

Use of Amine Terminated Liquid Natural Rubber as a Plasticiser in Filled NR and NBR Compounds

R. SRILATHAKUTTY, NEETHA JOHN, RANI JOSEPH and K. E. GEORGE

Dept. of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, India

(Received May 28, 1995)

Amine Terminated Liquid Natural Rubber (ATNR) was used as a plasticiser in filled NR and NBR compounds replacing oil/DOP. The scorch time and cure time were found to be lowered when ATNR was used as the plasticiser. ATNR was found to improve the mechanical properties like tensile strength, tear strength and modulus of the vulcanizates. The ageing resistance of the vulcanizates containing ATNR was superior compared to the vulcanizates containing oil/DOP.

KEY WORDS Amine terminated liquid natural rubber, natural rubber, nitrile rubber, mechanical properties, cure characteristics.

INTRODUCTION

Oil resistant elastomers like NBR have poor low temperature flexibility, because of the molecular structural features. As the acrylonitrile content is increased, the swell in oil is reduced resulting in an increase in low temperature stiffness.¹ Plasticisers are normally used to improve low temperature flexibility, but plasticisers may get leached out during service. According to Radhakrishnan *et al.*, liquid natural rubber can be used as a plasticiser in NBR, as liquid natural rubber can get vulcanized together with NBR the leaching of the plasticiser in oil can be minimised. Liquid natural rubber may have significant contribution in altering the flow properties of the rubber mix. Reduction in hardness due to plasticiser addition can be minimised as the liquid natural rubber gets covulcanized within the base rubber.

Depolymerisation of NR into shorter segments with reactive end groups is prerequisite for the production of new material such as hydroxyl terminated liquid natural rubber, carboxyl terminated liquid natural rubber etc.³ The introduction of desired terminal functional groups in the NR oligomers opened several ways to modify the functionality. Carboxyl terminated reactive liquid polymers (CT-RLP) have been extensively used for modification of epoxy resins. However at a higher loading of the CT-RLP, the cure rate of epoxy resins in the presence of amine cure agent is usually retarded and may require increasingly higher reaction temperatures.⁴ Amino com-

TABLE I
Formulations for NR-filled compounds

Ingredients	A	B	C	D	E	F
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	4	4	4	4	4	4
Silica	60	60	--	--	--	--
Clay	--	--	60	60	--	--
HAF black	--	--	--	--	50	50
Naphthenic oil	5	--	5	--	--	--
Aromatic oil	--	--	--	--	5	--
ATNR	--	5	--	5	--	5
HS	1	1	1	1	1	1
MBTS	0.8	0.8	0.8	0.8	0.8	0.8
TMED	0.2	0.2	0.2	0.2	0.2	0.2
S	2.5	2.5	2.5	2.5	2.5	2.5

pounds are used as accelerators for the vulcanization of natural rubber and nitrile rubber.

In this paper we investigate the effect of ATNR on curing of NR and NBR compounds containing various fillers like HAF black, precipitated silica and china clay. The mechanical properties of these compounds containing ATNR were compared with the conventional compounds. The ageing resistance of the vulcanizates was also compared.

2. Experimental

2.1 Materials Used

Natural rubber (NR) ISNR-5, Mooney viscosity [ML(1 + 4)100°C - 82] was supplied by the Rubber Research Institute of India, Kottayam. Nitrile rubber (NBR) (ACN content 28%) Aparene N512 NS was supplied by the Apar Polymers Ltd., India. Compounding ingredients, zinc oxide, steric acid, sulphur, aromatic oil,

TABLE II
Formulations for NBR-filled compounds

Ingredients	G	H	I	J	K	L
NBR	100	100	100	100	100	100
S	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
HS	1	1	1	1	1	1
Silica	60	60	--	--	--	--
Clay	--	--	60	60	--	--
HAF black	--	--	--	--	50	50
DOP	5	--	5	--	5	--
ATNR	0	5	0	5	0	5
MBTS	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5

naphthenic oil, dioctyl phthalate (DOP), carbon black (HAF N330), precipitated silica, china clay were of commercial grade. Dibenzthiazyl disulphide (MBTS) and tetramethylthiuram disulphide (TMTD) were rubber grade—supplied by Bayer India Ltd. Ethylene diamine (99 wt. %, density 0.9 g/ml at 20°C), toluene, methanol and tetrahydrofuran solvents were of reagent grade.

2.2 Preparation of Amine Terminated Liquid Natural Rubber (ATNR)

Natural rubber was masticated for 30 minutes at 50°C. 100 gms of the masticated NR was dissolved in 450 ml toluene and the solution was charged in to a flat bottomed borosilicate glass flask. 50 ml of ethylenediamine together with 50 ml of tetrahydrofuran was added and thoroughly mixed with the rubber solution. The solution was kept for UV irradiation for about 60 hours. After irradiation, the product was purified by repeated precipitation using methanol and dried in vacuum oven. The product was characterised by the method described elsewhere.⁵

NR and NBR were compounded as per formulations given in Tables I and II on a laboratory mixing mill (6 × 12') as per ASTM D 3182 (1982). The optimum cure times (time to attain 90% of the maximum torque) and scorch times (time to attain 10% of the maximum torque) of the compounds were determined by a Goettfert

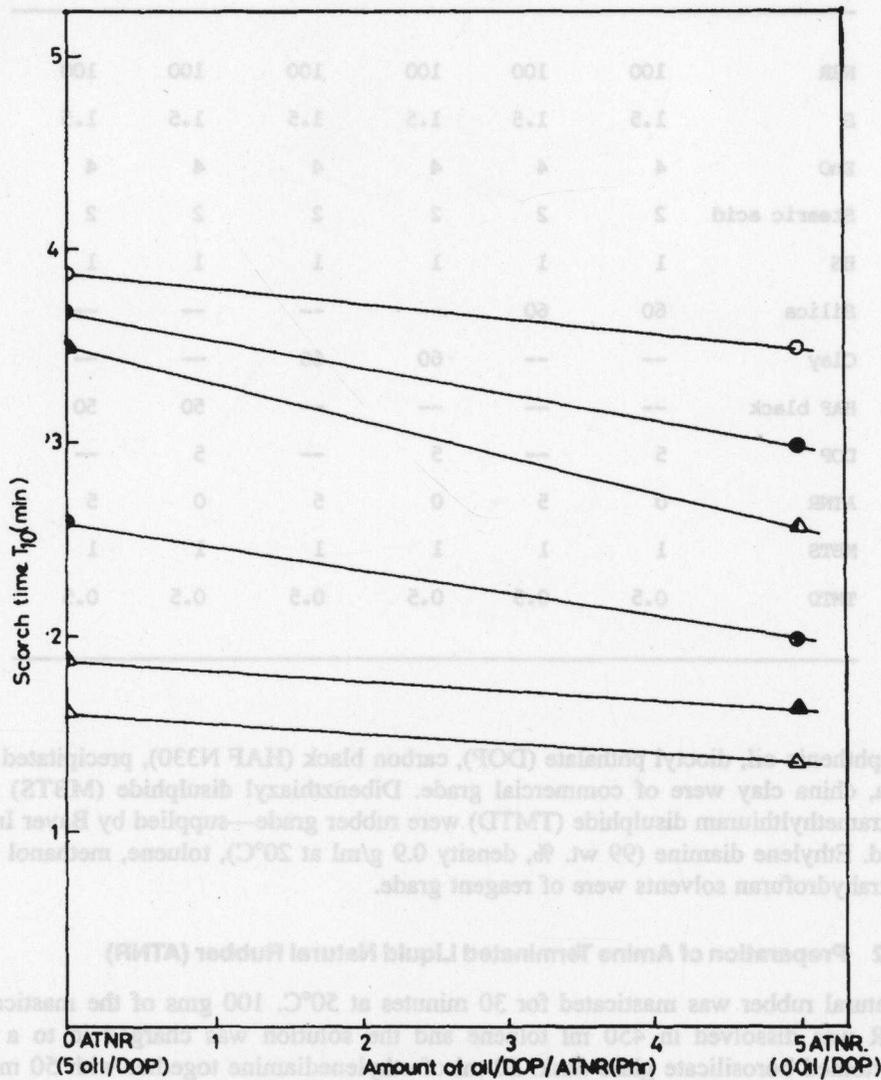


FIGURE 1 Variation of scorch time t_{10} (min) of filled NR and NBR compounds when oil/DOP was replaced by ATNR. ○, NR/silica; ●, NR/clay; △, NR/HAF; ◻, NBR/silica; ▲, NBR/clay; ▽, NBR/HAF.

Elastograph model 67.85 as per ASTM D 1646 (1981). These rubber compounds were moulded in an electrically heated hydraulic press at 150°C up to their respective optimum cure times. The tensile properties of the vulcanizates were evaluated on a Zwick UTM model 1445, at a crosshead speed of 500 mm min⁻¹ as per ASTM D 412-80. Tear resistance of the vulcanizates was evaluated as per ASTM D 624-81 using unicked 90° angled test specimens. The ageing resistance of the vulcanizates was studied by ageing for 24 and 48 hours at 100°C.

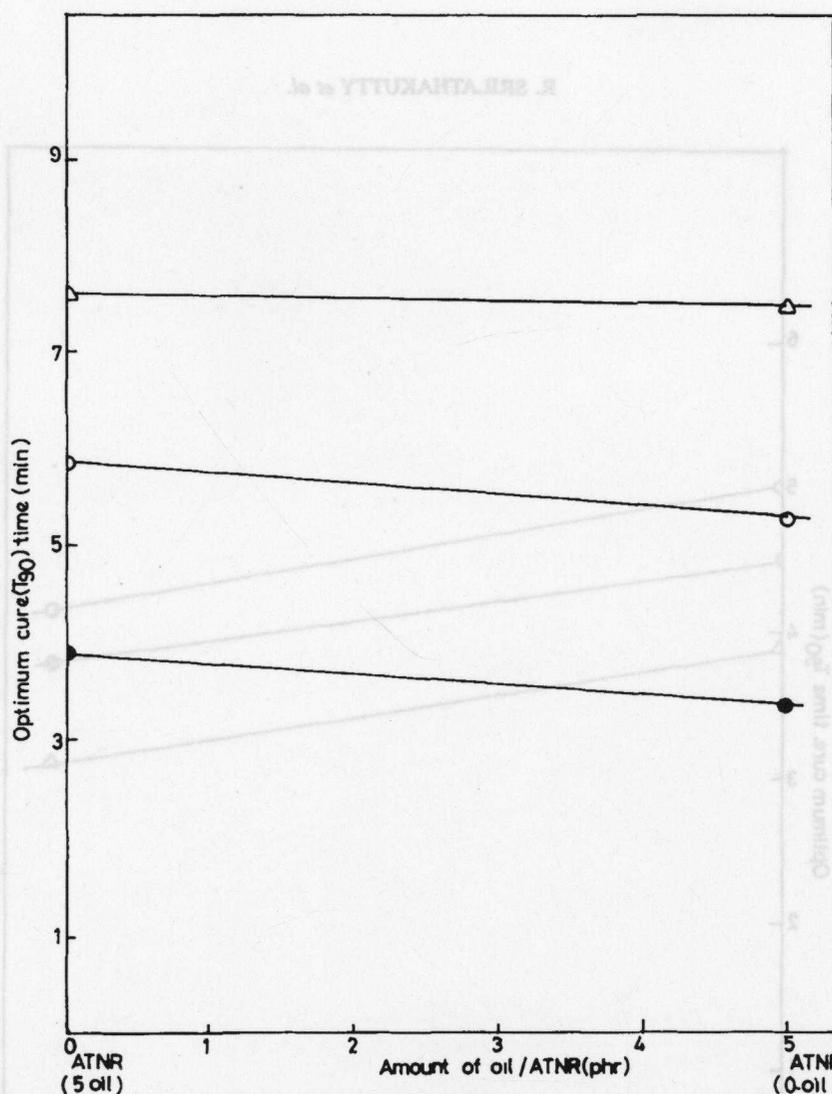


FIGURE 2 Variation of cure time t_{90} (min) of filled NR compound when oil was replaced by ATNR. Δ , NR/silica; \circ , NR/clay; \bullet , NR/HAF.

3. RESULTS AND DISCUSSION

Figure 1 shows the variation of scorch time when aromatic oil/naphthenic oil was replaced by ATNR in NR compounds and DOP in NBR compounds by ATNR. The compound containing ATNR shows a decrease in scorch time compared to compound containing aromatic oil/naphthenic oil. NR/carbon black filled and NR/clay filled compounds show a pronounced decrease in scorch time when aromatic oil/naphthenic oil was replaced by ATNR. This shows that ATNR accelerates the vulcanization of filled NR compounds. NR/silica filled compound shows marginal decrease in scorch

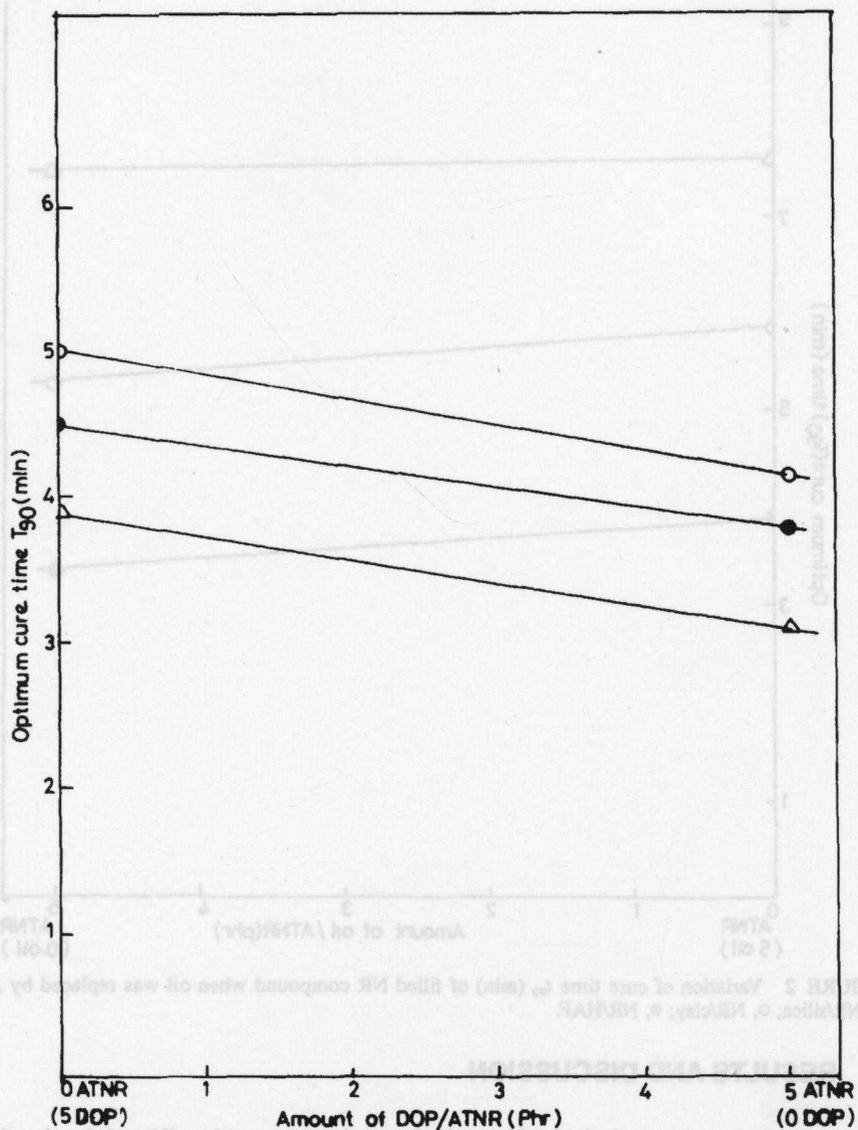


FIGURE 3 Variation of cure time t_{90} (min) of filled NBR compounds when DOP was replaced by ATNR. Δ , NBR/silica; \bullet , NBR/clay; \circ , NBR/HAF.

time. Similar trend is observed in the case of filled NBR compounds also. This shows that ATNR can accelerate the vulcanization of filled NBR compounds also.

Figure 2 shows the variation in cure time when naphthenic oil/aromatic oil was replaced by ATNR in NR filled compounds. The compounds containing ATNR shows a decrease in cure time. This may be due to the presence of amino group in ATNR which accelerate the curing of NR.⁷ NR/clay and NR/black filled compounds show considerable change in cure time compared to NR/silica filled compounds.

Figure 3 shows the variation in cure time when DOP was replaced by ATNR in

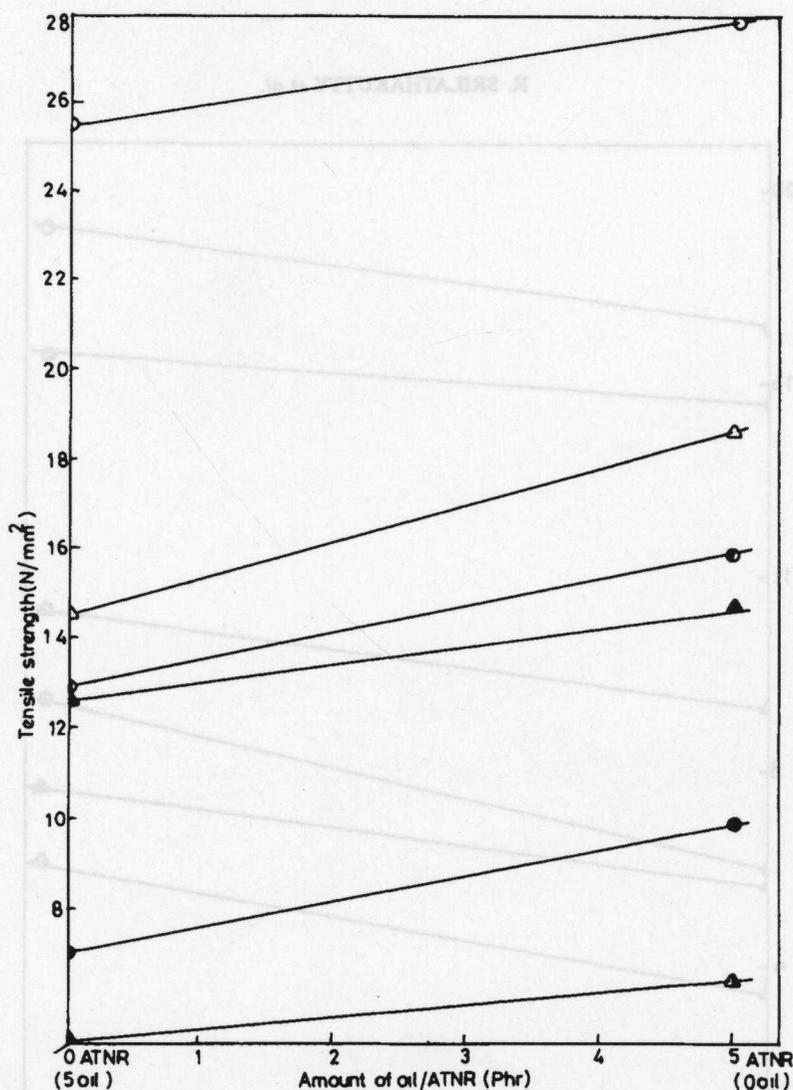


FIGURE 4 Variation of tensile strength of NR vulcanizates before and after ageing when oil was replaced by ATNR. Before ageing: \circ , NR/silica; Δ , NR/clay; \circ , NR/HAF. After ageing: \bullet , NR/silica; Δ , NR/clay; \blacktriangle , NR/HAF.

NBR compounds. In NBR compounds also a reduction in cure time was observed similar to natural rubber compounds. This shows that ATNR can accelerate the curing of NBR.⁶ NBR/clay filled and NBR/black filled compounds show a remarkable decrease in cure time. NBR/silica filled compounds show a marginal decrease in cure time.

Figure 4 shows the variation in tensile strength of the filled NR vulcanizates before and after ageing. The tensile strength of the NR filled vulcanizates containing ATNR was higher than that of compound containing aromatic oil/naphthenic oil. This may

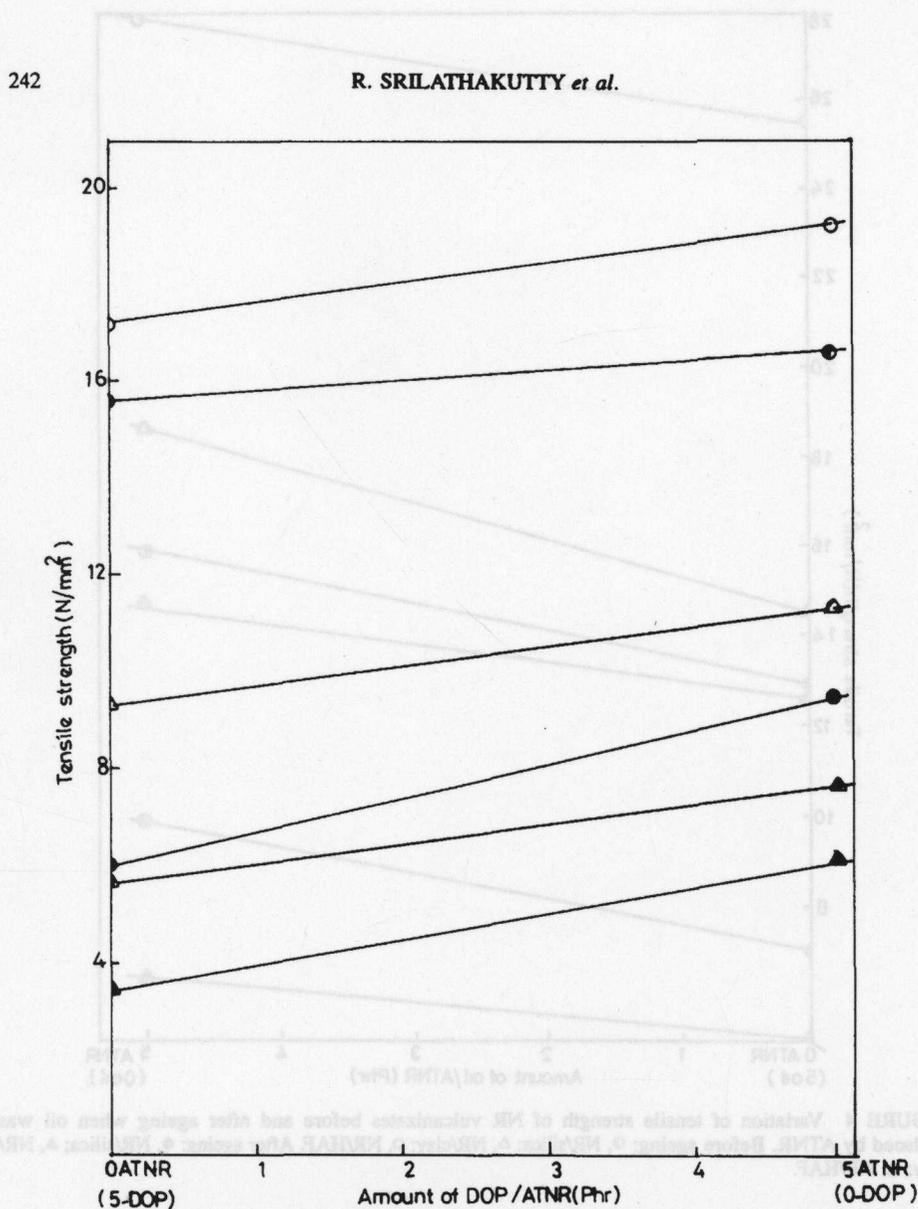


FIGURE 5 Variation of tensile strength of filled NBR vulcanizates before and after ageing when DOP was replaced by ATNR. Before ageing: Δ , NBR/silica; \bullet , NBR/clay; \circ , NBR/HAF. After ageing: Δ , NBR/silica; \blacktriangle , NBR/clay; \circ , NBR/HAF.

be due to the co-crosslinking of ATNR with NR. Tensile strength of NR/clay filled vulcanizates show a pronounced increase compared to NR/black and NR/silica filled compounds. This may be due to the improved polymer filler interaction produced by ATNR in clay filled NR vulcanizates. Ageing resistance of the filled NR vulcanizate containing ATNR was found to be superior in all cases. This shows that ATNR can improve the ageing resistance of NR vulcanizate may be due to the presence of amino group in ATNR.

Figure 5 shows the variation in tensile strength of filled NBR compounds before

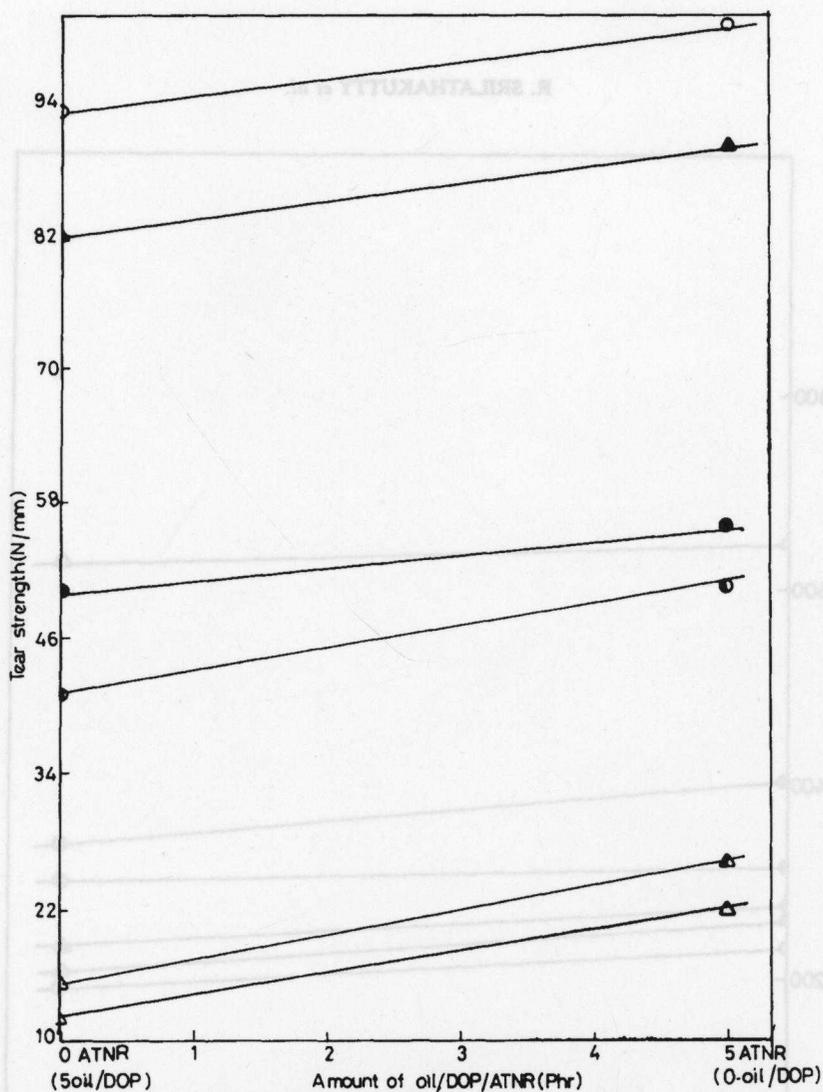


FIGURE 6 Variation of tear strength of filled NR and NBR vulcanizates when oil/DOP was replaced by ATNR. ●, NR/silica; △, NR/clay; ○, NR/HAF; ◻, NBR/silica; ▲, NBR/clay; ●, NBR/HAF.

and after ageing. Tensile strength of the filled NBR vulcanizates was higher than that of vulcanizates containing DOP. NBR/clay filled compounds show a remarkable increase in tensile strength compared to silica filled and black filled vulcanizates. This again shows that ATNR can improve the polymer filler interaction in clay filled NBR compounds. Vulcanizates containing ATNR show better ageing resistance. This shows that ATNR can act as a mild antioxidant in filled NBR compounds.

Figure 6 shows variation in tear strength of filled NR compounds when naphthenic oil/aromatic oil was replaced by ATNR. Tear strength of these vulcanizates containing ATNR was found to be superior compared to the vulcanizates containing oil.

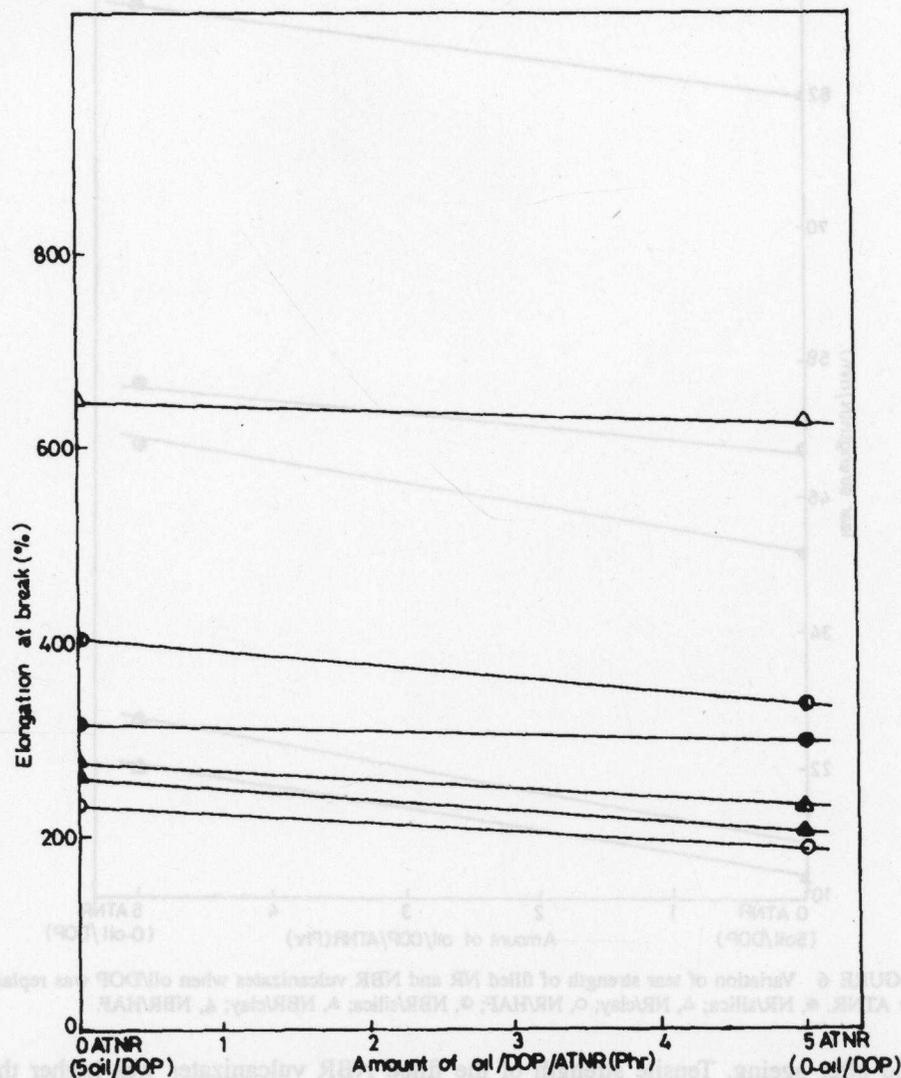


FIGURE 7 Variation of elongation at break (%) of filled NR and NBR vulcanizates when oil/DOP was replaced by ATNR. ●, NR/silica; △, NR/clay; ○, NR/HAF; ⊙, NBR/silica; ▲, NBR/clay; ▲, NBR/HAF.

NR/carbon black filled, NR/silica filled and NR/clay filled vulcanizate shows increase in tear strength when oil was replaced by ATNR. This shows that ATNR can act as a polymeric plasticiser and can get co-crosslinked with NR during final vulcanization. The tear strengths of NBR vulcanizates containing ATNR show a remarkable increase in tear strength compared to compounds containing DOP as shown in Figure 6. This again shows that the ATNR can act as a polymeric plasticiser and it gets co-crosslinked with NBR during the final vulcanization.

Figure 7 shows variation in elongation at break when aromatic oil/naphthenic oil was replaced by ATNR. Elongation at break found to be decreased when oil was

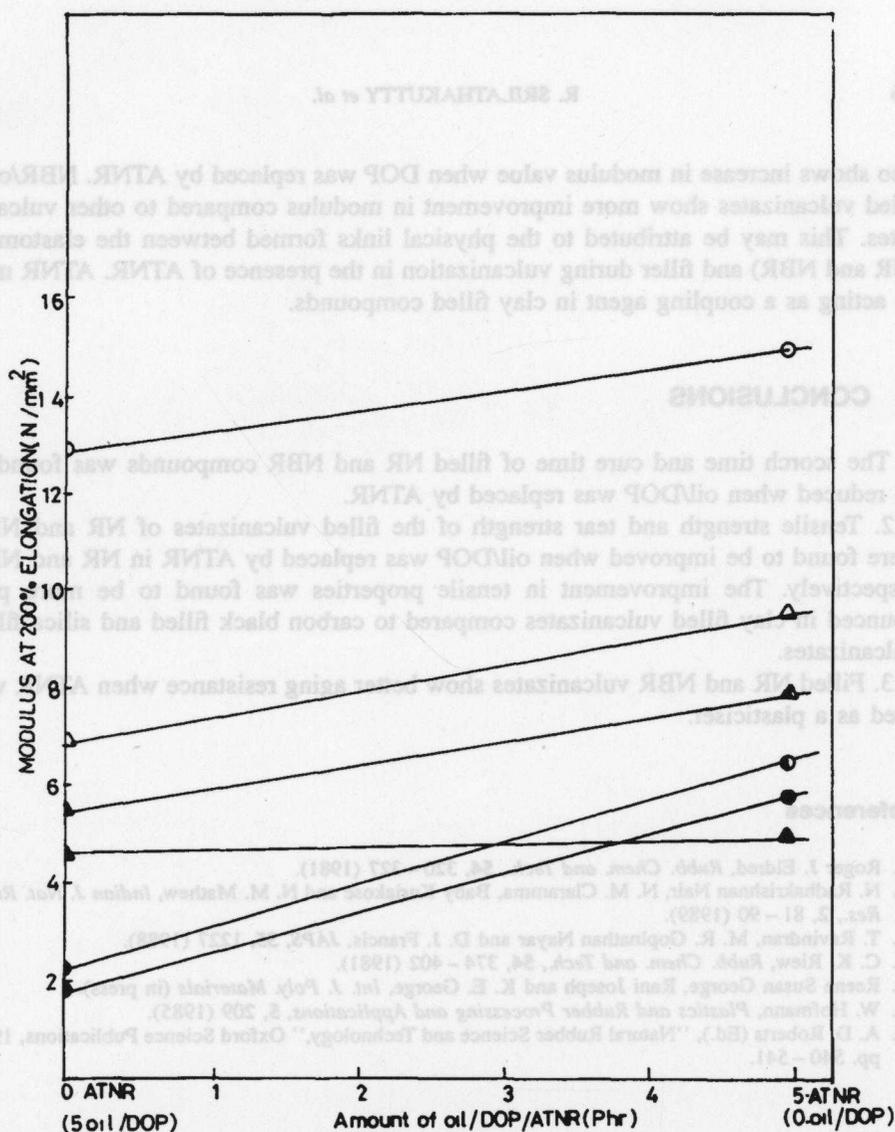


FIGURE 8 Variation of modulus at 200% elongation of filled NR and NBR vulcanizates. ▲, NR/silica; ●, NR/clay; △, NR/HAF; ◐, NBR/silica; ◑, NBR/clay; ○, NBR/HAF.

replaced by ATNR. This may be due to the increased polymer filler interaction through ATNR. ATNR may be acting as a coupling agent between the polymer and the filler. Similar trend was observed in filled NBR vulcanizates also as shown in Figure 7.

Figure 8 shows variation in modulus at 200% elongation when aromatic oil/naphthenic oil was replaced by ATNR. When oil was replaced by ATNR modulus of the filled NR vulcanizates was found to be increased. This improvement in modulus values may be due to the higher polymer filler interaction. Filled NBR compounds

also shows increase in modulus value when DOP was replaced by ATNR. NBR/clay filled vulcanizates show more improvement in modulus compared to other vulcanizates. This may be attributed to the physical links formed between the elastomers (NR and NBR) and filler during vulcanization in the presence of ATNR. ATNR may be acting as a coupling agent in clay filled compounds.

4. CONCLUSIONS

1. The scorch time and cure time of filled NR and NBR compounds was found to be reduced when oil/DOP was replaced by ATNR.

2. Tensile strength and tear strength of the filled vulcanizates of NR and NBR were found to be improved when oil/DOP was replaced by ATNR in NR and NBR respectively. The improvement in tensile properties was found to be more pronounced in clay filled vulcanizates compared to carbon black filled and silica filled vulcanizates.

3. Filled NR and NBR vulcanizates show better aging resistance when ATNR was used as a plasticiser.

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