Degussa AG.

The other ingredients used were of commercial grade.

Preparation of Compounds

The formulations of the compounds are given in Tables I and II. The rubbers in different proportions were blended in a two-roll laboratory mixing mill for 5 min and the blend was used for making the compounds. A two-stage mixing procedure was followed. The first stage was done in a laboratory model internal mixer (Shaw Intermix-MK3, size KO, Manchester, England) whereby the polymer, filler, and process aids were mixed.

Table II Formulation of Compounds (CBS–DPG Cure)

Ingredient	11	12	13	14	15	16	17	18	19
Nitrile rubber	100	97.5	95	90	85	80	75	100	100
ENR-50	—	2.5	5.0	10	15	20	25	—	—
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ultrasil VN$_3$	50	50	50	50	50	50	50	50	50
DOP	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
DPG[a]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.0	1.0
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Si-69	—	—	—	—	—	—	—	1.0	4.0

[a] Diphenyl guanidine.

Table III   Formulation of Mixes

Ingredient	20	21	22	23	24	25	26	27	28	29	30
Nitrile rubber	100	90	85	80	75	50	100	90	85	80	75
ENR-50	—	10	15	20	25	50	—	10	15	20	25
Ultrasil VN₃	—	—	—	—	—	—	50	50	50	50	50

The initial mixing temperature and rotor speed were 40°C and 60 rpm, respectively. The batch was dumped after 10 min. The curatives were incorporated in the second stage of mixing in a two-roll mill.

To assess the interpolymer interaction of NBR and ENR at the vulcanization temperature, a separate experiment was conducted. The rubbers in different proportions, as given in Table III (compounds 20–25), were blended in a laboratory model two-roll mixing mill for 5 min. Rheographs of the mixes at 150°C were taken and were used to quantify the polymer–polymer interaction resulting in crosslinks. To evaluate the added interaction of silica in the blend it was mixed with filler according to the formulation given in Table III (compounds 26–30), in a laboratory model internal mixer at a mixing temperature of 40°C at 60 rpm for 10 min. Rheographs of these mixes at 150°C were also taken.

Physical Testing

Cure characteristics of the compounds were determined using a Monsanto R-100 rheometer (Monsanto, St. Louis, MO) at 150°C. Test samples were molded using an electrically heated hydraulic press to their respective optimum cure times. Properties of the vulcanizates were tested according to the following standards:

Stress–strain properties: ASTM D 412-80 (Zwick UTM, model 1474)

Tear strength: ASTM D 624-91 (Zwick UTM)
Hardness: ASTM D 2240-95 (Shore A)
Resilience: ASTM D 1054 (Dunlop tripsometer)
Heat buildup: ASTM D 623 (Goodrich flexometer)
Compression set: ASTM D 395-89, Method B
Abrasion resistance: DIN 53516
Aging resistance: ASTM D 573-83

Bound Rubber Content

For the measurement of bound rubber content, samples of rubber compound were placed in a stainless steel cage and immersed in toluene at room temperature. The solvent was renewed after 3 days. After 7 days, the steel cage with the swollen sample was removed from the solvent. The samples were dried in air for 24 h and subsequently dried to constant weight in an oven at 115°C. The bound rubber of the polymer (R_B) was then calculated as described by Wolf et al.[6]

Volume Fraction of Rubber

The volume fraction of rubber in the swollen vulcanizate was determined by the equilibrium swelling of the vulcanized sample pieces in toluene at 30°C, according to the method suggested by Ellis and Welding.[7] A modified preswelling procedure,[8] which was designed to break polymer–filler bonds, was also used to determine the polymer–filler attachment on the effective number of network chains.

Table IV   Cure Characteristics (CBS Cure)

Parameter	1	2	3	4	5	6	7	8	9	10
Minimum torque, dN · m	9.0	10	12	26	26	20	21	18	8	12
Maximum torque, dN · m	39	38	42	74	84	78	83	80	57	52
Δ, Rheometric torque, dN · m (Max. − Min.)	30	28	30	48	58	58	62	62	79	40
Optimum cure time (t_{90}) at 150°C, min	74	63	52	52	50	49	49	58	56	16
Scorch time (ts_2) at 150°C, min	20.5	18.5	15.0	14.0	12.0	11.5	11.5	14.0	13.5	5.5
Cure rate index $[100/(t_{90} - ts_2)]$	1.57	2.25	2.70	2.63	2.63	2.67	2.67	2.27	2.35	9.5

Table V. Cure Characteristics (CBS–DPG Cure)

Parameter	11	12	13	14	15	16	17	18	19
Minimum torque, dN · m	21	26	26	26	26	27	26	17	14
Maximum torque, dN · m	98	98	98	102	105	106	106	100	114
Δ, Rheometric torque, dN · m (Max. − Min.)	77	72	72	76	79	79	80	83	100
Optimum cure time (t_{90}) at 150°C, min	49.5	32.0	32.0	30.5	27.5	25.5	26	39	34
Scorch time (ts_2) at 150°C, min	8.0	6.0	6.0	5.5	5.0	4.0	4.5	5.5	4.5
Cure rate index [$100/(t_{90} - ts_2)$]	2.3	3.9	3.9	4.0	4.5	4.7	4.7	3.0	3.4

RESULTS AND DISCUSSION

Cure Characteristics

The cure characteristics of the two sets of compounds, N-cyclohexyl-2-benzthiazyl sulfenamide (CBS) and CBS–diphenyl guanidine (DPG) combination, are given in Tables IV and V, respectively. Silica-filled nitrile rubber compounds, containing different concentrations of ENR and Si-69 as reinforcement modifiers, were compared with an Intermediate Super Abrasion Furnace black (ISAF)-filled nitrile rubber compound and an unmodified control compound. Cure characteristics of silica-filled compounds were found modified with incorporation of those modifiers. Maximum torque and differential torque were found to have increased with incorporation of ENR, indicating the likely formation of additional crosslinks by polymer–polymer and polymer–filler interactions. The polymer–polymer interaction resulting in chemical crosslinks was assessed through the rheometric study of compounds 20–25 of Table III. The respective rheographs are given in Figure 1. For mixes 20–25, a gradual increase in torque was noted with increasing concentration of ENR. The increased torque might have resulted from NBR–ENR interaction. It was reported earlier that acetonitriles can open the epoxy ring by the following mechanism[9]:
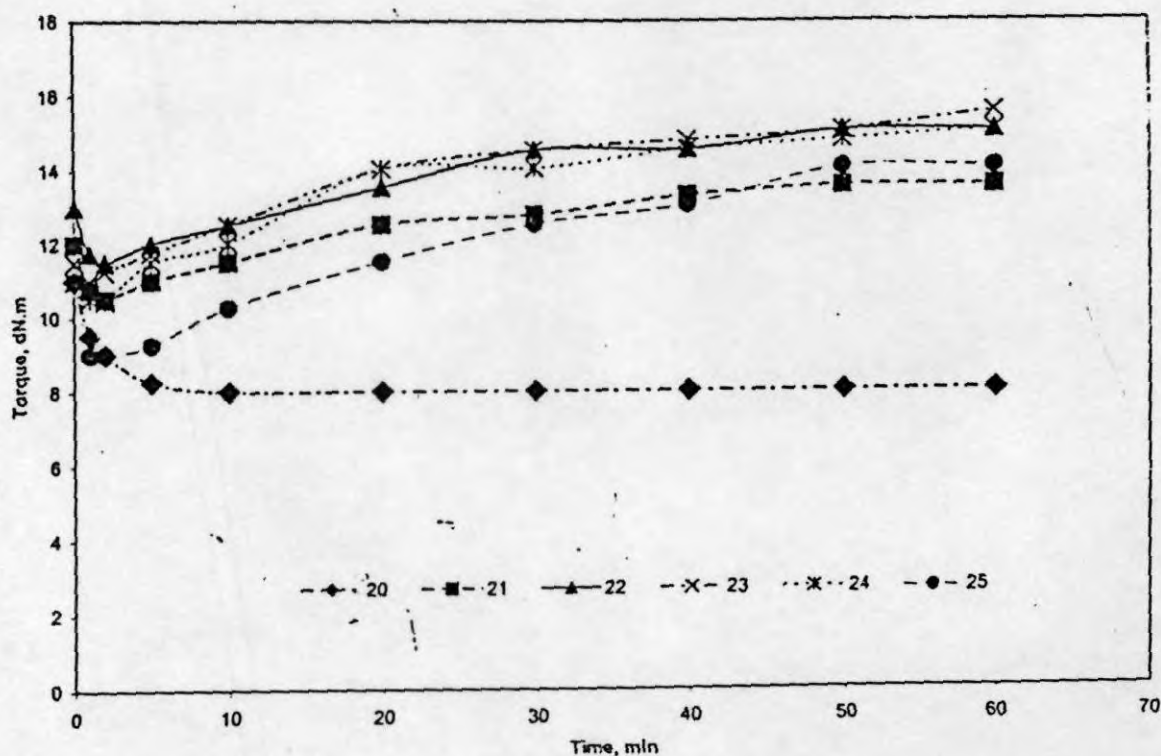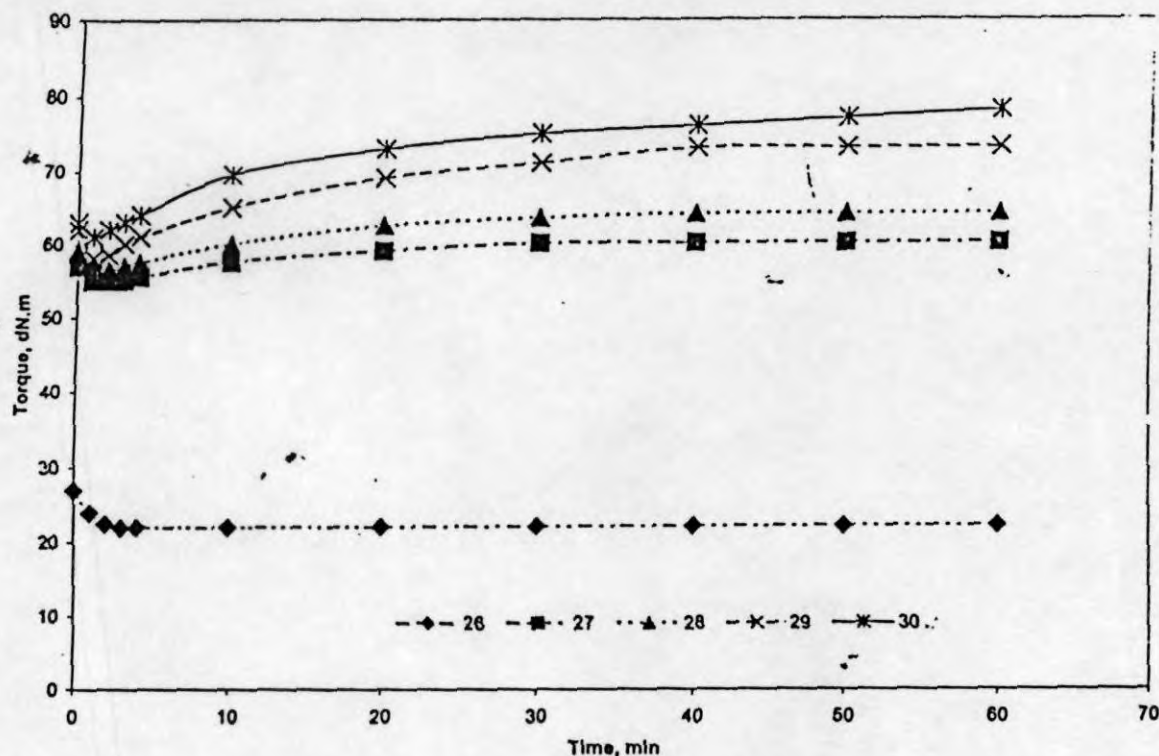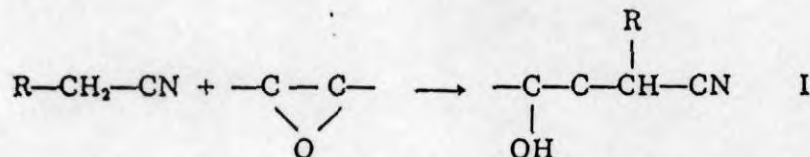

Figure 1 Rheograph of the gum compounds.

Figure 2 Rheograph of the filled compounds.

$$R-CH_2-CN + \underset{\underset{O}{\diagdown\diagup}}{-C-C-} \longrightarrow \underset{OH}{-C-C-}\overset{R}{\underset{|}{CH}}-CN \qquad I$$

A similar interaction might have occurred in the case of NBR–ENR blends, resulting in crosslinked structures, as evidenced from the

rheometric study. Earlier investigators[10] reported that the epoxy group of ENR can also react with the hydroxyl group of silica as follows.

$$\equiv SiOH + \underset{\underset{O}{\diagdown\diagup}}{CH_2-CHR} \longrightarrow \underset{OH}{\equiv SiOCH_2CHR} \qquad II$$

The contribution of rubber–silica interaction achieved through the incorporation of ENR was evaluated by rheometric study of compounds 26–30. The rheographs are given in Figure 2. The observed torque enhancement with ENR addition was higher in the filled mixes than that in the corresponding gum mixes. A comparison of the differential torque obtained from the rheographs of gum and filled mixes is shown in Table VI. The

increase in differential torque observed for the filled mix over the gum is taken as a measure of polymer–filler interaction. Enhanced differential torque with increased concentration of ENR showed a progressive improvement in rubber–filler interaction. Maximum torque and differential torque were found increased with incorporation of a coupling agent in a pattern similar to that obtained for compounds containing ENR as

Table VI Rheometric Data

Mix No./ Identification	Differential Torque, dN · m (Max − Min)	Increase in Differential Torque, dN · m (Filled − Gum)
21 (gum)	3	
27 (filled)	5	2
22 (gum)	3.5	
28 (filled)	8	4.5
23 (gum)	5	
29 (filled)	15	10
24 (gum)	5.25	
30 (filled)	17	11.75

modifier. The rheometric study of compounds given in Table III showed that ENR can serve as a coupling agent in a pattern similar to that of silane coupling agent, given that it can interact with both NBR and silica. ENR can interact with NBR through the crosslinks formed by the mechanism given in (I) and also through sulfur crosslinks, whereas silica interacts with the rubber through the mechanism given in (II). The NBR–ISAF composite exhibited higher values of maximum and differential torque than those of NBR–silica composites but lower compared to those containing modifiers.

With increased concentration of ENR, an increase in the minimum rheometric torque, an indication of compound viscosity was noted. The observed increased compound viscosity, in general, can be attributed to polymer–polymer and polymer–filler interactions.

The optimum cure time (t_{90}) and scorch time (ts_2) were found decreased and the cure rate index (CRI) increased with increased concentration of ENR, the values of which were closer to those of mixes containing a coupling agent. However, in carbon black–filled mixes, t_{90} and ts_2 were lower and CRI higher.

Bound Rubber

Bound rubber (R_B) measurement is conventionally being done to assess the rubber–filler interaction; the higher the bound rubber, the higher the polymer–filler interaction.[11] In the present experiment, the bound rubber content of a few selected NBR–silica mixes with and without modifiers and that in NBR–ISAF mix were measured. The results are given in Table VII. Silica-filled mixes containing modifiers and the NBR–ISAF mix showed higher R_B values than those of the unmodified samples. With an increase in concen-

tration of the silane coupling agent, an increase in bound rubber was noted. ENR-modified samples gave much higher R_B values than those of modified samples with coupling agent and NBR–ISAF mix. With increased concentration of ENR, an increase in R_B value was noted. The unusually high values might have resulted from the combined effects of polymer–filler interaction and the gel content resulting from the NBR–ENR interaction mentioned earlier. Tan et al.[11] reported that the gel content resulting from the polymer–polymer network can contribute to higher values of bound rubber. The higher R_B value in NBR–ISAF mix over that of the NBR–silica mix is attributed to the larger polymer–filler interaction for carbon blacks in NBR.[11]

Volume Fraction of Rubber

The volume fraction (V_r) of rubber obtained from swelling studies is an indication of the crosslink density of the sample. Data in Table VIII show the effect of modifiers on the V_r of different samples. NBR–silica composites containing modifiers showed higher V_r values than those of the unmodified. The increased volume fraction with the incorporation of modifiers can be attributed to increased crosslink density. It was seen that V_r

Table VII Bound Rubber

Mix No./Identification	Bound Rubber (R_B)
11 (NBR–Silica)	27.16
14 (NBR–10ENR–Silica)	40.44
15 (NBR–15ENR–Silica)	41.59
18 (NBR–2%Si-69)	29.12
19 (NBR–8%Si-69)	31.36
10 (NBR–ISAF)	34.81

Table VIII Volume Fraction of Rubber (CBS–DPG Cure)

Mix No.	V_r	V_r After NH_3 Treatment
11	0.2919	0.2490
12	0.3057	0.2586
13	0.3188	0.2692
14	0.3291	0.2775
15	0.3383	0.2845
16	0.3363	0.2843
17	0.3374	0.2849
18	0.3483	0.2793
19	0.3490	0.2796

progressively increased on increasing the ENR content up to a certain concentration. Crosslinks might have resulted from not only the NBR–ENR interaction but also the sulfur crosslinks. ENR–silica interaction also might have contributed to the higher V_r values. The silane coupling agent itself, also a crosslinking agent, gave higher V_r values for the composites containing it. The V_r after ammonia treatment is considered to be a quantification of the crosslinks, excluding the physically bonded polymer–filler bonds.[8] All the samples gave lower V_r values after ammonia treatment. The difference in V_r values, as obtained from swelling measurements in toluene in the original vulcanizate and the same after ammonia treatment, gives a measure of rubber–filler interaction. Samples containing the optimum concentration of ENR gave higher V_r values even after ammonia treatment, indicating the presence of permanent crosslinks in such composites that cannot be broken by ammonia.

Vulcanizate Properties

The technological properties of selected samples from mixes given in Tables I and II are shown in Tables IX and X, respectively, and in Figures 3 to 12.

Stress–Strain Properties

Stress–strain properties of selected samples from mixes given in Table I and II are represented in Figures 3 and 4, respectively.

It can be observed that the stress–strain properties were modified with the incorporation of ENR and are comparable to those of composites modified with silane coupling agent and the one containing ISAF.

Table IX Technological Properties (CBS Cure)

Parameter	1 (NBR–Silica)	4 (NBR–10ENR–Silica)	5 (NBR–15ENR–Silica)	8 (NBR–2%Si–69–Silica)	9 (NBR–8%Si–69–Silica)	10 (NBR–ISAF)
Modulus at 100% elongation, MPa	1.2	2.9	3.7	2.3	2.6	3.1
Modulus at 300% elongation, MPa	1.9	8.3	12.2	7.2	10.3	13.6
Tensile strength, MPa	14.7	20.4	21.8	23.2	23.6	23.4
Elongation at break, %	928	583	537	707	535	458
Tear strength, kN/in	41.4	63.6	65.3	66.2	65.4	64.7
Abrasion loss, mm³	108.4	85.6	84.5	82.7	81.4	77.2
Resilience, %	45.7	36.5	34.1	41.6	42.7	37.7
Hardness, Shore A	58	73	74	66	68	64
Compression set, %	55.2	36.6	35.9	34.1	31.3	32.5

Table X Technological Properties (CBS-DPG Cure)

Parameter	Mix No./Identification					
	11 (NBR–Silica)	14 (NBR–10ENR–Silica)	15 (NBR–15ENR–Silica)	18 (NBR–2%Si-69–Silica)	19 (NBR–8%Si-69–Silica)	10 (NBR–ISAF)
Modulus at 100% elongation, MPa	1.8	3.7	3.8	2.4	3.3	3.1
Modulus at 300% elongation, MPa	4.4	12.7	13.6	9.6	12.8	13.6
Tensile strength, MPa	19.5	21.5	23.7	23.8	23.9	23.4
Elongation at break, %	677	507	456	557	446	458
Tear strength, kN/m	55.9	65.3	66.0	67.5	64.7	64.7
Abrasion loss, mm^3	106.3	85.2	84.0	82.0	78.5	77.2
Resilience, %	43.4	41.8	42.8	42.8	43.9	37.7
Hardness, Shore A	70	74	74	72	72	64
Heat buildup, ΔT°C	71	61	59	65	61	65
Compression set, %	41.2	34.5	34.0	33.4	31.0	32.5

Modulus

Variations in tensile modulus of ENR-modified composites for the two systems of cure are given in Figure 5. For both cure systems, a slight increase in 100% modulus was observed with increased concentration of ENR and coupling agent; further, the modulus values for NBR/ENR blend containing 15 parts of ENR were higher than those observed with a coupling agent and were closer to those of NBR–ISAF composite. Modulus at 300% elongation is also given in Figure 5. Incorporation of ENR into the silica composites was found to have improved the modulus for both systems of cure. The increased crosslink density resulting from polymer–polymer and polymer–filler interactions might have contributed to the modulus enhancement. This is also supported by the V_r values. The silane coupling agent, which is itself a crosslinking agent, increases the crosslink density of the composites, thereby enhancing the modulus.[12] The modulus was found to increase by increasing the concentration of the coupling agent. For the CBS-accelerated composite the modulus increase was more pronounced with higher concentrations of ENR and the value obtained with 15 parts of ENR was even higher than that obtained for composites containing 8% Si-69. The secondary accelerator system improved the modulus in all cases. For this system also, the modulus achieved for silica-filled NBR modified with 15 parts of ENR was found to be higher than that of the same modified with Si-69 and the value was closer to that of the NBR–ISAF composite.

Tensile Strength and Elongation at Break

Improved tensile strength and reduced elongation at break (EB) are considered as criteria for higher filler reinforcement.[13] Figure 6 shows the variation in tensile strength and EB of ENR-modified composites for the two cure systems. These two properties are also related to the nature and number of crosslinks. For the CBS cure system, tensile strength showed an increase up to 15 parts of ENR and then decreased, whereas EB showed a continuous decrease with increased ENR concentration. Up to 5 parts of ENR, the changes were not very marked, beyond which a sharp difference in both cases was noticed. Increased tensile strength and reduced EB with increased concentration of ENR can be attributed to increased interaction between the polymers and with polymer and filler. Improved tensile strength and re-
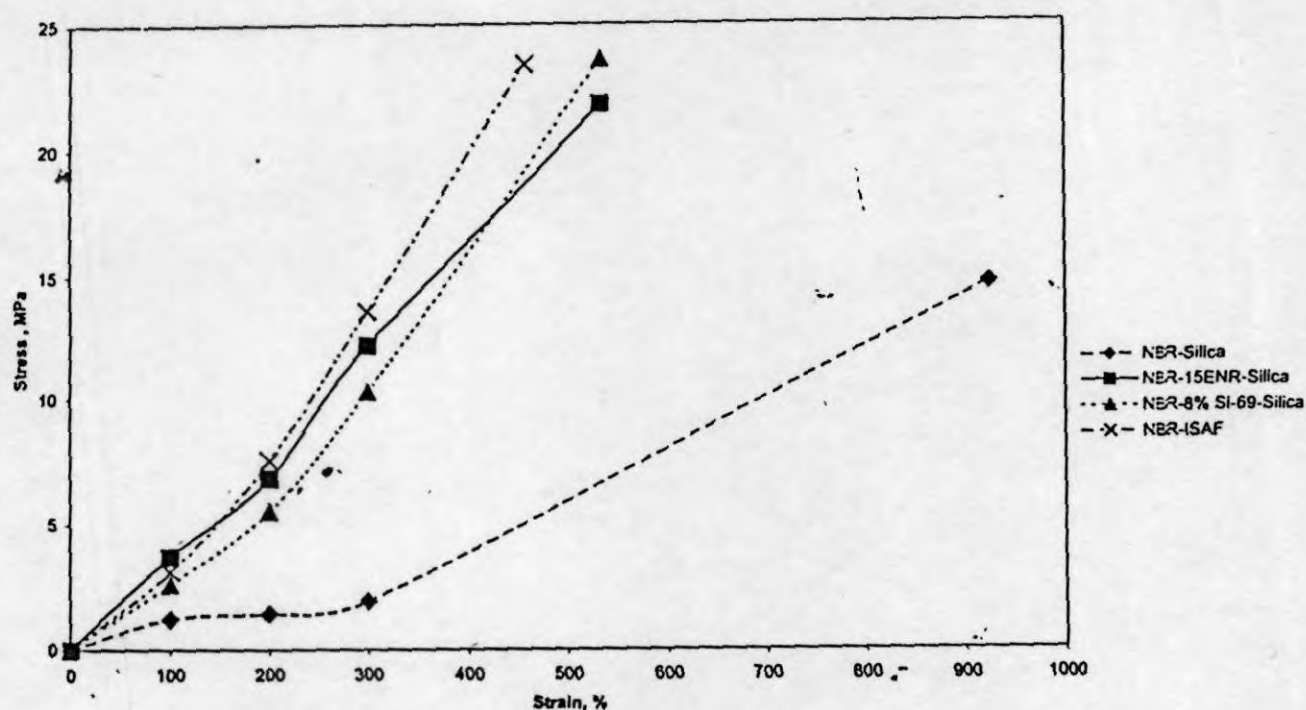
Figure 3   Comparision of the stress–strain property (CBS cure).

duced EB achieved with ENR addition for the CBS-based cure systems were found further enhanced by the incorporation of a secondary accel-

erator. Here also tensile strength showed an increase up to 15 parts of ENR and then decreased, whereas EB showed a continuous decrease with
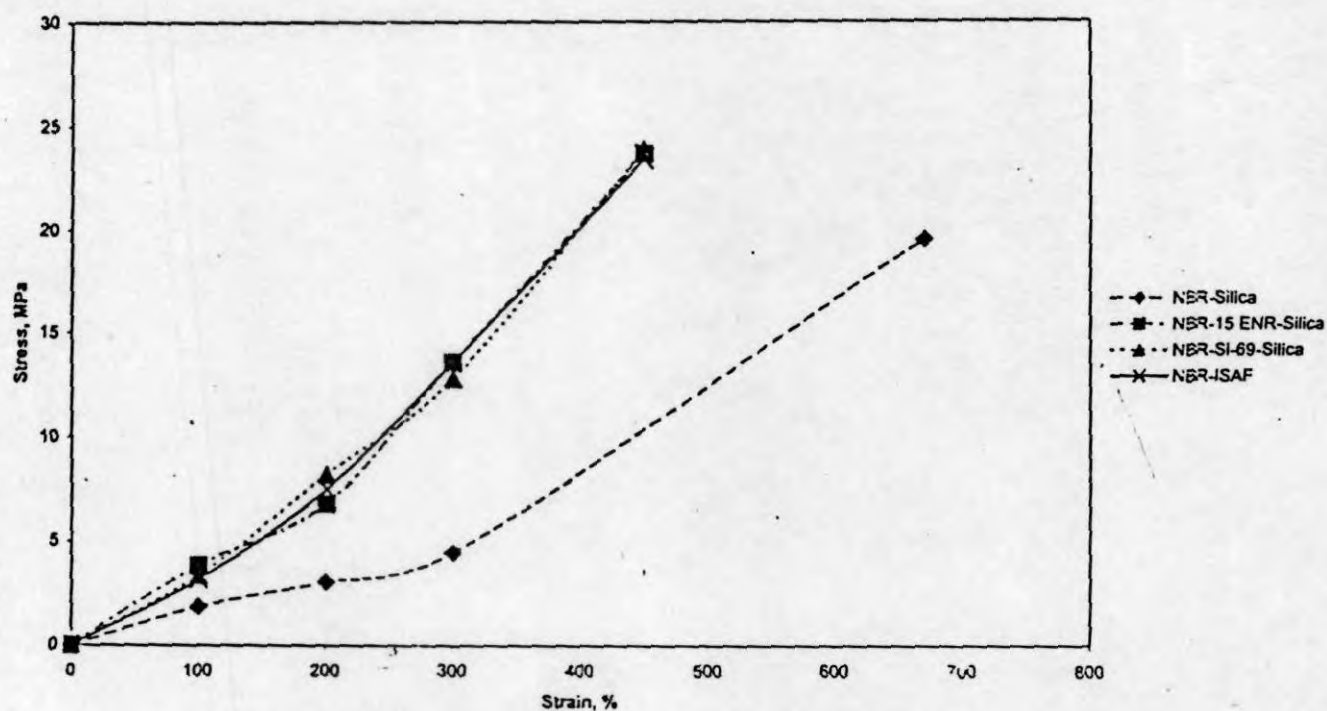

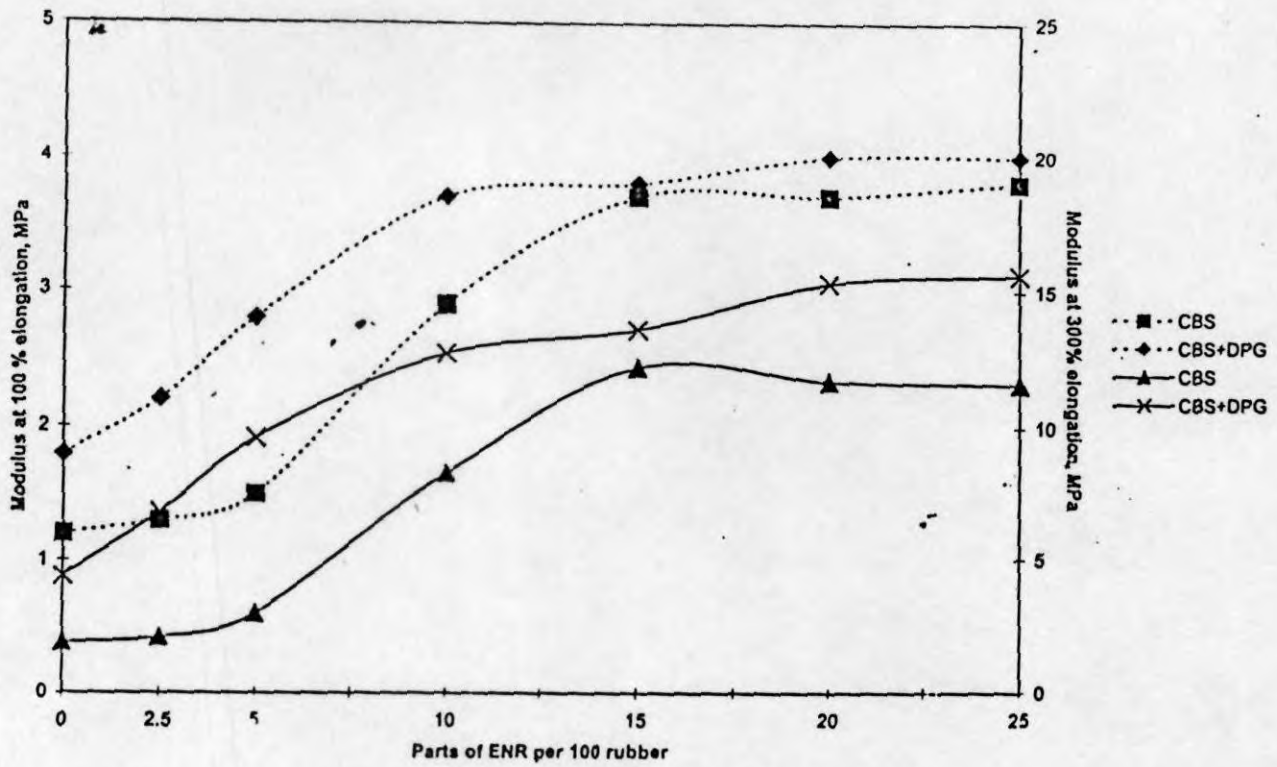Figure 4   Comparision of the stress–strain property (CBS–DPG cure).
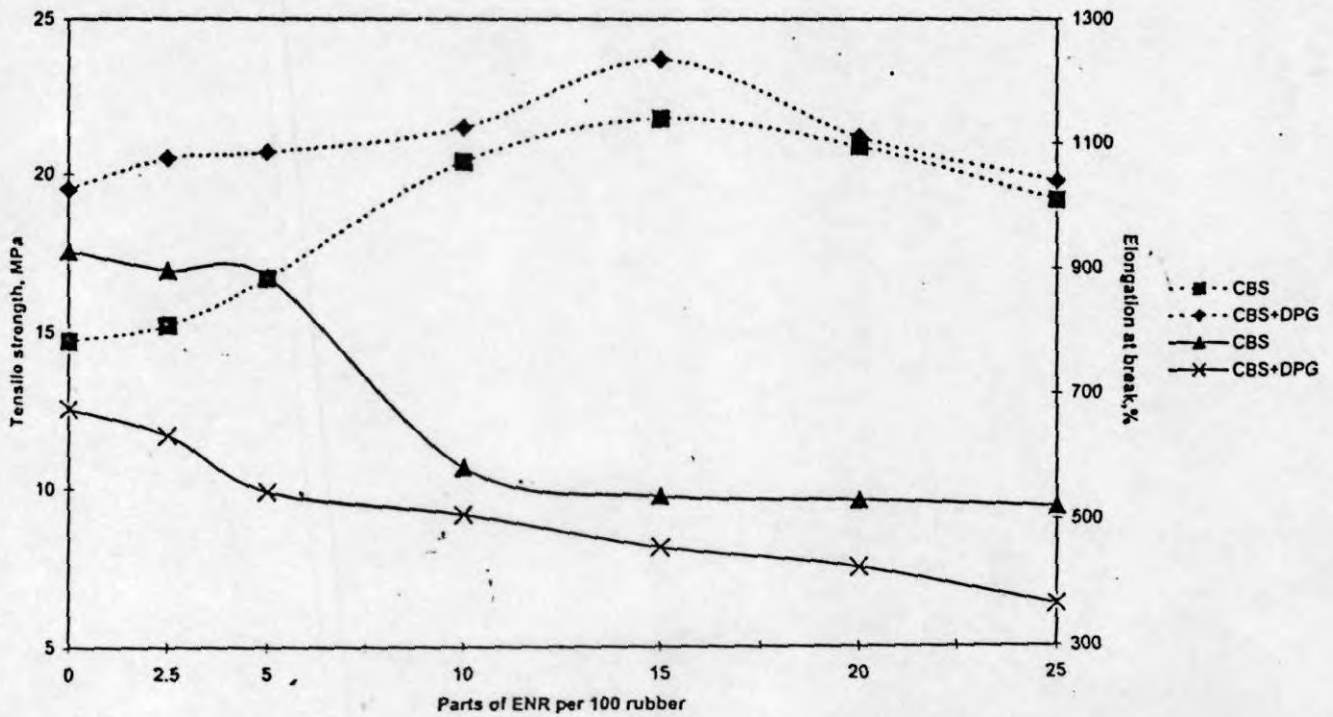
Figure 5   Variation in modulus with ENR incorporation.

Figure 6   Variation in tensile strength and elongation at break with ENR incorporation.
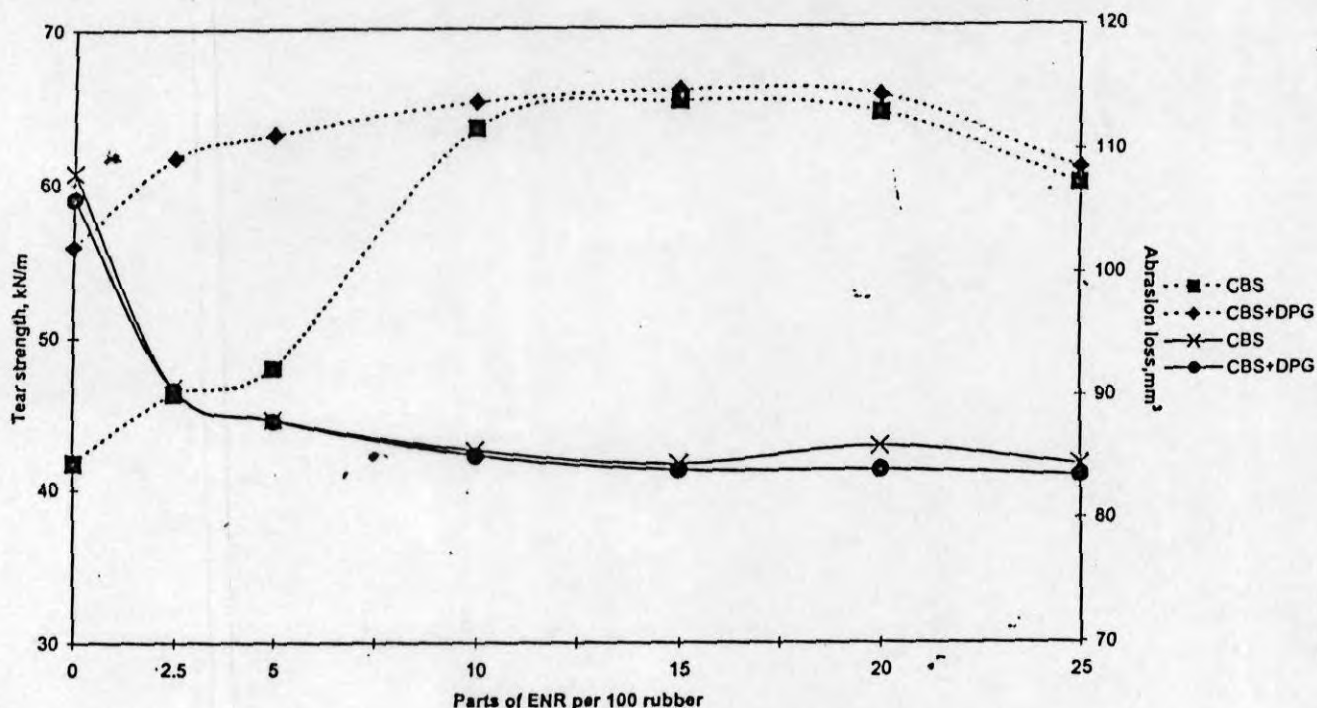
Figure 7   Variation in tear strength and abrasion loss with ENR incorporation.

increase in concentration of ENR. Higher concentrations of coupling agent could not impart any further enhancement in tensile strength while EB decreases. From Tables IX and X it was observed that 15 parts of ENR incorporation was sufficient for obtaining tensile strength values comparable to those of Si-69-modified and NBR–ISAF composites. EB values obtained with 15 parts of ENR were closer to those of NBR modified with 8% coupling agent and NBR–ISAF composite.

Tear Strength and Abrasion Resistance

Variations in tear strength and abrasion loss for different compositions of silica-filled NBR/ENR blends for the two cure systems are given in Figure 7. Improvements in tear strength and abrasion resistance are measures of enhanced filler reinforcement.[14] For both cure systems, tear strength showed an increase up to 15 parts of ENR and then showed a decrease with increased concentration of ENR. With the CBS cure system, beyond 5 parts of ENR incorporation, the increase in tear strength was sharp. Improved tear strength observed for composites modified with a coupling agent and ISAF could also be achieved for the NBR–silica composite modified with a limiting concentration of ENR, as can be observed from the data given in Tables IX and X.

Substitution of NBR with ENR and incorporation of a coupling agent in NBR–silica composites improved their abrasion resistance to a greater extent than that of the unmodified for both cure systems. With the binary accelerated system, the improvement in abrasion resistance observed over that of the CBS system was only marginal. NBR–ISAF and NBR–silica containing a coupling agent showed the maximum resistance; however, the NBR–silica composite modified with 15 parts of ENR cured with both systems exhibited comparable values, as can be seen from Tables IX and X.

Improved tear strength and abrasion resistance observed for the ENR-modified composites can be attributed to the enhanced polymer–polymer and polymer–filler interactions achieved through ENR.

Resilience and Hardness

Figure 8 shows the variation in resilience and hardness of NBR–silica composites modified with varying proportions of ENR for both cure systems. With the CBS cure system, resilience showed a continuous decrease, whereas hardness showed an increase and then remained almost steady with increased concentration of ENR. The changes were not very marked up to 5 parts of
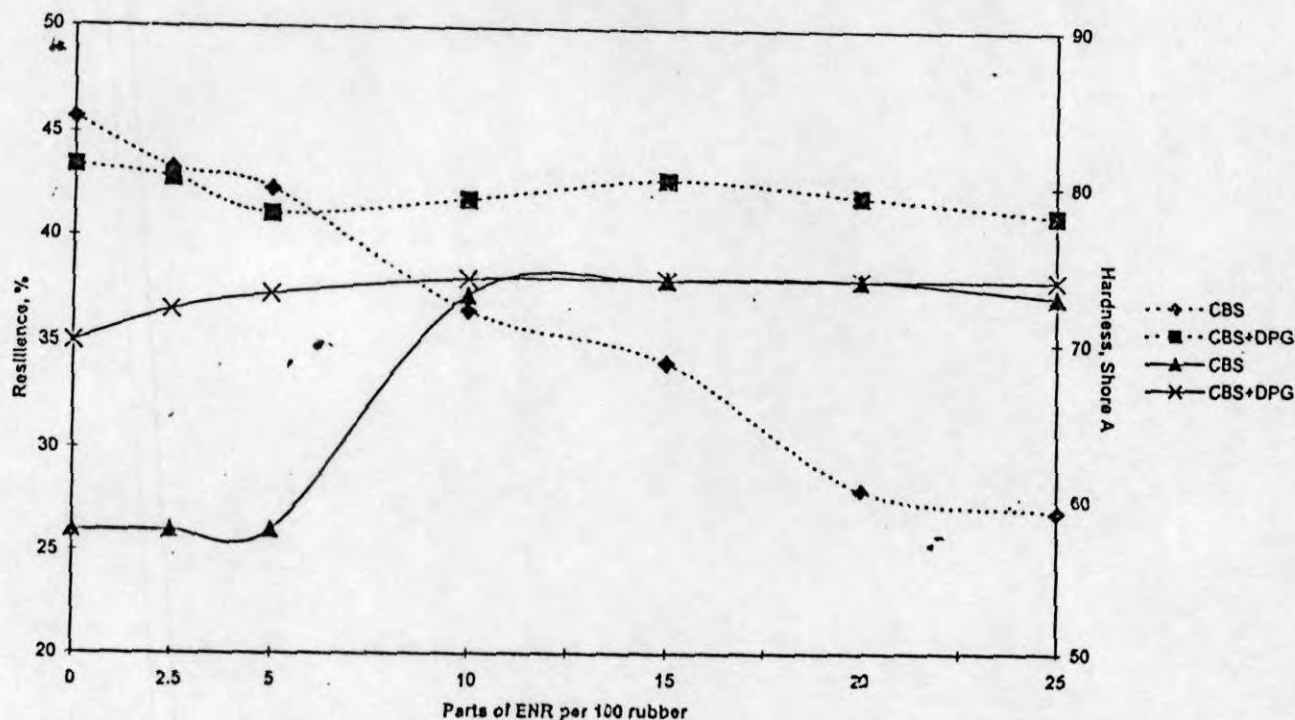
Figure 8   Variation in resilience and hardness with ENR incorporation.

ENR, beyond which a sharp fall in resilience and an increase in hardness were noted. For the CBS-DPG combination, no marked difference in resilience was noticed with ENR incorporation. For both cure systems, beyond 10 parts of ENR, hardness remained almost closer, whereas lower resilience values were noted for the CBS system. This discrepancy may be the result of the difference in the nature of crosslinks formed. For the CBS cure system, the optimum cure times of the mixes were higher than those for the corresponding binary system. This might have produced more NBR-ENR crosslinks, resulting in reduced polymer mobility and hence reduced resilience.

From Tables IX and X it was observed that the resilience value obtained for the composite modified with 15 parts of ENR for the binary cure system was closer to that of those modified with the silane coupling agent. The resilience of the unmodified silica-filled compound was scarcely altered with the change in cure system. The resilience value observed (Table IX) for the carbon black–based composite was closer to that of the silica-filled composite modified with ENR. The hardness values obtained for the composites modified with a limiting concentration of ENR for both cure systems were higher than those modified with Si-69 and NBR-ISAF composite. This may be attributable to increased crosslink density

resulting from ENR incorporation, as reflected in the V_r values.

Compression Set and Heat Buildup

Variations in compression set and heat buildup for different compositions of silica-filled NBR/ENR blends for the two systems of cure are given in Figure 9. For both cure systems, a reduction in compression set with incorporation of ENR was noted, which can be attributed to the increased crosslink density achieved through it. With increased concentration of coupling agent a reduction in compression set was noted. The set values obtained for NBR–silica composites modified with an optimum concentration of ENR was closer to that obtained for the coupling agent, as is seen from Tables IX and X.

With the dual accelerated system, there was a reduction in heat buildup up to 15 parts of ENR, after which there was a slight increase with increased ENR concentration. Reduction in heat buildup observed with ENR incorporation can be attributed to the increased crosslinks resulting from the interaction between the polymers and between the polymer and filler. Higher concentrations of coupling agent can allow a considerable reduction in heat buildup. With 15 parts of ENR
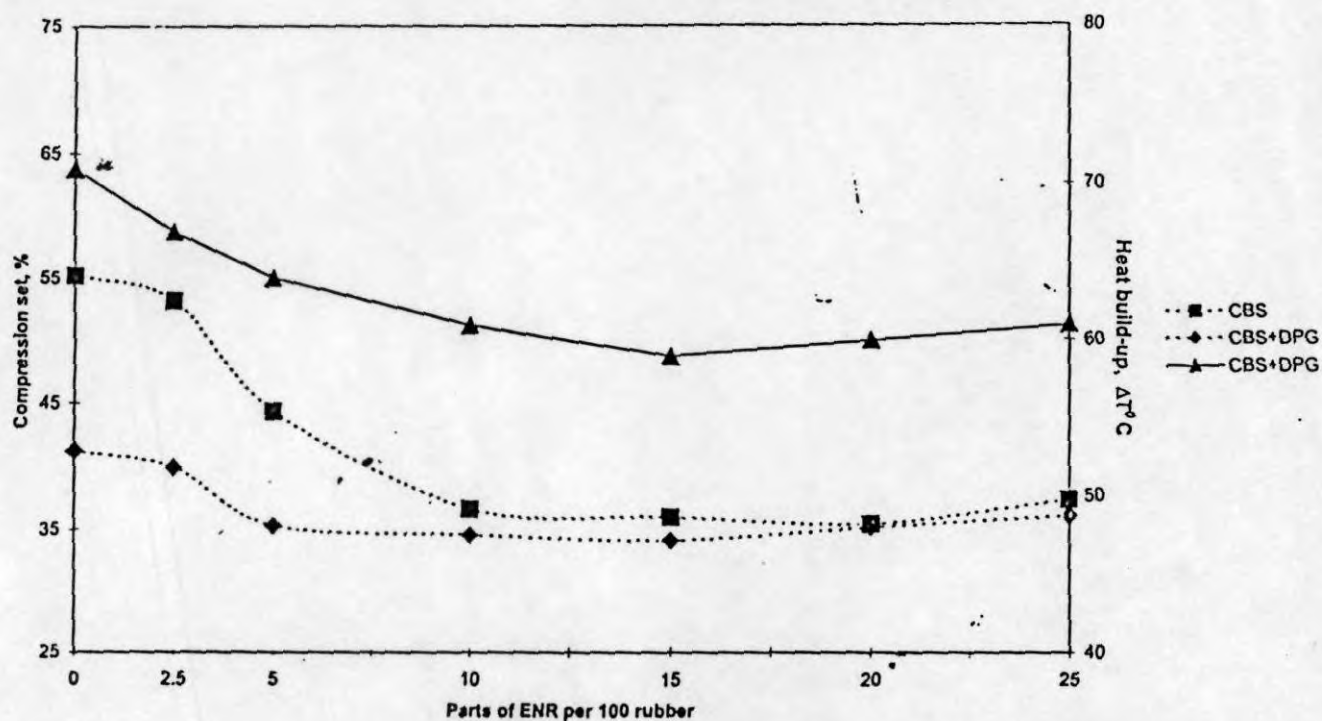
Figure 9   Variation in compression set and heat buildup with ENR incorporation.

incorporation, the heat development was lower than that achieved for NBR–Si-69–silica and NBR–ISAF, as observed from Table X. With the CBS cure system, because of the low modulus values shown by unmodified silica composite and also those with small proportions of ENR, it was difficult to carry out the test.

Aging Resistance

The aging resistance of the vulcanizates was assessed by determining the tensile properties before and after aging. Figures 10 and 11 show the aging resistance in tensile strength and modulus for the dual accelerator system of a few selected
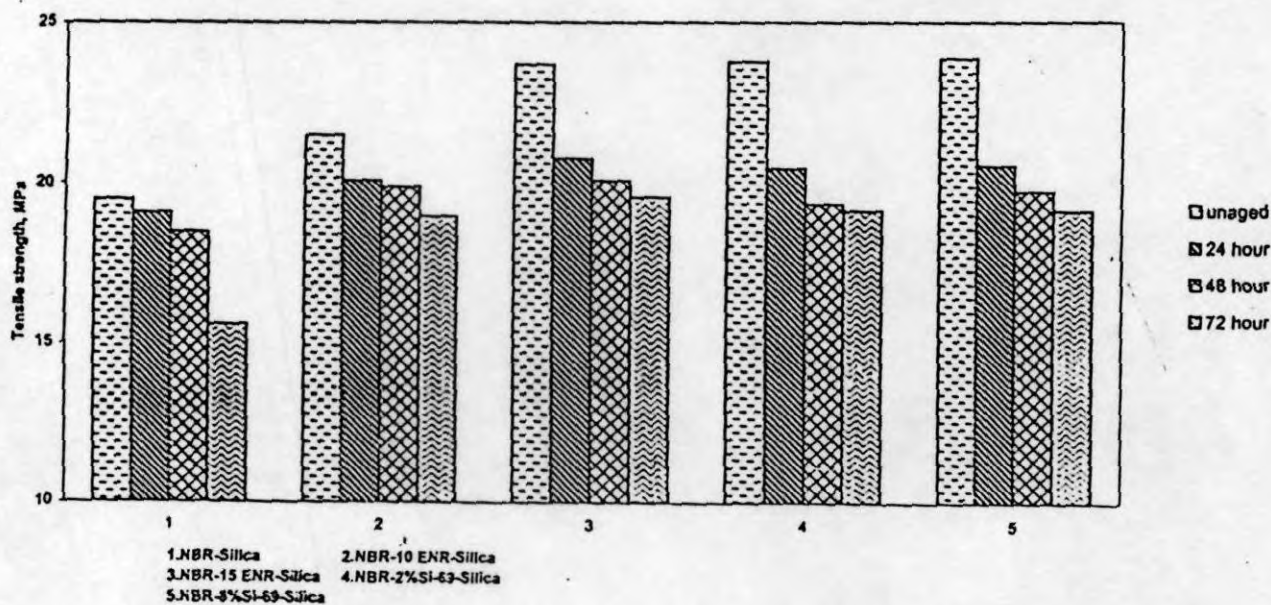

1.NBR-Silica   2.NBR-10 ENR-Silica
3.NBR-15 ENR-Silica   4.NBR-2%Si-69-Silica
5.NBR-8%Si-69-Silica

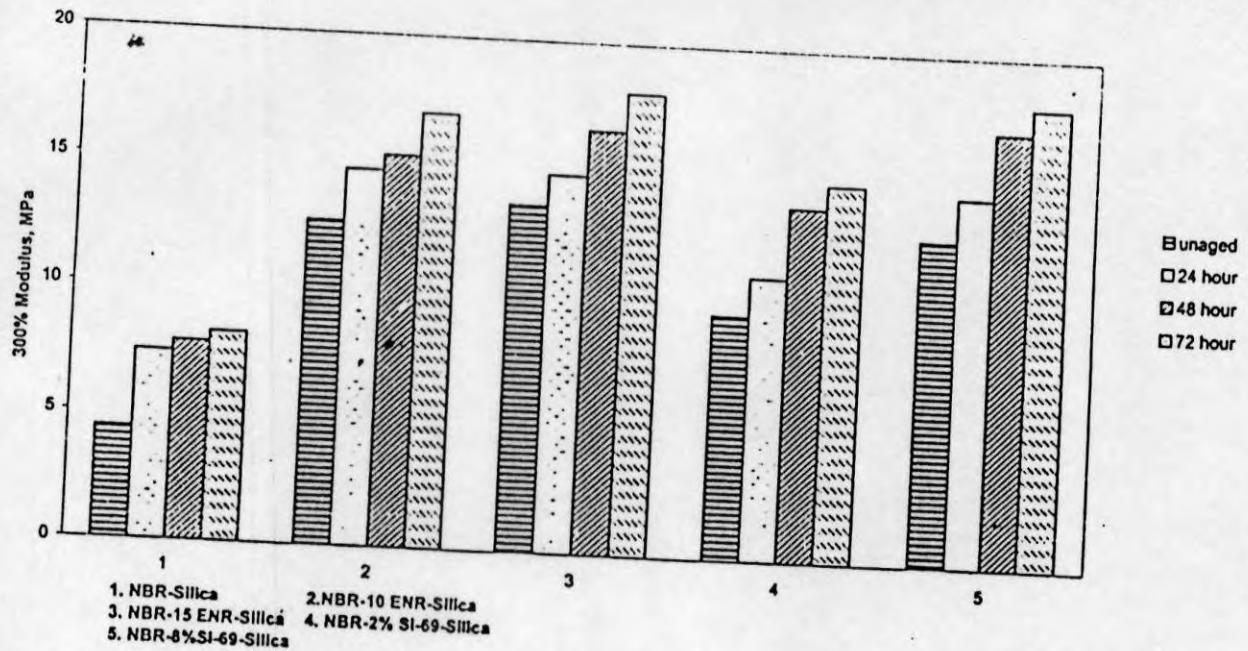Figure 10   Effect of aging on tensile strength.

Figure 11 Effect of aging on 300% modulus.

samples, that is, NBR–silica, NBR–ENR–silica, and NBR–Si-69–silica, after aging at 100°C for 24, 48, and 72 h. Retention of strength and modulus for the ENR-substituted samples were better than those of the unmodified sample and were comparable to those of the Si-69–modified sample.

Tear strength values for the binary accelerated system, after aging for 24, 48, and 72 h, are given in Figure 12. Retention of tear strength was greater for the ENR-substituted composites than that of the unmodified samples and was closer to that modified with the coupling agent.
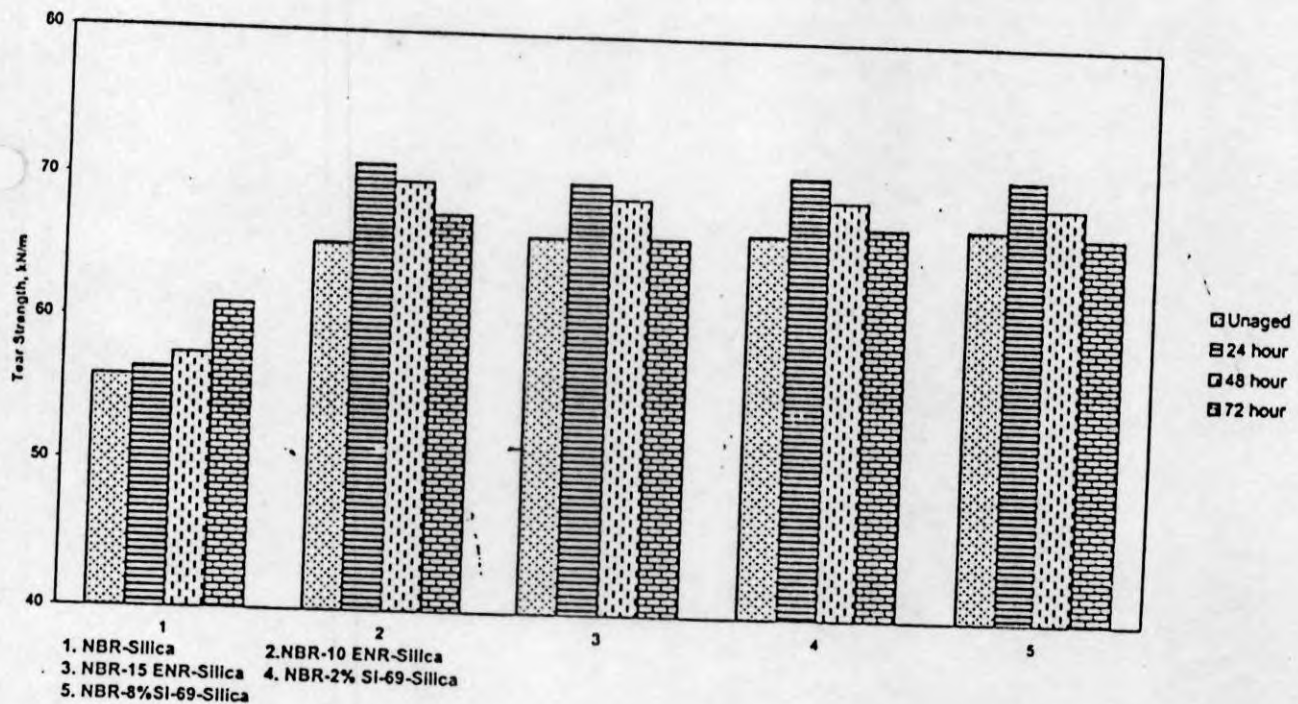

Figure 12 Effect of aging on tear strength.

CONCLUSIONS

Incorporation of ENR in NBR–silica composites can modify the technological properties of the latter. ENR could serve the function of a coupling agent between silica and nitrile rubber. NBR and ENR can form self-crosslinked structures and ENR also could link with silica particles at the vulcanization temperature, thus functioning as a coupling agent. Observations from bound rubber, rheometric studies, and volume fraction support this view. These composites were also compared with those of NBR–silica modified with coupling agent and NBR–ISAF. Incorporation of an optimum concentration of ENR in NBR–silica composites gave technological properties comparable to those containing a coupling agent and NBR–ISAF. Both single and binary accelerated systems showed improvements in properties with ENR addition. ENR-substituted composites exhibited aging resistance comparable to that of those modified with a coupling agent. The overall property enhancement indicates that ENR can serve as a reinforcement modifier for silica-filled nitrile rubber.

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