Natural Rubber Research, 21 (1&2): 76-83, 2008

EPOXIDISED NATURAL RUBBER: A MODIFIER FOR CHINA CLAY FILLED NITRILE RUBBER

K. Mariamma George, Jacob K. Varkey, Benny George, K.T. Thomas and N. M. Mathew
Rubber Research Institute of India, Kottayam-686009, Kerala, India

George, K.M., Varkey, J. K., George, B., Thomas, K.T. and Mathew, N.M. (2009). Epoxidised natural rubber: A modifier for china clay filled nitrile rubber. *Natural Rubber Research*, **21**(1&2):76-83.

China clay, a semi-reinforcing filler is used for rubber products which do not require very high mechanical properties. Silane coupling agents or activators like diethylene glycol (DEG) are used in such formulations to enhance the polymer filler interaction. The use of small proportions of ENR as reinforcement modifier in china clay filled NBR was attempted and was compared with activator and silane coupling agent. Cure characteristics changed with the addition of all the three modifiers. ENR and silane modified systems showed better modulus, strength and other physical properties indicating better polymer-polymer and polymer-filler interactions. ENR-substituted composites also exhibited ageing resistance comparable to that realised with the coupling agent. For the composites containing china clay and ISAF black, ENR substitution reduced the cure time and improved the tensile and tear strength, though the values were lower than those containing the coupling agent. The overall property enhancement indicated that ENR can function as a reinforcement modifier in china clay filled nitrile rubber.

Key words: China clay, Epoxidised natural rubber, Nitrile rubber, Reinforcement modifier.

INTRODUCTION

Nitrile rubber (NBR), which remains amorphous under all conditions, requires the use of reinforcing fillers in the manufacture of products that need good mechanical properties. Hydrated silica imparts better physical properties to polar rubbers, compared to hydrocarbon rubbers. Kaoline clay, also called kaolinite or china clay, (Waddell and Evans, 2001; Florea, 1986) is hydrous aluminium silicate [$Al_2Si_2O_5(OH)_4$], consisting of platelets with alternating layers of silica and alumina. Clays have been used as fillers (extenders) in compounding of rubbers as they are relatively cheap although the resulting vulcanizates have inferior properties. The clay filled compounds have better processability but the surface properties of clays cause difficulties in their use as a reinforcing agent in hydrocarbon rubbers (Dannenberg, 1975). The filler surface is highly polar and hydrophilic as a result of its polysiloxane structure and the presence of numerous silanol groups. Generally a silane coupling agent (Si 69) or an activator like diethylene glycol (DEG) is used to enhance polymer-filler interaction and thereby the level of reinforcement (Murakami *et al.*, 1999).

Correspondence: Mariamma George (Email: mariamma@rubberboard.org.in)

Waddell (1996) reported the use of clay in rubber lubricant and tyre sealant formulations. Clays have been used in inner liner and white sidewall compounds. China clay loaded NBR compounds have been used for light coloured fuel hose and conveyor belt covers. NBR and epoxidised natural rubber (ENR) can form blends with good compatibility (Feijie and Jianhe, 1993). ENR could also serve as a reinforcement modifier in silica filled nitrile rubber (George *et al.*, 2002).

The objective of the present study was to examine the possibility of using ENR in small proportions, as a reinforcement modifier in china clay filled nitrile rubber, substituting DEG or silane coupling agent. NBR replaced with ENR was compared with silane modified and unmodified NBR-china clay/ISAF black compounds.

EXPERIMENTAL

Materials

Nitrile rubber (Aparene N 423-NS) with acrylonitrile content (33 %) supplied by Apar Industries Ltd. (India) was used. ENR 50 was obtained from the Rubber Research Institute of India and had 50 mole % epoxidation with a Mooney viscosity of 118. China clay (Grade KCG/SD) manufactured by English Indian Clays, Thiruvanathapuram (Table 1) was used as filler. Silane coupling agent Si 69- [bis (3-triethoxypropyl)-silyl tetra sulphide] used was manufactured by Degussa AG, Germany. The other ingredients were of commercial grade.

Preparation of compounds

The formulations of china clay filled compounds are given in Table 2. Samples were prepared in a two-roll laboratory-mixing mill. For compounds 2 to 6, rubbers as per the given proportions were pre-blended in the mixing

Table 1. **Composition of china clay**

Parameter	Value
Grade	KCG/SD
pH	8.50
Moisture content, %	1.00
Bulk density, kg/L	0.65
Specific surface area, m^2/g	16.00
Oil absorption, g/100 g	45.00
< 2 micron, w/w %	75.00
> 300 mesh, w/w %	0.05
Specific gravity	2.60

Table 2. **Formulation of china clay filled compounds**

Ingredient	Parts by weight of ingredients								
	Compound No.								
	1	2	3	4	5	6	7	8	9
Nitrile rubber	100	97.5	95	90	85	80	100	100	100
ENR 50	-	2.5	5	10	15	20	-	-	-
China clay	70	70	70	70	70	70	70	70	70
DOP	7	7	7	7	7	7	7	7	7
DEG	-			-	-		1.8	3.5	-
Si-69	-			-	-		-	-	1.4
Others (common to all compounds)	Zinc oxide- 4.0, Stearic acid- 1.0, CBS-1.5, Antioxidant HSL- 1.0, Sulphur- 1.5								

Table 3. **Formulation of china clay/ISAF black filled compounds**

Ingredient	Parts by weight of ingredients		
	Compound No.		
	10	11	12
Nitrile rubber	100	85	100
ENR 50	-	15	-
China clay	35	35	35
ISAF black	35	35	35
DOP	7	7	7
Si 69			1.4
Others (common to all compounds)	Zinc oxide- 4.0, Stearic acid- 1.0, CBS-1.5, Antioxidant HSL- 1.0, Sulphur- 1.5		

mill for 5 minutes. The china clay/ISAF black filled compounds were prepared as per the formulation given in Table 3 in a laboratory model internal mixer (at 70 rpm) at a mix temperature of 50°C for 8 minutes.

To asses 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 4 (compounds 13-18), were blended in a laboratory model two-roll mixing mill for 5 minutes. Rheographs of the mixes at 150 °C were recorded and used to quantify the polymer-polymer interaction resulting in crosslinks.

Cure characteristics of the compounds were determined using a rheometer (Monsanto Rheometer R-100, USA) at 150°C. Test samples were moulded using an electrically heated hydraulic press to their respective optimum cure times. Tensile properties of the vulcanizates were tested according to ASTM D 412-98 (Zwick UTM, model 1474). The tear strength (ASTM D 624-00, Zwick UTM), hardness: (ASTM D 2240-04, Shore A), resilience (ASTM D 1054-02, Dunlop Tripsometer), heat build-up (ASTM D 623-99, Goodrich flexometer), compression set

Table 4. **Formulation of mixes**

Ingredient	Parts by weight of ingredients					
	Compound No.					
	13	14	15	16	17	18
Nitrile rubber	100	90	85	80	75	50
ENR-50	-	10	15	20	25	50

Table 5. **Cure characteristics of china clay filled compounds**

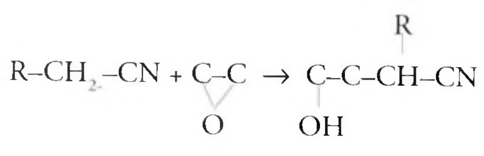
Parameter	Compound No.								
	1	2	3	4	5	6	7	8	9
Minimum torque, dN.m	1.9	2.1	2.3	3.4	3.4	3.6	1.6	1.7	1.8
Maximum torque, dN.m	19.5	19.9	20.5	22.5	23.8	23.2	19.4	22.1	22.1
Optimum cure time (t_{90}) at 150°C, min	15.7	13.5	13.0	11.0	10.0	12.0	14.0	13.4	22.3
Cure rate index [$100/(t_{90}$- ts_2)]	15.6	38.5	40.0	45.5	47.6	34.5	13.7	13.6	7.3
Mooney viscosity, ML (1+4) at 100°C	54.1	58.6	61.2	75.3	76.5	80.6	47.9	44.1	49.5
Scorch time at 120°C, min	65.0	58.7	55.7	44.9	45.0	50.1	42.7	32.9	61.4

(ASTM D 395-03, Method B), abrasion resistance (DIN 53516) and ageing resistance (ASTM D 573-04) were also tested. The volume fraction (Vr) of rubber in the swollen vulcanizate was determined by the equilibrium swelling of the vulcanized sample in toluene at 30°C, according to the method suggested by Ellis and Welding (1964). The ageing resistance of the vulcanizates was assessed by determining the tensile properties before and after ageing at 100°C for 24 and 72 hours.

RESULTS AND DISCUSSION

Cure characteristics of china clay filled compounds

Cure characteristics and Mooney viscosity measurements of the nine (Table 2) china clay filled compounds are presented in Table 5. The minimum and maximum 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 of compounds 13-18 (Table 4) was assessed from the rheographs (Fig. 1). A gradual increase in torque was noted with increasing concentration of ENR. The increased torque might have resulted from NBR-ENR interaction. Lee and Neville (1967) reported that acetonitriles can open the epoxy ring as shown below:



A similar interaction might have occurred in the case of NBR-ENR blends resulting in crosslinked structures. With increase in the concentration of ENR, an increase in the minimum rheometric torque which is an indication of the compound viscosity, was

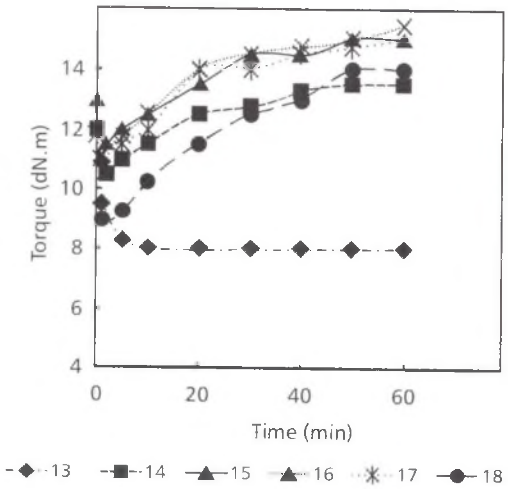


Fig. 1. Rheograph of NBR/ENR blends

noted. The high compound viscosity can be attributed to polymer-polymer and polymer-filler interactions. Mooney viscosity, which is a measure of processability, also increased with the addition of ENR. A slight reduction in the minimum rheometric torque and Mooney viscosity was noted for the DEG incorporated samples. The optimum cure time (t_{90}) and scorch time (ts_2) were found to have decreased with increase in concentration for ENR up to 15 parts. The DEG and ENR modified samples gave the lowest cure values. Cure rate index (CRI) increased for ENR substituted samples. However, in the mix containing the silane coupling agent, t_{90} was higher and ts_2 and CRI were lower than those of the unmodified sample. The property improvement was higher for the sample modified with 15 parts of ENR.

Volume fraction of rubber

The volume fraction (Vr) of rubber obtained from swelling studies is an indication of the crosslink density of the sample. Table 6

Table 6. **Volume fraction of rubber**

Compound No.	Vr
1	0.3161
2	0.3190
3	0.3205
4	0.3265
5	0.3295
6	0.3270
7	0.3066
8	0.3105
9	0.3437

shows the effect of modifiers on the Vr of different samples. NBR-china clay composites containing silane coupling agent and ENR as modifiers showed higher Vr values than those of the unmodified. The increase in volume fraction with the incorporation of modifiers can be attributed to increased crosslink density. It was seen that Vr 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 from the sulphur crosslinks. The silane coupling agent being a crosslinking agent, have shown higher Vr values for its composite.

Mechanical properties

The mechanical properties of the vulcanizate are given in Table 7. A slight increase in 100 % modulus was observed with increase in concentration of ENR. The values were higher than those observed with the DEG modified samples and closer to that of the mix modified with the silane-coupling agent. Incorporation of ENR into the clay composites was found to have improved the 300 % modulus. The enhancement in modulus could be due to increase in crosslink density as has been reported in compounds containing silane coupling agent (Debnath *et al.,* 1989). The NBR-china clay composite modified with DEG gave modulus value lower than those of the unmodified composite.

Tensile strength showed an increase up to 15 parts of ENR and then decreased, whereas EB showed a continuous decrease with increased ENR concentration, with values

Table 7. **Mechanical properties of china clay filled compounds**

	Compound No.								
Parameter	1	2	3	4	5	6	7	8	9
100% Modulus, MPa	2.0	2.3	2.4	2.5	2.6	2.7	1.6	1.5	2.7
300% Modulus, MPa	3.6	4.0	4.3	5.5	5.8	5.4	2.6	2.5	6.6
Tensile strength, MPa	13.5	14.1	14.9	15.7	16.0	15.5	15.2	11.3	16.8
Elongation at break, %	690	680	650	620	620	595	718	660	618
Tear strength, N/mm	30.8	33.7	34.9	35.4	37.4	34.5	29.4	28.1	39.0
Abrasion loss, mm^3	220	165	164	160	162	168	262	295	140
Resilience, %	50.6	54.3	52.8	50.6	49.4	49.2	45.8	47.0	50.0
Hardness, Shore A	54	53	54	56	58	60	54	54	56
Compression set, %									
70°C, 22 h	27	33	32	30	27	30	29	28	18
100°C, 22h	66	79	74	68	65	70	72	70	55
Heat build-up, ΔT, °C	45	43	43	41	41	40	41	45	41

comparable to that of the mix modified with the coupling agent. With lower concentration of DEG (2.5 % of the filler) tensile strength and EB increased over the control (compound 1) but with double the concentration of DEG both the properties decreased. Improved tensile strength and reduced elongation at break (EB) are considered as criteria for higher filler reinforcement (Boonstra, 1982). These properties are also related to the nature and number of crosslinks.

Improvements in tear strength and abrasion resistance are measures of enhanced filler reinforcement (Waddell and Evans, 2001). Tear strength showed an increase up to 15 parts of ENR and was comparable to that achieved using the coupling agent. With the addition of DEG, the tear strength was lower, but comparable to that of the control sample. Substitution of NBR with ENR and incorporation of the coupling agent improved the abrasion resistance of NBR-clay composites, the latter showing the maximum. The DEG modified composites gave lower abrasion resistance.

Resilience showed an increase with the incorporation of small proportions of ENR, but the value decreased with increasing concentrations of ENR. No marked difference in resilience was noticed for the silane and ENR (15 parts) modified composites. Lower resilience values were observed for the DEG modified composites. Hardness, a measure of the modulus of the rubber compound, showed an increase with increasing concentrations of ENR. The hardness values of the composites modified with higher concentrations of ENR and silane were higher than those modified with DEG and the control.

A marked reduction in compression set was noted for the silane-modified composite whereas for the composites modified with ENR the values were generally high except when the concentration of ENR was 15 parts. A higher set value was observed for the DEG modified composite. A reduction in heat build-up was observed for the silane modified composite and lower concentration of DEG but at the higher concentration there was no change.

In general, the improvements in mechanical properties of compound containing ENR and silane coupling agent could be due to enhancement in polymer-polymer and polymer filler interaction leading to better crosslinking.

Cure characteristics of china clay/ISAF black filled compounds

Cure characteristics of the mixed filler system are presented in Table 8. In the mixed filler system there was no torque increase with the incorporation of ENR. Mooney viscosity also remained same for these compounds. Optimum cure and scorch times were lower for the ENR modified composite (No.11) whereas these were higher for the silane modified one (No.12)

Table 8. **Cure characteristics of china clay/ISAF black filled compounds**

Parameter	Compound No.		
	10	11	12
Minimum torque, dN.m	2.2	2.3	2.1
Maximum torque, dN.m	20.0	19.8	22.2
Optimum cure time (t_{90}) at 150°C, min	11.5	10.0	24.0
Cure rate index [$100/(t_{90} - ts_2)$]	13.2	15.8	5.6
Mooney viscosity, ML (1+4) at 100°C	66	68	66
Scorch time at 120°C, min	26	24	28

Mechanical properties of china clay/ISAF filled compounds

Mechanical properties of the vulcanizates are given in Table 9. A slight increase in the modulus was observed with the incorporation of ENR though lower than that with the coupling agent. Tensile and tear strengths were higher whereas EB was lower on modification by ENR. The tensile and tear strength values under ENR modification were lower than that with the coupling agent. No marked difference in resilience and hardness was observed with use of either of the modifiers. Reduction in compression set value was noted for the silane modified composite whereas that of ENR modified and unmodified composites were comparable. Heat build-up and abrasion loss decreased for both ENR and silane modified composites and the values were comparable.

Table 9. **Mechanical properties of china clay/ISAF filled compounds**

Parameter	Compound No.		
	10	11	12
100% Modulus, MPa	2.9	3.2	4.0
300% Modulus, MPa	7.3	8.6	11.1
Tensile strength, MPa	16.5	17.9	23.1
Elongation at break, %	630	569	550
Tear strength, N/mm	51.8	56.8	60.7
Resilience, %	41.0	41.0	40.5
Hardness, Shore A	70	70	71
Compression set, %			
70°C, 22 h	33.1	32.8	28.1
100°C, 22 h	69.3	66.7	63.1
Heat build-up, ΔT, °C	40	36	36
Abrasion loss, mm^3	152	131	128

Ageing resistance

Ageing resistance of the vulcanizates was assessed by determining the tensile properties before and after ageing at 100°C for 24 and 72 hours. Figures 2 and 3 show the retention in tensile strength and modulus of clay filled compounds and Figures 4 and 5 for the clay/ISAF filled compounds. Retention of tensile strength and modulus for the ENR substituted clay filled samples were comparable to that of the silane modified and the unmodified whereas for the mixed filler system it was comparable to the unmodified compound.

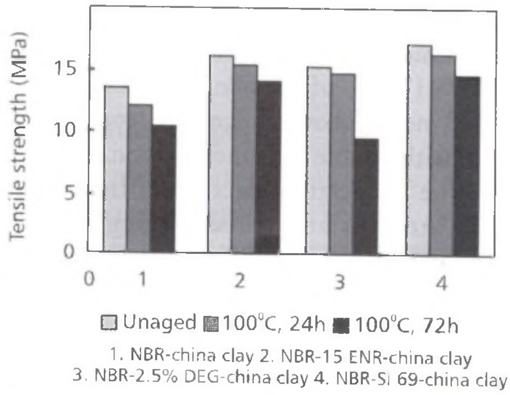


Fig. 2. Effect of ageing of china clay filled NBR on tensile strength

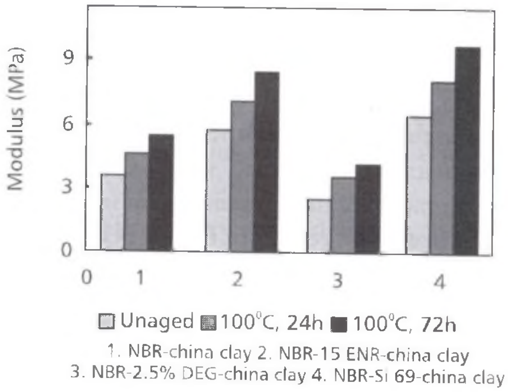


Fig. 3. Effect of ageing of china clay filled NBR on 300% modulus

CONCLUSION

Blending of small proportions of ENR in NBR-china clay composites gave vulcanizate

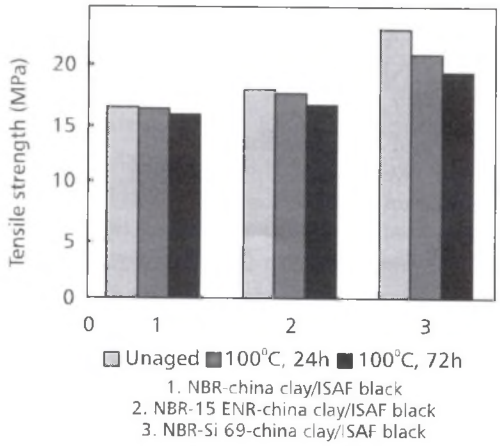


Fig. 4. Effect of ageing of china clay/ISAF black filled NBR on tensile strength

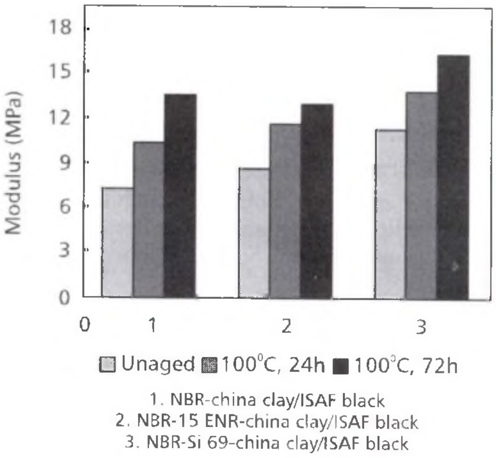


Fig. 5. Effect of ageing of china clay / ISAF black filled NBR on 300% modulus

properties and ageing resistance comparable to those modified with silane coupling agent. Replacing 15 parts of NBR with ENR 50 gave comparable tensile strength, modulus, elongation at break and tear strength to that modified with the coupling agent. For composites containing china clay and ISAF black, ENR substitution reduced the cure time and improved tensile and tear strength, though the values were lower than those containing the coupling agent. The overall property enhancement indicated that ENR can function as a reinforcement modifier in china clay filled nitrile rubber.

REFERENCES

Boonstra, B.B. (1982). Reinforcement by fillers. In: *Rubber Technology and Manufacture*, (Ed. C.M. Blow). Butter worth scientific, Stone ham pp. 227-261.

Dannenberg, E.M. (1975). The effect of surface chemical interaction on the properties of filler-reinforced rubbers. *Rubber Chemistry and Technology*, **48**: 410.

Debnath, S., De, S.K., Khastgir, D. (1989). Effects of silane coupling agents on mica-filled styrene butadiene rubber. *Journal of Applied Polymer Science*, 37: 1449-1464.

Ellis, B and Welding, G.N. (1964). Estimation, from swelling, of the structural contribution of chemical reactions to the vulcanization of natural rubber. *Rubber Chemistry and Technology*, **37**: 571-575.

Feijie, L., Jianhe, L. (1993). A study of epoxidised natural rubber-Nitrile / butadiene rubber blends. *Proceedings of the IRRDB Symposium, Tun Abdul Razak Laboratory, Hertford*, England, pp. 16-28.

Florea, T.G. (1986). Elastomer reinforcement with chemically modified and specialty clays, Elastomerics, **118**: 22-27.

George, K.M., Varkey, J.K., Thomas, K.T. and Mathew, N.M. (2002). Epoxidised natural rubber as a reinforcement modifier for silica-filled nitrile rubber. *Journal of Applied Polymer Science*, **85**: 292-306.

Lee, H and Neville, K. (1967). In Handbook of Epoxy Resins: (Eds. H. Lee and K. Neville). McGraw-Hill, New York, pp. 5-32.

Murakami, K., Osanai, S., Shigekuni, M., Iro, S., Tanahashi, H., Kohjiya, S. and. Ikeda, Y. (1999). Silica and silane coupling agent for *in situ* reinforcement of acrylonitrile-butadiene rubber. *Rubber Chemistry and Technology*, **72**:119-129.

Waddell, W.H., Evans, L.R. (1996). Use of non-black fillers in tire compounds. *Rubber Chemistry and Technology*, **69**: 377-423.

Waddell, W.H., Evans, L.R. (2001). Precipitated silica and non-black fillers. *Rubber Technology*, (Ed. J. S. Dick). Hanser gardener Inc., Cincinnati pp. 325-343.