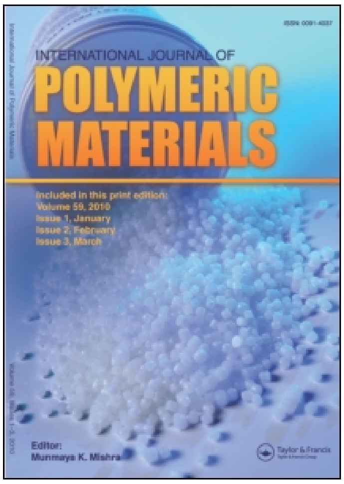

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Study of Polyschiff's Base as a Protective Agent in Natural Rubber

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Photochemical degradation of natural rubber (NR) yield amine-terminated liquid natural rubber (ATNR) when carried out in solution in presence of ethylene diamine. The ATNR on reaction with glyoxal yielded polyschiff's base. This polyschiff's base was found to improve the ageing resistance of natural rubber.

KEY WORDS Natural rubber, ageing resistance, polyschiff's base

1. INTRODUCTION

The developments in product design and improvements in compounding have increased service life for rubber products. Many amine and phenolic type antioxidants are commercially available. However, most of the antioxidants suffer from fairly high volatility and extractability in water or other fluids. The removal of antioxidants from the polymer during service has an adverse effect on the useful life of the product.[1] Transition metal ions like cobalt, iron, manganese and copper act as catalyst for hydroperoxide decomposition. These metal ions reduce the activation energy of the hydroperoxide decomposition. They are, therefore, effective prooxidants and the activity depends on the availability of oxidised and reduced states of comparable stability.[2] Complexing agents which have the ability to coordinate the vacant orbitals of transition metal ions to their maximum coordination number and thus inhibit the coordination of hydroperoxides to the metal ions are therefore effective as metal deactivators and hence inhibitors to metal catalysed autooxidation.

This paper describes the preparation of polyschiff's base starting from amine terminated liquid natural rubber which was prepared by the photochemical degradation of natural rubber.[3] This polyschiff's base was tried as antioxidants in natural rubber vulcanizate. The ATNR gets attached to the natural rubber during sulphur vulcanization and the polyschiff's base becomes nonvolatile and nonextractable. The efficiency of this rubber bound polyschiff's base is compared with that of conventional antioxidant in dry rubber vulcanizates.

TABLE I

Formulations

Materials				
NR	100	100	100	100
ZnO	5	5	5	5
Stearic acid	2	2	2	2
MBTS	0.6	0.6	0.6	0.6
TMTD	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5
Carbon black	40	40	40	40
Aromatic oil	5	5	5	5
Accinox ZC	--	1.0	--	--
Polyschiff's base	--	--	1.0	2.0
Cure characteristics				
T_{10} (Scorch time) in minutes	2.1	2.1	1.7	1.6
T_{90} (Optimum cure time) in minutes	4.0	3.9	3.7	3.5
Vulcanizate properties				
Compression set (%)	35.24	30.29	30.03	30.12
Hardness (Shore A)	48	49	50	51

2. EXPERIMENTAL

2.1 Materials

Natural rubber (ISNR-5, Mooney viscosity (ML (1 + 4) 100°C) 85.3 supplied by the Rubber Research Institute of India. Ethylene diamine (99 wt.%, density 0.9 g/ml at 20°C). Glyoxal solution (40%). Toluene, methanol and tetrahydrofuran solvents were of reagent grade, dried and distilled before use. Zinc oxide, stearic acid, benzothiazyl disulphide, tetramethyl thiuram disulphide, sulphur, carbon black (HAF N 330), aromatic oil, Accinox ZC (N-1,3-dimethyl N'-phenyl *p*-phenylene diamine) used were commercial grade.

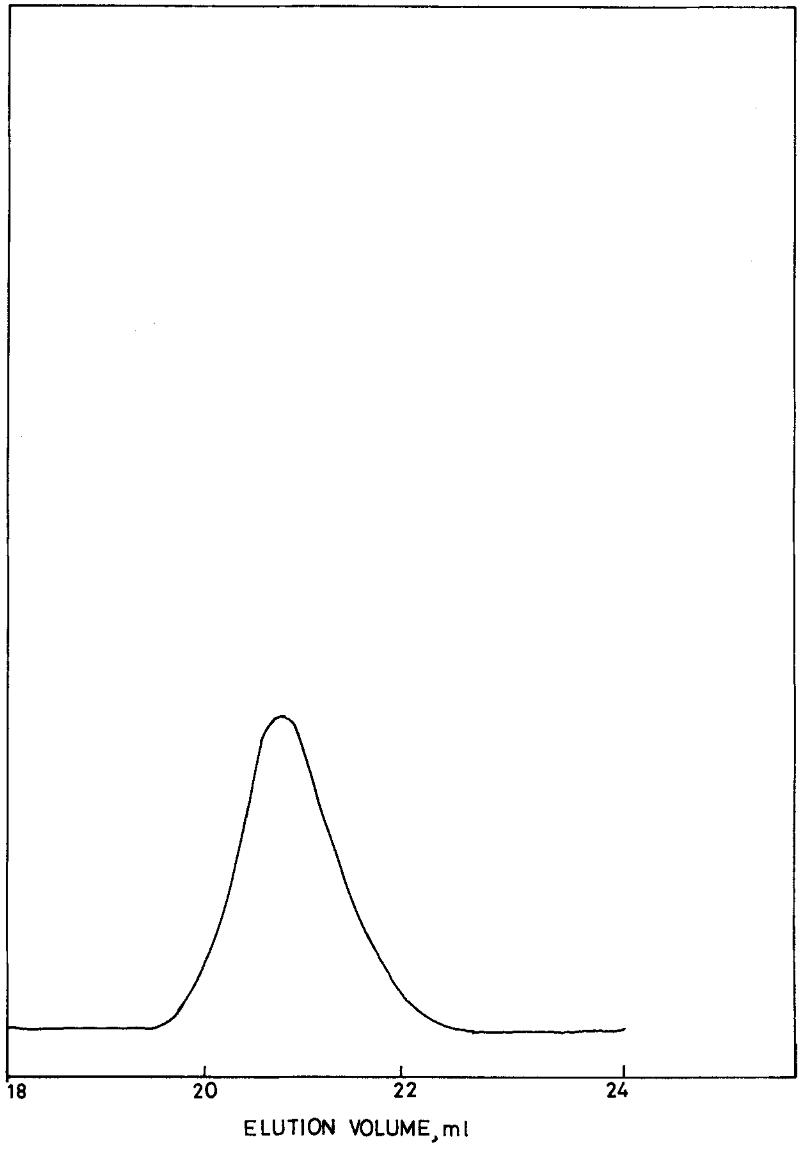

FIGURE 1 GPC trace of ATNR.

2.2 Preparation of 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 into a flat-bottomed borosilicate glass flask. 50 ml of ethylene diamine together with 50 ml of tetrahydrofuran was added and thoroughly mixed with the rubber solution. The solution was kept in sunlight for irradiation. After about 60 h of irradiation, the

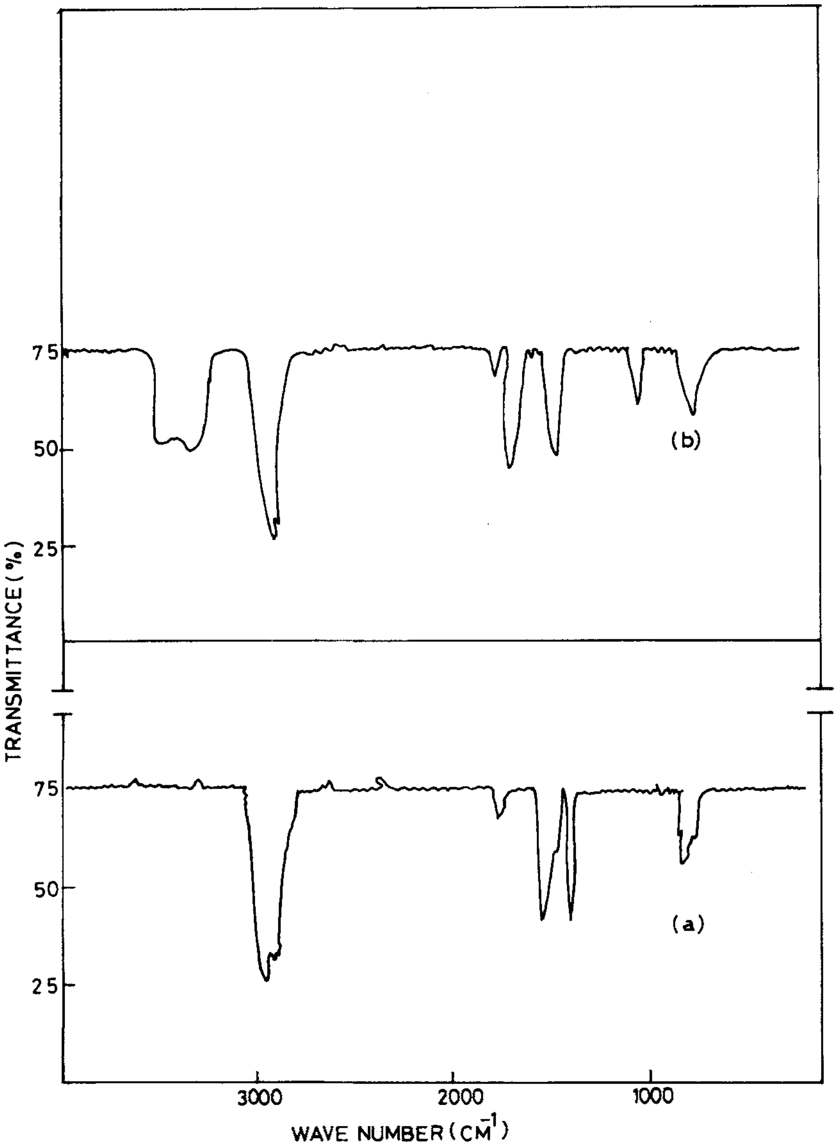

FIGURE 2 IR spectra of (a) raw natural rubber, (b) ATNR.

product was washed with methanol and dried in vacuum. The sample for analysis was purified by repeated precipitation by methanol from a toluene solution and dried in a vacuum oven.

2.3 Preparation of Polyschiff's Base

5 gms of the purified ATNR sample was dissolved in 20 ml of toluene and 25 ml 40% glyoxal was added. The polyschiff's base formed was precipitated with

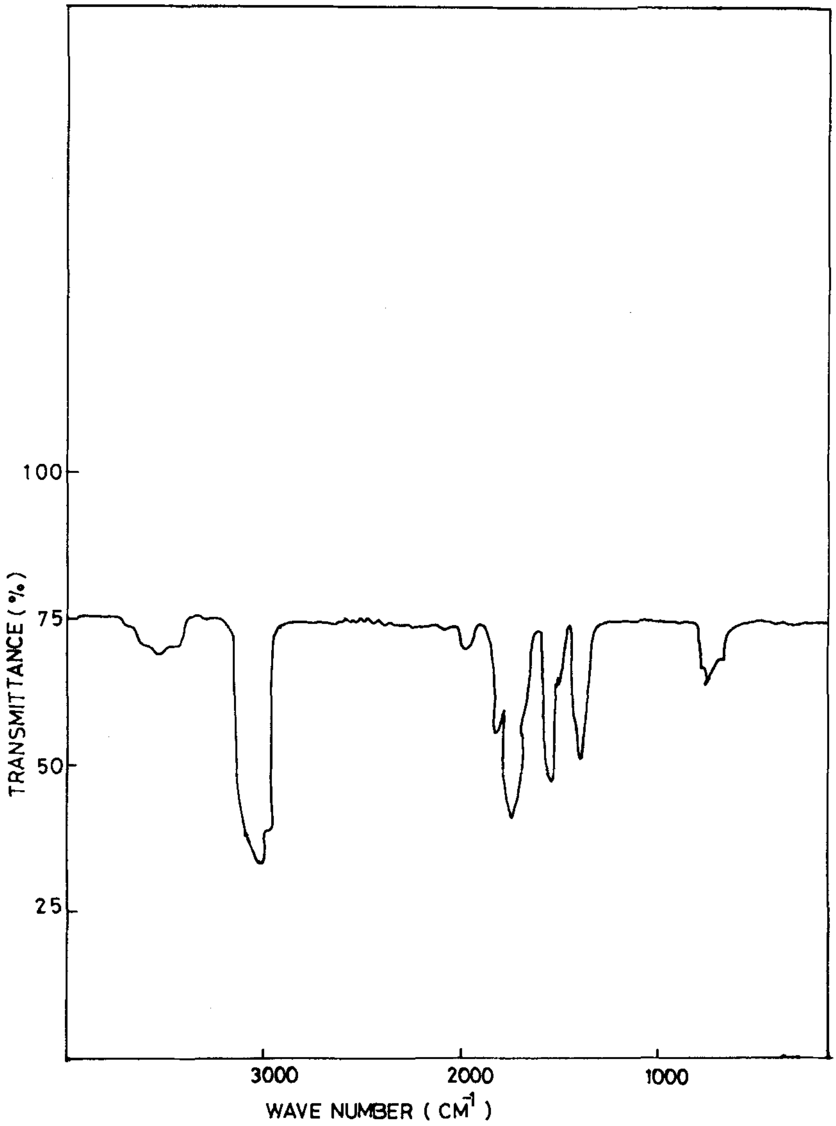

FIGURE 3 IR spectrum of the polyschiff's base.

excess methanol and dried in vacuum. This polyschiff's base was tried as a metal deactivator in natural rubber as per formulation given in Table I.

NR was masticated and compounded as per the formulation given in Table I according to ASTM procedure. The optimum cure times (time to reach 90% of the maximum torque) of the compounds were determined on a Göttfert Elastograph model 67.85 as per ASTM D-1646 (1981). Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure times. Dumbell-shaped tensile test pieces were punched out of

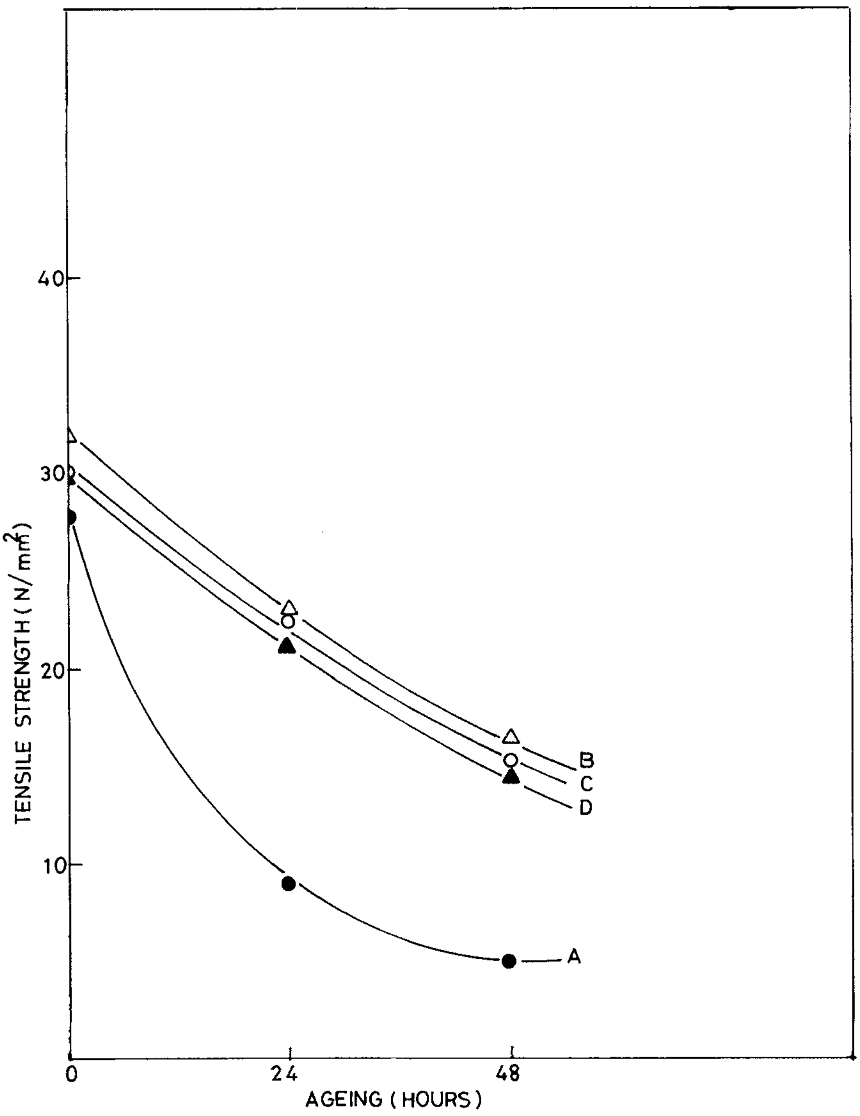

FIGURE 4 Variation in tensile strength with ageing at 100°C (A) without antioxidant, (B) 1 phr Accinox ZC, (C) 1 phr polyschiff's base, (D) 2 phr polyschiff's base.

these sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine model 1445 using a cross-head speed of 500 mm/min as per ASTM D-412-80. The ageing resistance of the vulcanizates was studied by ageing the vulcanizates for 24 h and 48 h at 100°C in an air oven and then measuring the retention in tensile properties. The tear strength, hardness and compression set were measured according to relevant ASTM standards.

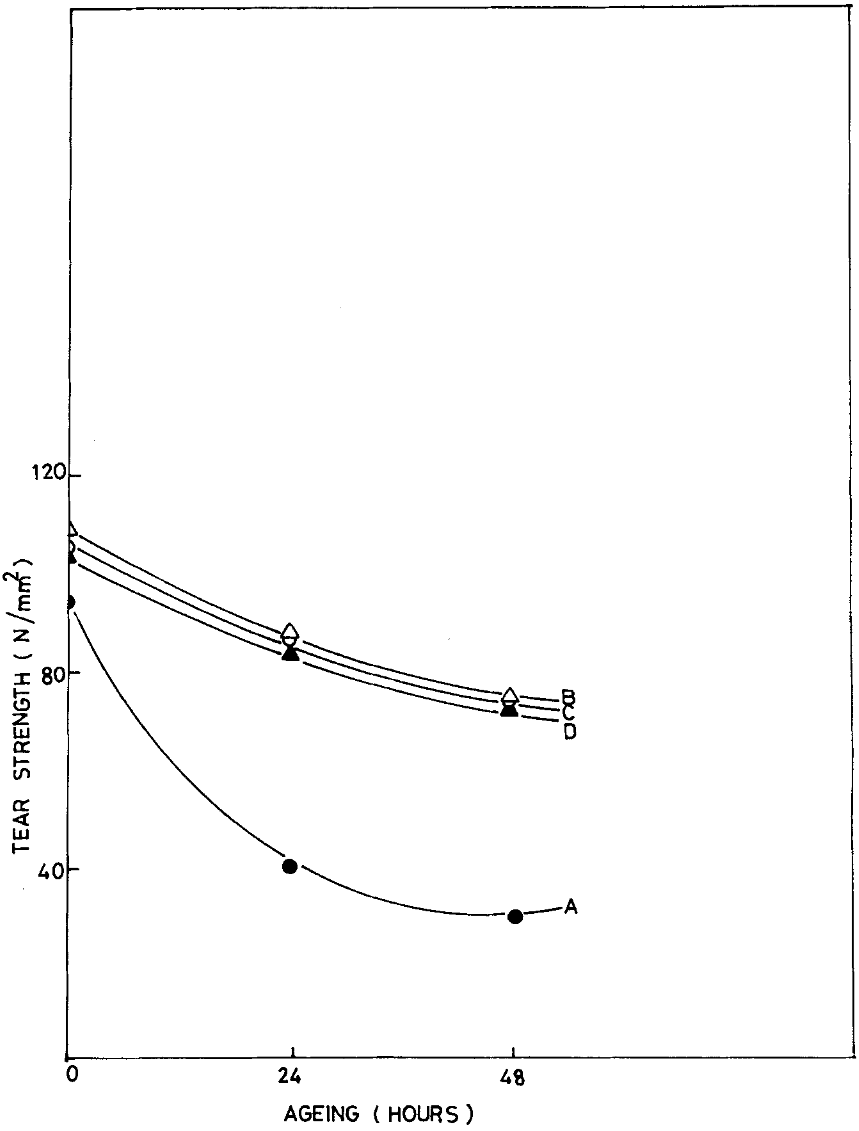

FIGURE 5 Variation in tear strength with ageing at 100°C. (A) without antioxidant, (B) 1 phr Accinox ZC, (C) 1 phr polyschiff's base, (D) 2 phr polyschiff's base.

2.4 Characterisation of ATNR

The average molecular weight of ATNR was measured by gel permeation chromatograph (GPC) (Waters Associates, Model 6000A solvent delivery system with differential refractometer R-401).

IR spectrum was recorded in a Beckman spectrometer at 20°C in NaCl plate cell.

Aminogroup was estimated volumetrically using a standard procedure.[4]

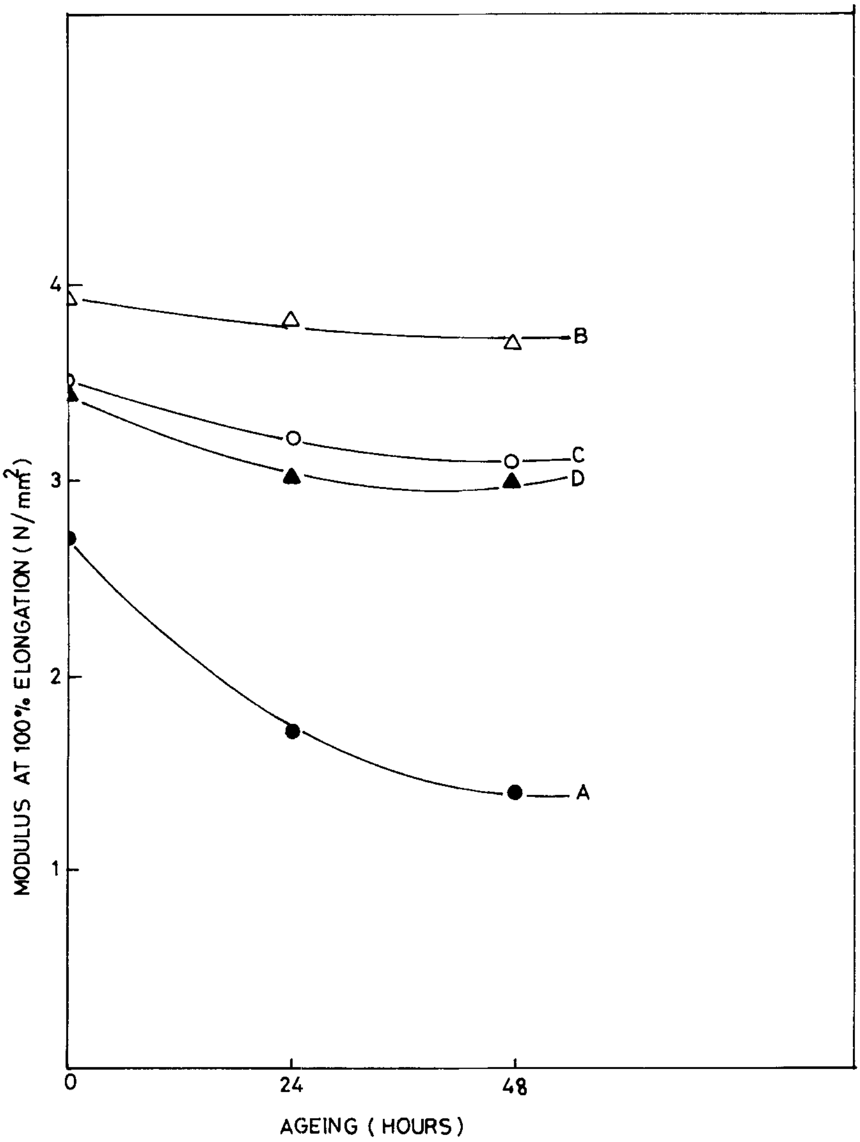

FIGURE 6 Variation in modulus at 100% elongation with ageing at 100°C (A) without antioxidant, (B) 1 phr Accinox ZC, (C) 1 phr polyschiff's base, (D) 2 phr polyschiff's base.

2.5 Characterisation of Polyschiff's Base

IR spectrum was recorded in a Beckman spectrometer at 20°C in a NaCl plate cell.

3. RESULTS AND DISCUSSION

Figure 1 shows the GPC trace of the ATNR. The molecular weight ($\overline{MW}$) of the product is found to be about 2100 which confirms the efficiency of the depolymerisation of natural rubber in solution by sunlight.

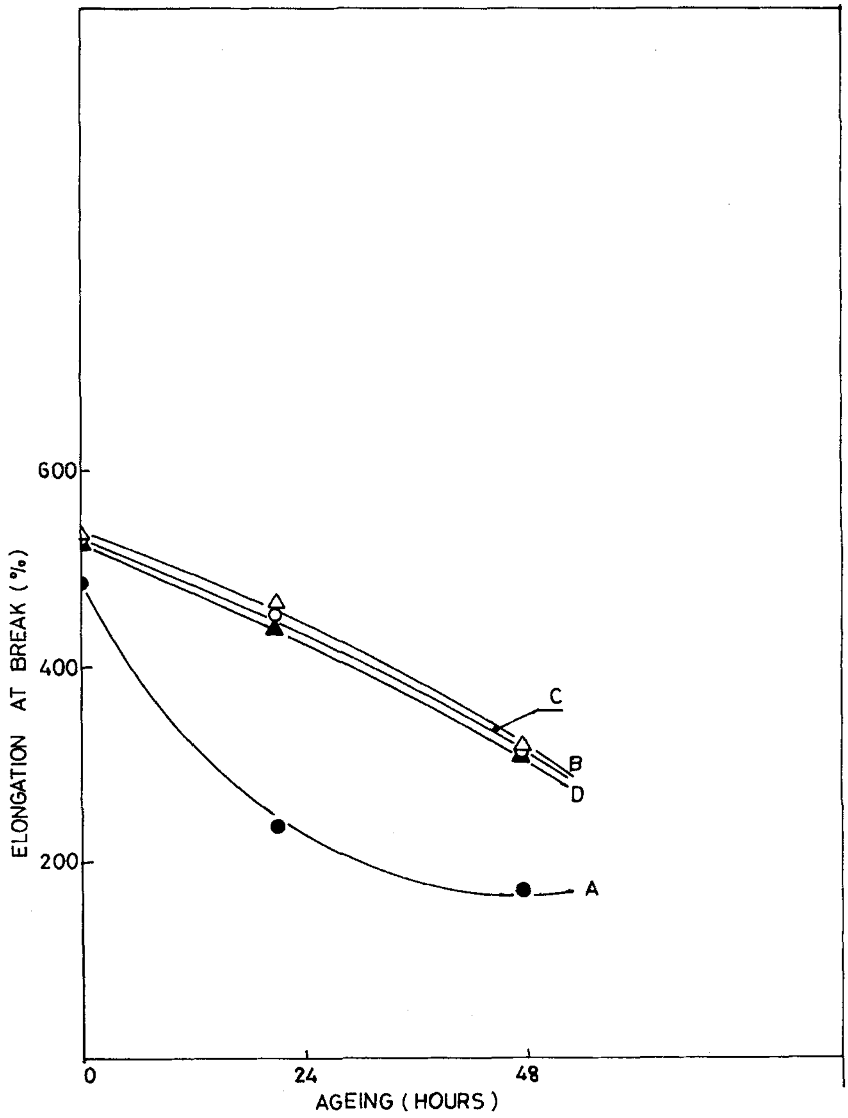

FIGURE 7 Variation in elongation at break with ageing at 100°C (A) without antioxidant, (B) 1 phr Accinox ZC, (C) 1 phr polyschiff's base, (D) 2 phr polyschiff's base.

Amino group estimation by acetylation gave an average value of 47.74 mg of KOH/g of the sample which corresponds to a functionality of 1.79. This value, being slightly less than 2, indicates side reactions to a lower extent. Hence the depolymerised product may be assumed to contain amino groups.

Figure 2 shows the IR spectrum of NR and ATNR. Peaks are observed at 3600–3200 cm^{-1} (broad N—H stretching), 3200–3040 cm^{-1} (C—H stretching), 1650–1590 cm^{-1} (N—H bending), 1660 cm^{-1} (C=C Cis-vinylene), 1450 cm^{-1} (C—H bending), 1100 cm^{-1} (C—H stretching) and at 885 cm^{-1} (—CH_3). This further confirms the presence of aminogroup in the depolymerised natural rubber.

Figure 3 shows the IR spectrum of the polyschiff's base. The additional peak observed at 1685 cm^{-1} corresponds to the C=N stretching vibrations. This confirms the formation of a polyschiff's base.

Table I shows the cure characteristics of the compounds. The compounds containing the polyschiff's bases are found to show a slight reduction in the scorch time and cure time which may be due to accelerating effect of amino compounds.[6]

Figure 4 shows the variation in tensile strength of the vulcanizates with ageing. The compound without antioxidant shows very poor ageing resistance. The retention in tensile strengths of the vulcanizates containing the polyschiff's base is comparable to that of the compound containing 1 phr antioxidant after 24 and 48 hrs ageing at 100°C. And so is the retention in tear strength (Figure 5) modulus (Figure 6) and elongation at break (Figure 7). This shows that the polyschiff's base can complex with pro-oxidant metals like iron, copper, manganese and thus improve the ageing resistance. The compression set and hardness of the vulcanizates are given in Table I. These properties are similar for the vulcanizates containing polyschiff's base and the conventional antioxidant.

4. CONCLUSION

The polyschiff's base formed by the reaction of ATNR with glyoxal can act as a metal deactivator and thus improve the ageing resistance of NR compounds.

Acknowledgment

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