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NATURAL RUBBER/EPOXIDISED NATURAL RUBBBER/ POLYVINYL CHLORIDE TERNARY THERMOSET BLENDS

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INTRODUCTION

Elastomers have been blended with polyvinyl chloride (PVC) for different purposes. Addition of PVC to acrylonitrile butadiene rubber (NBR) can improve the mechanical properties, resistance towards solvent, ozone, weathering, u.V, and fire of NBR. Blends of natural rubber (NR) and PVC do not exhibit good mechanical properties (2). The superior mechanical properties exhibited by NBR/PVC over NR/PVC can be attributed to the better interfacial adhesion (3). Francis et. al have tried different polymers viz. nitrile rubber, ethylene vinyl acetate copolymer (EVA) and polyether ester block copolymer (Hytrel) as compatibilizers for property improvement of NR/PVC blends, but none of them was found effective (2). It was reported earlier that PVC can form miscible blends with 50 mole % epoxidised natural rubber (ENR50) (4). Wan Aizan and Abdullah (5) have reported on the ternary blends of NR/ENR/PVC with the rubber phase uncrosslinked.

This paper describes use of ENR as a compatibilizer in NR/PVC blend based thermosets in comparison with those of a commercial medium acrylonitrile NBR/PVC based thermoset.

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EXPERIMENTAL

1. Materials

Natural rubber -	ISNR-5, pilot crumb rubber factory, Rubber Board, Kottayam.
ENR50 (50 Mole % - epoxidised natural rubber)	Prepared by epoxidising NR latex using performic acid generated in situ(6)
Nitrile rubber (33% acrylonitrile)	Aparence 423 NS, Apar Polymers Ltd, Bombay
Poly(vinyl chloride)	ER092, K Value, 67 M/s IPCL, Baroda.

The other ingredients used were of rubber grade.

2. Preparation of blends and compounding

PVC was compounded with the required quantity stabilisers and plasticizer in a Haake Rheocord 90, at 100°C, at 60 rpm for 15 minutes (7). Binary blends of NR/PVC, ENR/PVC, NBR/PVC and ternary blends of NR/ENR/PVC were also prepared in the Rheocord at 150°C and at 60 rpm for 12 minutes. Compounding of the blends were also done in the same equipment at 60°C, at 60 rpm for 8 minutes.

3. Vulcanisation and testing

Cure characteristics of the compounds were determined using a Monsanto Rheometer R-100 at 150°C. The test samples were prepared by vulcanising the compound at 150°C up to their optimum cure times (t95) in an electrically heated laboratory hydraulic press.

Tensile properties and tear strength of the vulcanisates were determined as per ASTM D 412-80 on a Zwick UTM model 1474. Ageing was carried out as per ASTM D 573. Compression set, hardness and ozone resistance were tested as per ASTM D 395 - 89 method B, D 2240-95 and D 1149-86 sample B respectively. Abrasion loss was determined according to DIN 53516.

RESULTS AND DISCUSSION

Formulations of the different compounds are given in Table 1. The compounds based on ternary blends were so designed that the natural rubber part of a 70/30 NR/PVC blend was substituted by increasing the proportions of ENR viz. 2.5,5,10,15,20 and 70 parts. A 70/30 medium acrylonitrile

NBR/PVC blend also was compared with the above blends.

Cure characteristics of the compounds made from the above blends are given in Table 2. Cure properties were slightly affected when ENR was introduced into the binary blend. Compared with NR/PVC, the ternary blends showed minor increase in maximum torque and cure rate index while NBR/PVC showed lower cure rate index.

Figures 1, 2 & 3 give the effect of incorporation of ENR in NR/PVC blends on its tensile properties and are compared with those of ENR/PVC and NBR/PVC. Variations in properties on ageing are also depicted in the figures. Changes in modulus are given in Fig. 1. Triblends showed a dip in the modulus with 2.5 parts of ENR, followed by a rise with higher quantities up to about 15 parts and a second dip with still higher quantities. NR/ENR/PVC blends beyond a critical concentration of ENR, showed higher modulus than the binary blends. Modulus observed for the ENR50/PVC blend is closer to that of the NBR/PVC blend of the same composition. Moduli of NR/PVC, ENR/PVC and the ternary blends showed an increase on ageing, while the change is only marginal for NR/PVC blend. Tensile strength values for the different blends are given in Fig. 2. In the case of the ternary blends, strength properties were found to increase with incorporation of ENR beyond a critical concentration up to about 15 parts. Triblends with very small quantities of ENR exhibited poor strength compared to the binary blend. With larger quantities, again a drop in strength properties was observed. ENR/PVC blend showed considerably lower strength values compared to that of NR/PVC of the same composition and the ternary blends. Samples from compounds 1 and 2 showed sharp fall in strength on ageing whereas the other blends retained considerable strength even after ageing. Better strength properties and improved ageing resistance showed by the ternary blends having a limiting concentration of ENR over NR/PVC binary blend might have resulted from the compatibilizing action of ENR. Earlier workers also have reported that the thermal stability of the blends is highly dependent on their compatibility (8, 9). Elongation at break (EB) values of the different blends are depicted in Fig.3. Compared to NR/PVC, triblends having ENR beyond 2.5 parts showed lesser EB. This might have resulted from a better interfacial adhesion between NR and PVC achieved through ENR thereby imparting more PVC character to NR. NBR/PVC blend showed higher EB, than the ternary blend with the optimum concentration of ENR. For all the blends EB decreased on ageing and is more prominent for NR/PVC than the ternary blends. The corresponding change is the least with NBR/PVC.

Figure 4 give the variations in tear strength of NR/PVC blends with incorporation of ENR and also the values for ENR/PVC and NBR/PVC. Tear strength dropped, on substitution of 2.5 parts of NR with ENR and then progressively increased up to 15 parts followed by a decrease on further addition. Changes in tear strength, on ageing of different blends also are depicted in the same figure. The ternary blends with a certain optimum concentration of ENR showed better retention of tear strength on ageing, comparable with that of NBR/PVC.

Figures 5 and 6 give the variation in hardness, compression set and abrasion loss of various blends. For the triblends only a nominal decrease in hardness was noted with up to 20 parts by weight of ENR. Variation in compression set values of the ternary blends showed an opposite trend to that of the strength properties. An initial high set was observed with small quantities of ENR, followed by a reduction with larger quantities and a further rise with still larger proportions. Ternary blend with the optimum concentration of ENR showed comparable set values as that of NBR/PVC. Abrasion loss decreased continuesly to a minimum with about 15 parts of ENR and then increased with further rise in ENR content of the triblend. Unlike other properties, the abrasion loss observed for the ternary blend having optimum concentration of ENR is higher than that observed for the NBR/PVC blend.

Photographs of the samples exposed to 50 pphm ozone for 70 hours at 40°C are given in Fig.7. NR/PVC and NR/ENR/PVC with up to 10 parts of ENR failed in about 2.5 hours (crack initiated). Samples of NBR/PVC, ENR/PVC and ternary blends with more than 15 parts of ENR showed very good ozone resistance. As can be seen from the photograph, no visible crack was observed after exposure of those samples for even 70 hours.

Higher modulus, better strength properties, lower compression set and abrasion loss and resistance towards ageing and ozone observed for the ternary blends with optimum concentration of ENR over NR/PVC may have resulted from a better interfacial adhesion of NR and PVC achieved through the compatibilizing action of ENR. The probable interaction between ENR and PVC may be either through chemical reactions, hydrogen bonding or through polar interactions (4,10,11).Also it is likely that ENR can bind with NR through sulphur bridges. Compared to NR/PVC, the drop in modulus, tensile and tear strength and the higher compression set and EB observed for the ternary blends with small quantities of ENR may be a consequence of the inadequate interface modification of NR and PVC. The drop in modulus, tensile and tear strength and hardness observed for the binary ENR/PVC and the ternary blends beyond a critical concentration of ENR might have resulted from the plasticising action of ENR on PVC.

CONCLUSIONS

Ternary thermoset blends of NR/ENR/PVC with an optimum concentration of ENR showed superiority in physical properties and resistance towards ageing over NR/PVC. Ternary blends with more than 15 parts of ENR by weight showed very good ozone resistance comparable with that of ENR/PVC The improvement in properties showed by the ternary blends over NR/PVC blend might have resulted from the interface modification of the latter by ENR.

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Table 1. Formulation of mixes

Ingredients	Mix number							
	1	2	3	4	5	6	7	8
Natural rubber (ISNR5)	70	67.5	65	60	55	50	-	-
Epoxidised natural rubber (ENR 50)		2.5	5	10	15	20	70	-
Nitrile rubber (33% acrylonitrile)	-	-	-	-	-	-	-	70
PVC [a]	30	30	30	30	30	30	30	30
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Antioxidant HS [b]	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
TBBS [c]	1.17	1.17	1.17	1.17	1.17	1.17	1.17	1.17

a). The required quantity of PVC compound was added so as to get an equivalent of PVC as shown in Table 1.

b) Polymerised 1.2 dihydo 2, 2, 4 trimethyl quinoline

c) t-butyl benzothiazole sulphenamide

Table 2 - *Cure characteristics*

Property	Mix Number							
	1	2	3	4	5	6	7	8
Minimum torque (dNm)	6	7	8	8	8	7	4	8
Maximum torque (dN.m)	38	37	37	39	39.5	37	33	32
Scorch time (t2), minutes	3.2	3.5	3.5	3.2	3.2	3.0	2.5	4.0
Cure rate Index 100/t90-t2	10	11.7	11.1	10.7	10.7	11.7	10	2.8

t2 - Time to reach 2 units above the minimum rheometric torque

t90 - Time to reach 90 percent of the maximum torque

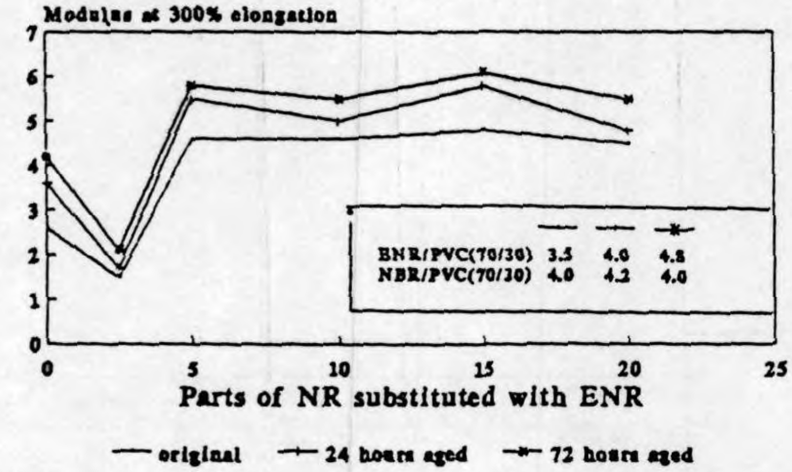

FIG.1 Variations in modulus of NR/PVC(70/30) with increased substitution of NR with ENR

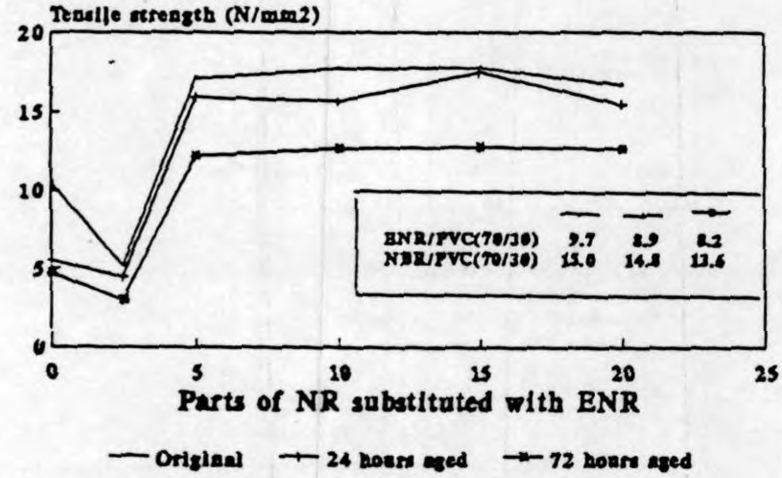

FIG.2 Variations in tensile strength of NR/PVC(70/30) with increased substitution of NR with ENR

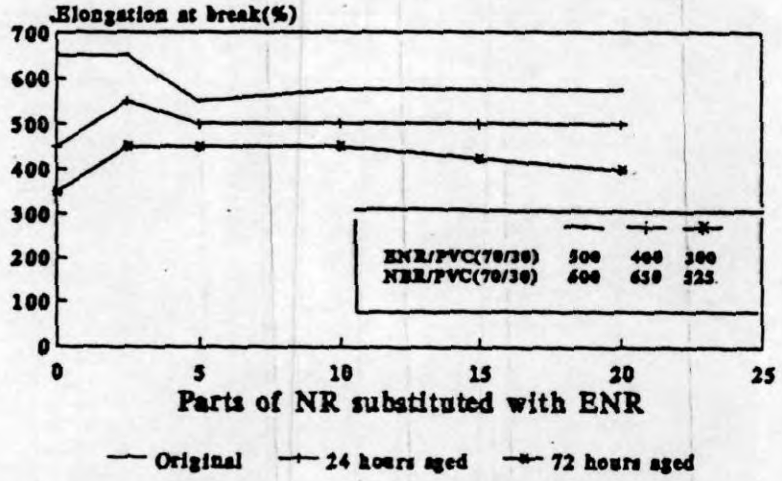

FIG.3 Variations in elongation at break(%) of NR/PVC(70/30) blends with substitution of NR with ENR

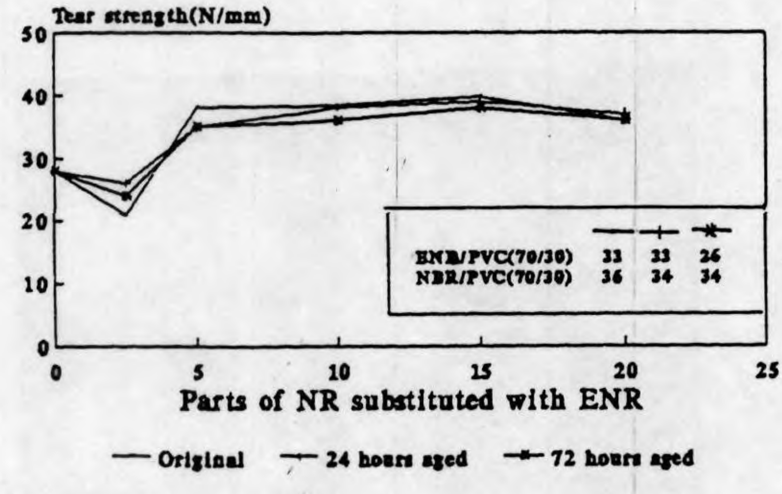

FIG.4 Variations in tear strength of NR/PVC(70/30) with substitution of NR with ENR

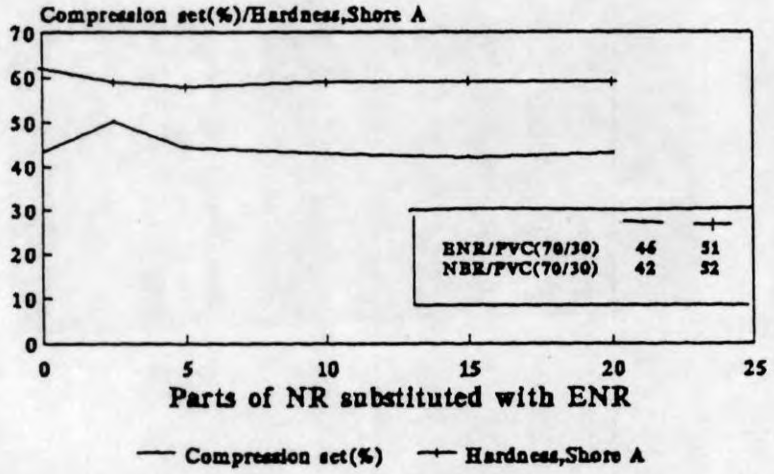

FIG.5 Variations in compression set and hardness of NR/PVC(70/30) blends with substitution of NR with PVC

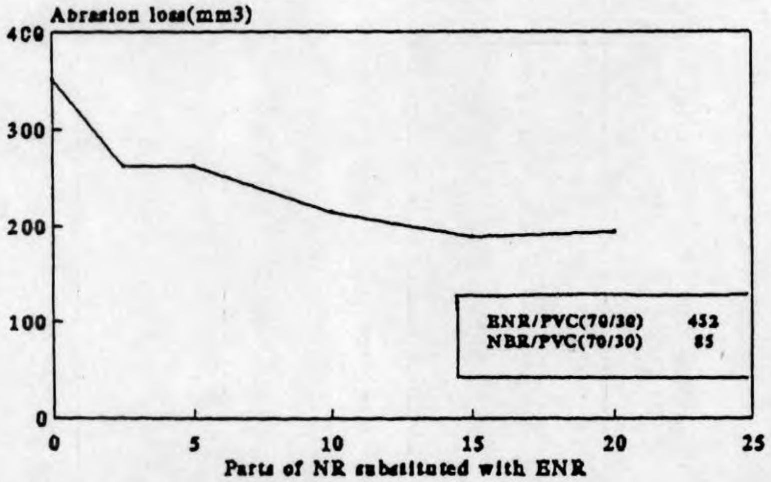

FIG.6 Variations in abrasion loss(mm3) of NR/PVC(70/30) blends with substitution of NR with ENR

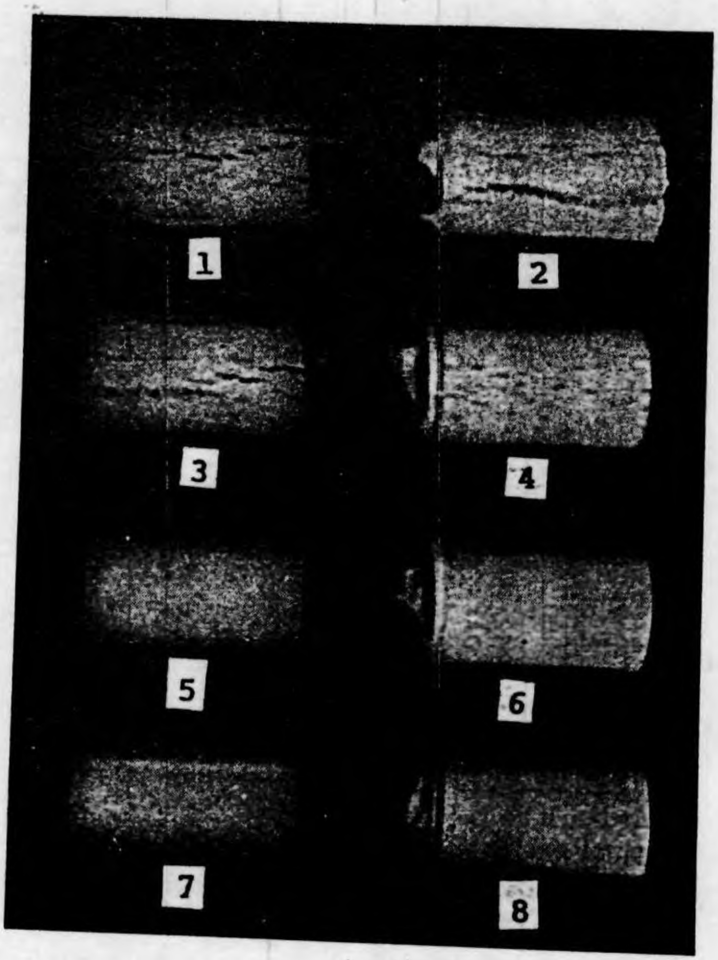

Fig. 7 - Photograph of samples from compounds 1 to 8 exposed to ozone for 70 hours