

Silica Filled Rubbers – Epoxidised Natural Rubber as a Reinforcement Modifier in Comparison with a Silane

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Introduction

Most of the rubber products are made to meet the requirements of specific applications, mainly through reinforcement usually with particulate fillers. Among conventional particulate fillers, silica is comparable to carbon black as an important reinforcing filler used in the rubber industry. Recently the use of silica is increasing due to the characteristic properties it offers to the rubber product such as high tear strength, good abrasion resistance, low heat build up and ageing resistance¹. In tires, use of silica as a reinforcing filler in place of carbon black could reduce its rolling resistance². Silica as a reinforcing filler in rubber also has some disadvantages like poor processability, cure retardation and inferior technological properties. Use of silane coupling agents have been found to control these detrimental effects^{3,4}. High cost of silane is a limitation to its large scale use. Rubbers differ in their silica reinforcing capability depending on its molecular constitution viz, natural rubber (NR) and styrene butadiene rubber (SBR) being non-polar hydrocarbon rubbers are less reinforcing than polar acrylonitrile butadiene rubber (NBR)⁵. However in all these rubbers silanes are to be used for getting maximum reinforcement.

Epoxidised natural rubber (ENR) is a modified form of NR made by epoxidising NR. Earlier workers have reported that epoxy group of ENR can react with the silanol group of silica^{6,7}. It is known that silica exhibits better reinforcement in ENR than in NR⁸. ENR can be considered as functionally similar to silane coupling agent, as it also is bifunctional viz, the epoxy group capable of reacting with silanol group and the unsaturation capable of forming sulphur cross links with the bulk of the rubber. Edward et al have reported that improved silica reinforcement could be achieved in epoxy functionalized NBR and SBR over the unmodified^{9,10}.

The work reported is based on the observations made from the studies on the use of ENR in small quantities as a reinforcement modifier in silica filled NR, SBR and NBR in comparison with the corresponding silane modified systems.

Experimental

Materials

Natural rubber: ISNR-5 obtained from crumb rubber factory, Rubber Board, Kottayam. Styrene butadiene rubber : SBR 1502, manufactured by M/s. Synthetics and Chemicals, Bareilly, India.

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

Epoxidised natural rubber: ENR-50 (50 mol.% epoxidised natural rubber – prepared at Rubber Research Institute of India by epoxidising NR latex using performic acid generated in situ¹¹).

Precipitated silica: Ultrasil VN₃, manufactured by Degussa (India).

Coupling agent: Si 69 (Bis (3-ethoxy propyl) – silyl tetra sulfide), manufactured by Degussa AG.

Other ingredients used were of rubber grade.

Preparation of compounds

The formulation of the mixes made are given in Table 1, 2 and 3. The rubber or combination of rubbers were initially either masticated or mastication-cum blending was done in a laboratory two roll mill for 5 minutes. The resultant material was used for further mixing in the internal mixer. All the ingredients except the curatives were mixed in the internal mixer set at 40°C, 60 rpm for 10 minutes. Curative addition and final homogenization was done in the two roll mixing mill.

Physical testing

Cure characteristics of the compounds were determined using a Monsanto Rheometer (R-100) at 150°C. Test samples were moulded using an electrically heated hydraulic press to their respective optimum cure times at 150°C. Vulcanized samples were tested for stress-strain properties, tear strength, resilience, hardness, heat build up, compression set and ageing resistance as per the respective ASTM standards. Abrasion resistance was tested as per DIN 53516.

Volume fraction of rubber(V_r)

The volume fraction of rubber in the swollen vulcanisate was determined by the equilibrium swelling of the vulcanized sample pieces in toluene at 30°C, according to the method suggested by Ellis and Welding¹².

Dynamic mechanical analysis

Dynamic mechanical analysis was carried out using DMA 2980, Dynamic mechanical analyzer (TA Instruments, U.S.A) at a frequency of 1 Hz and a heating rate of 1°C/minute.

Results and Discussion

Cure characteristics

The cure characteristics of the various compounds made from the three rubbers viz, NR, SBR and NBR are given in Table 4, 5 and 6 respectively. With NR-Silica systems the maximum torque showed a slight decrease with ENR addition of up to 20 parts, while silane modification showed an enhancement. Torque enhancement might have occurred as a result of the extra cross links formed between the sulphur in the coupling agent and the rubber chains. No significant difference was noted for the scorch and cure time of ENR and silane modified.

With SBR-Silica and NBR-silica system the minimum and maximum torque increased with ENR addition. This might have resulted from the additional rubber to rubber cross links formed between the major rubber phase and ENR, either independent or zinc compound assisted reaction^{1,13}. ENR-silica reaction also may have contributed to the torque enhancement. Zinc oxide also is known to enhance the viscosity of silica filled rubber compounds³. For the ENR modified SBR/silica and NBR/silica compounds, scorch and cure time decreased with ENR incorporation. Cure retardation caused by the polarity of silica surface got masked by ENR and the fast curing nature of ENR over SBR and NBR might have reduced the scorch and cure time.

Vulcanisate properties

Modulus, tensile strength and elongation behaviour of the silica filled vulcanisates from NR, SBR and NBR are given in figures 1,2 and 3 and that of the corresponding silane modified vulcanisates are given in Table 7. Modulus and tensile strength increased with ENR incorporation for all the three rubbers with marked improvement obtained for the NBR/ENR/silica system.. Elongation at break (EB), in general decreased with ENR incorporation for all the three rubbers and the drop is comparatively higher for the ENR modified NBR. With incorporation of ENR in NR/silica and SBR/silica systems, the improvement in stress-strain properties were almost at par with that obtained using a silane coupling agent at 2% concentration (based on filler). In the case of NBR/ENR/silica system, properties closer to that obtained using a higher concentration of silane coupling agent (8% on filler) could be achieved.

Variations in tear strength and abrasion loss for different compositions of silica filled NR, SBR and NBR are given in figures 4 and 5. Corresponding values of the silane modified are given in Table 7. For all the three rubber- silica systems, tear strength and abrasion resistance improved with ENR addition over the unmodified vulcanisates. Tear strength values obtained for various systems modified using ENR at optimum concentration were almost closer to those of the silane modified vulcanisates. Abrasion loss values of the ENR modified NR/Silica and SBR/Silica systems are comparable to those of the 2% silane modified system, while the corresponding NBR/Silica system showed better abrasion resistance.

Hardness increased and the resilience decreased with ENR addition (Figures 6 and 7). Values of hardness for the ENR containing samples are comparable to those obtained for the silane - modified system. Resilience values of ENR modified vulcanisates were lower than those obtained for the silane modified. High damping nature of ENR might have caused the lower resilience exhibited by those samples containing it. Silica filled NR vulcanisates showed a marginal increase in heat build up with ENR addition (Figure 8). However heat build up decreased with the incorporation of ENR in SBR/silica and NBR/silica vulcanisates. Respective silane modified system showed the lowest heat build up (Table 7). For the ENR containing NR/silica vulcanisates a marginal rise in compression set over the unmodified was observed. While, for the silane modified NR/silica system, set decreased considerably. ENR modified SBR and NBR exhibited lower set value, comparable to that of the silane modified (Figure 9 and Table 7). These variations could be due to the differences in the chemical constitution of the rubbers and the resultant inter- rubber interactions occurred in the blend system¹³.

Volume fraction of rubber(Vr)

A comparison of the Vr values of the three silica filled rubber samples is given in figure 10 and the respective silane modified in Table 7. An enhancement in Vr was obtained for all the ENR modified samples. The increase in Vr might have resulted from the cross - links formed between the rubber-rubber and or rubber - filler interactions. With ENR modified SBR and NBR, Vr values were comparable to those of the silane modified.

Ageing resistance

High temperature resistance of the selected vulcanisates was assed by ageing at 100°C for a period of 48 hours. Results obtained are given in figure 11 and 12. Both in modified and unmodified systems, modulus increased after ageing. However, the aged modulus values are higher for ENR modified samples over the unmodified. For all the three rubbers, tensile strength obtained after ageing was comparable for the respective ENR and silane modified and the unmodified.

Dynamic mechanical analysis

In the field of tires, silica reinforcement of rubber is important as it offers low rolling resistance. Wet grip and low rolling resistance are important requirements for tires. It is difficult to achieve these two properties together. $\tan \delta$ at 0° C and 60° C can be taken as a measure of wet grip and rolling resistance respectively². Higher the $\tan \delta$ at 0° C, better the wet grip and lesser the $\tan \delta$ at 60° C, lower will be the rolling resistance. $\tan \delta$ values of the silica filled NR and SBR modified with ENR and silane in comparison with the unmodified is given in figures 13 and 14. It can be observed that with ENR incorporation $\tan \delta$ at 0° C enhances and that the value at 60° C is not altered much. By ENR incorporation, in addition to the betterment achieved in silica reinforcement, wet grip also can be improved without adversely affecting the rolling resistance.

Conclusions

Incorporation of ENR into silica filled NR, SBR and NBR has improved its reinforcing capability in these rubbers. The enhancement of technological properties might have resulted from the modification of the interface between silica and the major rubber phase by ENR. It also might have contributed to the rubber-filler bonding and or rubber-rubber bonding as is indicated by the higher V_r values.

In the tire field applications, ENR modified silica composites can enhance the wet grip, without adversely affecting the rolling resistance.

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Table 1 : Formulation of mixes (NR based)

Ingredients*	A1	A2	A3	A4	A5	A6	A7	A8
Natural rubber (ISNR 5)	10 0	97.5	95	90	85	80	10 0	100
Epoxidised natural rubber (ENR 50)	-	2.5	5	10	15	20	-	-
Silane coupling agent (Si 69)	-	-	-	-	-	-	1	4

* Compounds given in Table 1 also contain the ingredients given below.

Zinc oxide 5, stearic acid 2, Naphthenic oil 5, N-cyclohexyl-2-benzthiazyl sulphenamide (CBS) 1.5, Diphenyl guanidine (DPG) 1.5, sulphur 2.5 and ultrasil VN₃ 50

Table 2 : Formulation of mixes (SBR based)

Ingredients*	B1	B2	B3	B4	B5	B6	B7	B8
Styrene butadiene rubber (SBR - 1502)	100	97.5	95	90	85	80	100	100
Epoxidised natural rubber (ENR 50)	-	2.5	5	10	15	20	-	-
Silane coupling agent (Si 69)	-	-	-	-	-	-	1	4

* Compounds given in Table 2 also contain the ingredients given below.

Zinc oxide 5, stearic acid 2, Naphthenic oil 10, N-cyclohexyl-2-benzthiazyl sulphenamide (CBS) 1.5, Diphenyl guanidine (DPG) 2, sulphur 2 and ultrasil VN₃ 50

Table 3 : Formulation of mixes (NBR based)

Ingredients*	C1	C2	C3	C4	C5	C6	C7	C8
Acrylonitrile butadiene rubber (N-423-NS)	10 0	97.5	95	90	85	80	10 0	100
Epoxidised natural rubber (ENR 50)	-	2.5	5	10	15	20	-	-
Silane coupling agent (Si 69)	-	-	-	-	-	-	1	4

* Compounds given in Table 3 also contain the ingredients given below.

Zinc oxide 4, stearic acid 1, Dioctyl phthalate 5, N-cyclohexyl-2-benzthiazyl sulphenamide (CBS) 1, Diphenyl guanidine (DPG) 1.5, sulphur 1.5 and ultrasil VN₃ 50

Table 4 : Cure characteristics (A1 to A8)

Ingredients*	A1	A2	A3	A4	A5	A6	A7	A8
Minimum torque, dN.m	8	8	8	8	8	12	12	6
Maximum torque, dN.m	92.5	92	92	88	88	88	92	100
Scorch time (ts ₂) at 150°C	2.5	3	3	3	3	3	2	3
Optimum cure time (t ₉₀) at 150°C	5.5	6	6	6	6	6	5	7

Table 5 : Cure characteristics (B1 to B8)

Ingredients*	B1	B2	B3	B4	B5	B6	B7	B8
Minimum torque, dN.m	14	17	16	16	16	15	14	16
Maximum torque, dN.m	90	94	95	96	94	93	96	112
Scorch time (ts ₂) at 150°C	9	8.8	6.5	6	7	7.5	6	6
Optimum cure time (t ₉₀) at 150°C	15.5	15	11.5	11	13	13.5	11.5	13.5

Table 6 : Cure characteristics (C1 to C8)

Ingredients*	C1	C2	C3	C4	C5	C6	C7	C8
Minimum torque, dN.m	21	26	26	26	26	27	17	14
Maximum torque, dN.m	98	98	98	102	105	106	100	114
Scorch time (ts ₂) at 150°C	8	6	6	5.5	5	4	5.5	4.5
Optimum cure time (t ₉₀) at 150°C	49.5	32	32	30.5	27.5	25.5	39	34

Table 7 : Technological properties (silane modified)

Property	NR/Silica		SBR/Silica		NBR/Silica	
	A7	A8	B7	B8	C7	C8
Modulus at 300% elongation, MPa	12	15	10	15	9.6	12.8
Tensile strength, MPa	27	27.5	16.6	20	24	24
Elongation at break, %	530	470	479	286	557	446
Tear strength, KN/m	111	110	51	57	68	65
Abrasion loss, mm ³	144	111	125	92	82	79
Hardness, Shore A	66	72	66	70	72	72
Resilience, %	60	59	59	58	43	44
Compression set, %	24	25	18	16	33	31
Heat build up, °C	23	24	34	30	65	61
Volume fraction of rubber (V _r)	0.163	0.179	0.229	0.267	0.337	0.348

Fig.1: Variation of modulus with ENR content

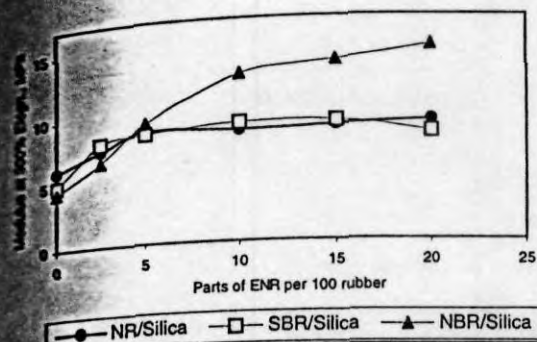


Fig.2: Variation of tensile strength with ENR content

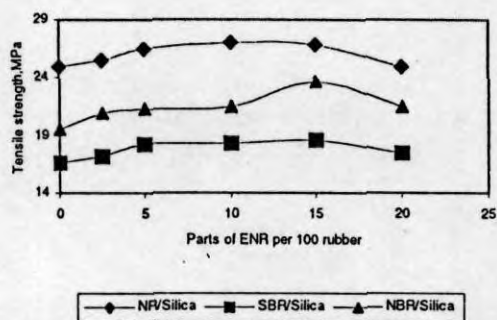


Fig.3: Variation of elongation at break, (%) with ENR content

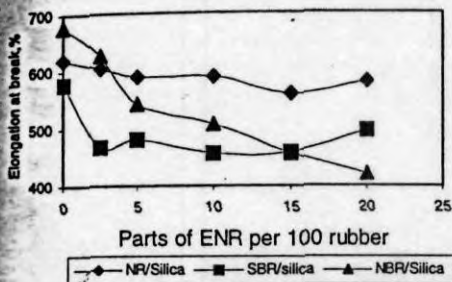


Fig.4: Variation of tear strength with ENR content

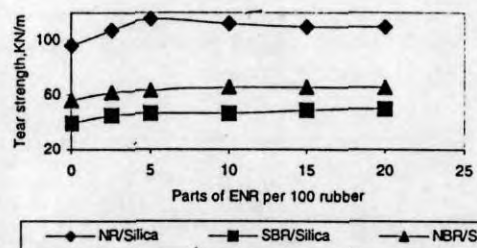


Fig.5: Variation of abrasion loss with ENR content

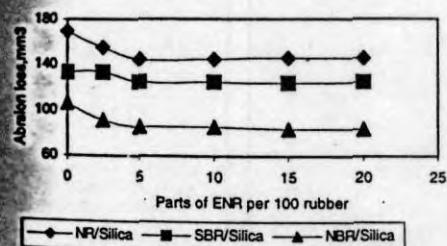


Fig.6 Variation of hardness with ENR content

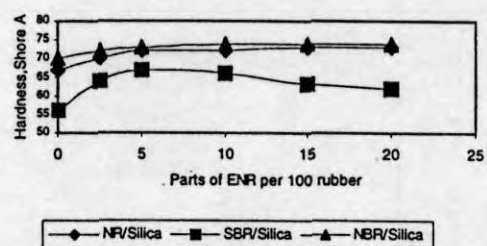


Fig.7: Variation of resilience with ENR content

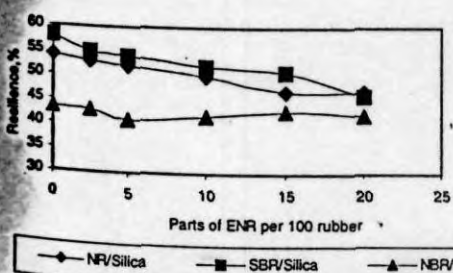
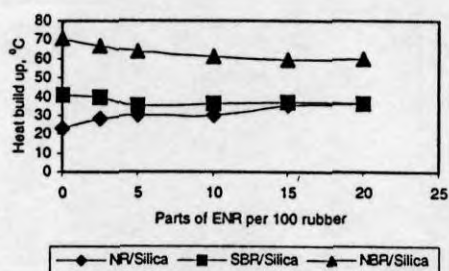


Fig.8: Variation of heat build up with ENR content



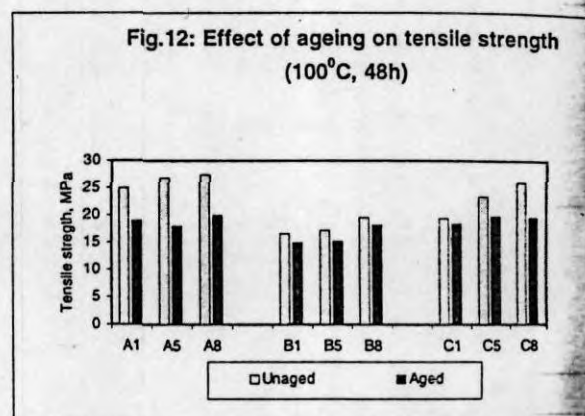
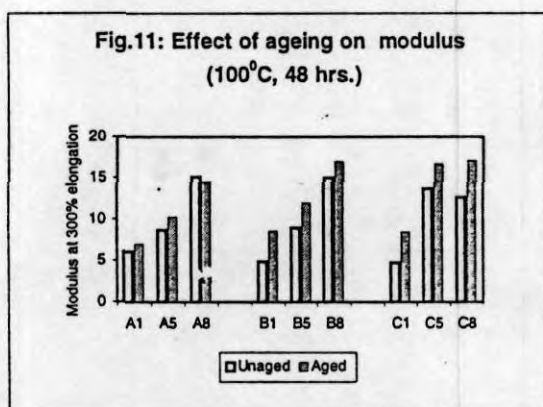
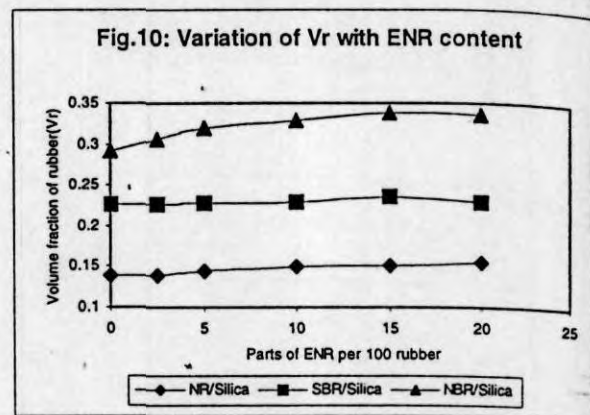
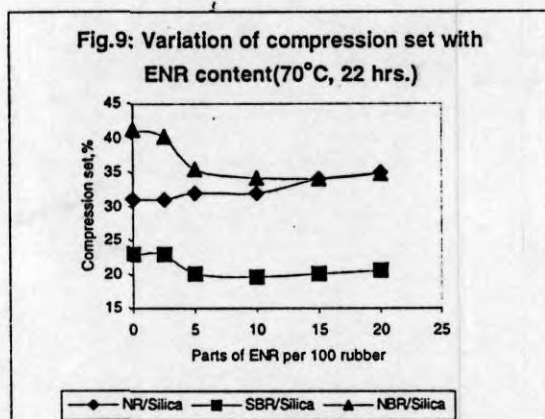


Fig.13. Dynamic mechanical analysis(NR/Silica)

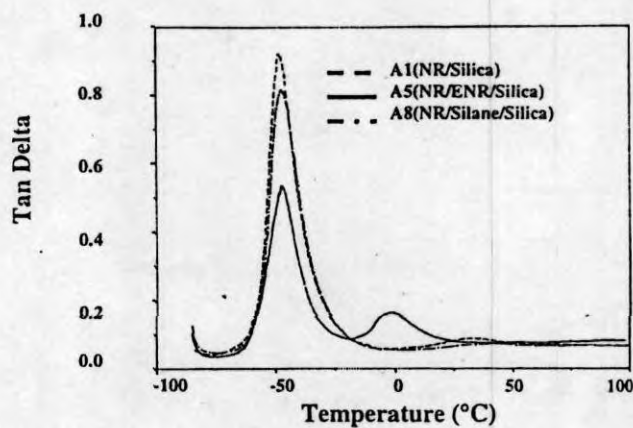


Fig.14. Dynamic mechanical analysis(SBR/Silica)

