

Studies on Natural Rubber Bound *Para*-Phenylenediamine Antioxidants in NBR

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SYNOPSIS

Para-phenylenediamine (PD) was chemically attached to depolymerized natural rubber by a photochemical reaction. The rubber bound PD was characterized by TLC, ¹H-NMR, IR, and TGA. The efficiency and permanence of the bound PD were compared with conventional antioxidants in NBR vulcanizates. The rubber bound PD was found to be less volatile and more resistant to water and oil extraction. The vulcanizates showed improved aging resistance in comparison to vulcanizates containing conventional antioxidants. The liquid rubber bound antioxidant reduces the amount of plasticizer required for compounding. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Nitrile rubber based polymers used in the fabrication of seals for use in contact with mineral oil based hydraulic fluids require protective antioxidant stabilization in order to retain their elastomeric properties for a useful period in service. But when they are subjected to continuous contact with hydraulic fluids under high temperature, the low molecular weight additives will be lost by extraction or volatilization. One method to overcome this problem is to develop polymer bound antioxidants. There are two basic approaches to obtain polymeric antidegradants. One is to copolymerize various monomers having an antioxidative active moiety with elastomeric monomers. The other is by the direct combination of conventional antioxidant with modified elastomers.^{1,2} Nitrile rubber containing copolymerized *N*-(4-anilinophenyl) methacrylamide was first reported by Meyer et al.³ Ajiboye and Scott reported the azobis-isobutyronitrile initiated addition of mercaptans in nitrile bound rubber (NBR) latex that can be used as a masterbatch antioxidant for blending with unstabilized NBR.⁴ Bonding of antioxidants to NBR by a combination of triazine thiol,

N-methylol methacrylamide, and antioxidant were described by Mori et al.⁵ This article describes the chemical binding of *para*-phenylenediamine (PD) to depolymerized natural rubber by photochemical reaction and subsequent use of the product in NBR compounds. The rubber part of the bound antioxidant gets attached to nitrile rubber during sulfur vulcanization and the antioxidant becomes nonvolatile and nonextractible. The efficiency and permanence of these bound antioxidants were compared with conventional antioxidants in filled NBR vulcanizates.

EXPERIMENTAL

Materials

Acrylonitrile-butadiene rubber (NBR; N 553) was supplied by Apar Polymers Ltd., India. Compounding ingredients, ZnO, stearic acid, dioctylphthalate, and carbon black (HAF, N 330) were commercial grade. Dibenzthiazyl disulfide (MBTS), tetramethylthiuram disulfide (TMTD), Vulkanox 4020 (*N*-phenyl-*N'*(1,3 dimethylbutyl)-*p*-phenylenediamine), Vulkanox HS (polymerized 2,2,4 trimethyl-1,2-dihydroquinoline) were rubber grade supplied by Bayer India Ltd. Methanol, acetone, and toluene were of reagent grade and used as such. Light oil, gear oil, transformer oil, and engine oil were commercial

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Table I Formulations for Testing Antioxidants

Sample	X	A	B	C	D
Acrylonitrile-butadiene rubber (NBR) (phr)	100	100	100	100	100
Sulfur	1.5	1.5	1.5	1.5	1.5
Zinc oxide	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Carbon black (HAF, N 330)	40.0	40.0	40.0	40.0	40.0
Diethylphthalate	5.0	1.0	5.0	5.0	1.0
Dibenzthiazyl disulfide	1.0	1.0	1.0	1.0	1.0
Tetramethyl thiuram disulfide	0.5	0.5	0.5	0.5	0.5
Vulkanox 4020	—	—	1.0	—	—
Vulkanox HS	—	—	—	1.0	—
NR-PD	—	5.0	—	—	—
Depolymerized rubber	—	—	—	—	5.0
Cure characteristics					
Cure time (min)	3.9	2.6	3.6	3.8	4.0
Scorch time (min)	2.2	1.6	2.1	2.2	4.9

phr, parts per hundred rubber; NR-PD, *para*-phenylenediamine bound to depolymerized natural rubber.

grade. PD (Analar grade) from Central Drug House (India) was used.

Preparation of Natural Rubber (NR) Bound PD

NR was masticated for 30 min at 50°C; 100 g of it was dissolved in 1 L toluene and the solution was charged into the photochemical reactor, a glass vessel of 3-L capacity fitted with a water condenser and mechanical stirrer. A high pressure mercury vapor lamp in a quartz immersion well was placed in the solution. After 60-h exposure to a part of depolymerized rubber solution, 25 g PD dissolved in acetone was added slowly with stirring and irradiation was continued. Samples taken, after 1, 2, 3, 4, 5, 6, 7, 10, 12, and 15 h of exposure after adding PD were poured into an excess of methanol with stirring; liquid rubber precipitated. The unreacted PD was removed by repeated reprecipitation using a toluene-methyl alcohol (1 : 1 v/v) mixture, and the product was dried in a vacuum oven. The rubber bound antioxidant was obtained in the form of a viscous liquid. Samples taken after different times of exposure were added in nitrile rubber compounds according to formulations given in Table I. The optimum exposure time for preparing rubber bound antioxidant was determined by studying the retention in tensile strength after aging the vulcanizates at 100°C for 48 h. Maximum retention in tensile strength was obtained for vulcanizates containing the rubber bound samples produced by exposure for 6 h and above, so time of UV irradiation after adding PD was fixed at 6 h. The bound antioxidants were pre-

pared by irradiating depolymerized rubber with PD for 6 h. The rest of the depolymerized rubber solution was irradiated continuously. Samples were taken after 1, 2, 3, 4, 5, 6, 7, 10, 12, and 15 h of exposure, precipitated as above, and employed in nitrile rubber compounds with the formulations given in Table I.

Analysis of Bound Antioxidant

Analysis of the bound antioxidant was carried out by using thin layer chromatography (TLC), infrared spectroscopy (IR), proton magnetic resonance spectroscopy (¹H-NMR), and thermogravimetric analysis (TGA). TLC was carried out using silica gel as the adsorbent. A mixed solvent combining benzene and ethyl acetate (4 : 1 v/v) was used as the developing solvent for all samples. Diazotization using nitrous acid fumes was carried out to detect the antioxidants and iodine for depolymerized NR.⁶

IR spectra were taken on a Perkin-Elmer Model 377 IR spectrometer.

The ¹H-NMR spectra of the samples were recorded from a solution in CCl₄ using a JEOL-JNM spectrometer.

TGA was carried out using a Dupont TG-DSC standard model at a heating rate of 10°C/min.

Molecular weight of the rubber bound antioxidant (\bar{M}_n) was calculated using the Mark-Houwink-Sakurada equation by measuring the intrinsic viscosity using an Ubbelohde viscometer and substituting the values of K (5.02×10^{-2} mL/g) and a (0.667) of NR.

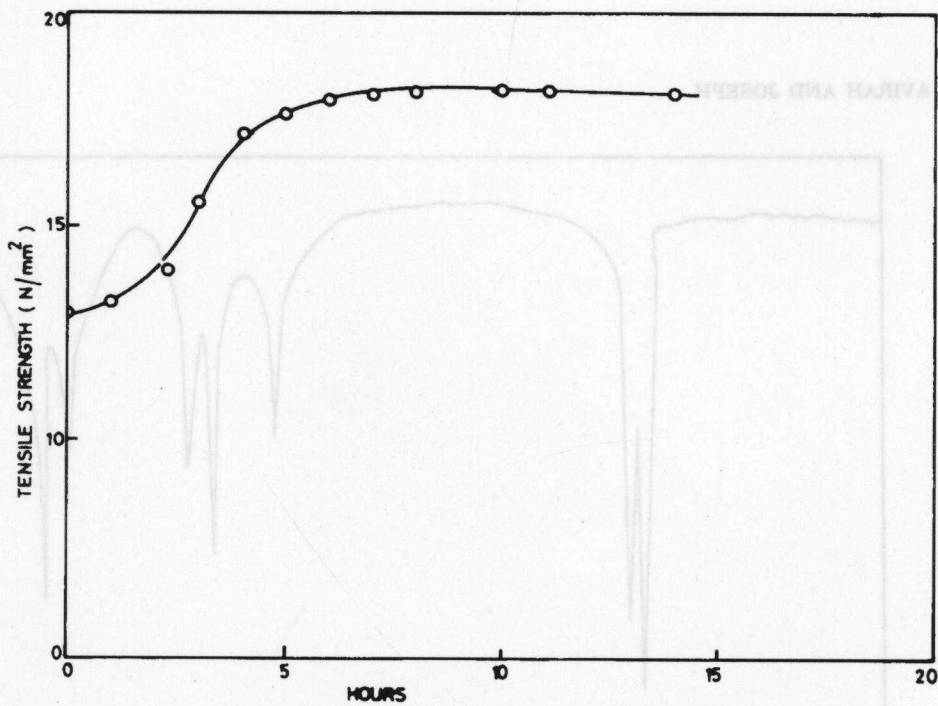


Figure 1 Variation of tensile strength after aging with exposure time.

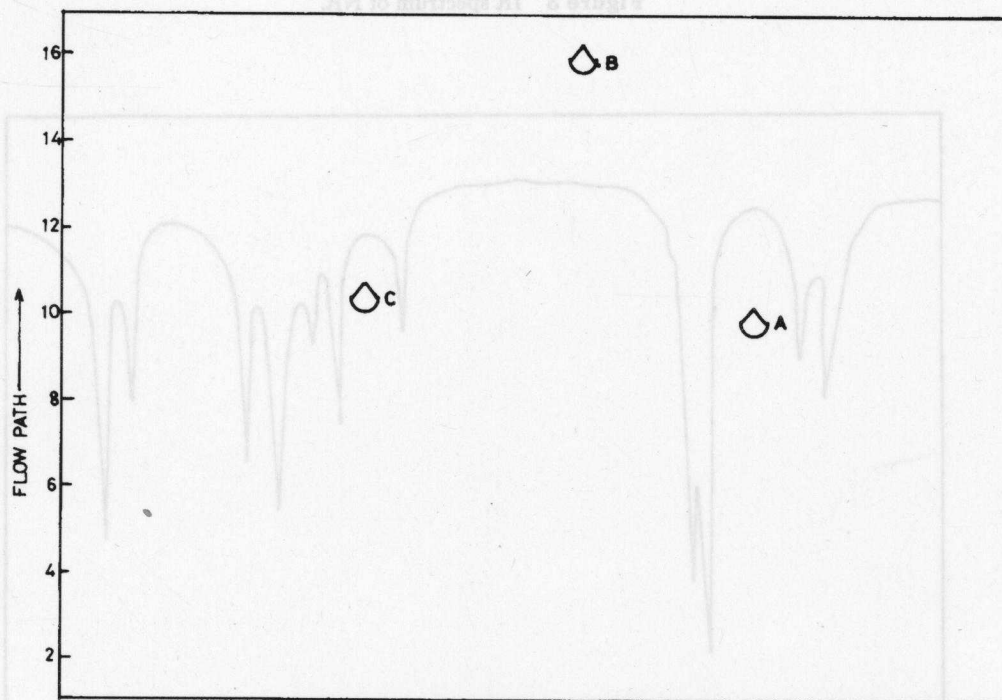


Figure 2 TLC of compounds: (A) NR-PD, (B) PD, (C) depolymerized NR.

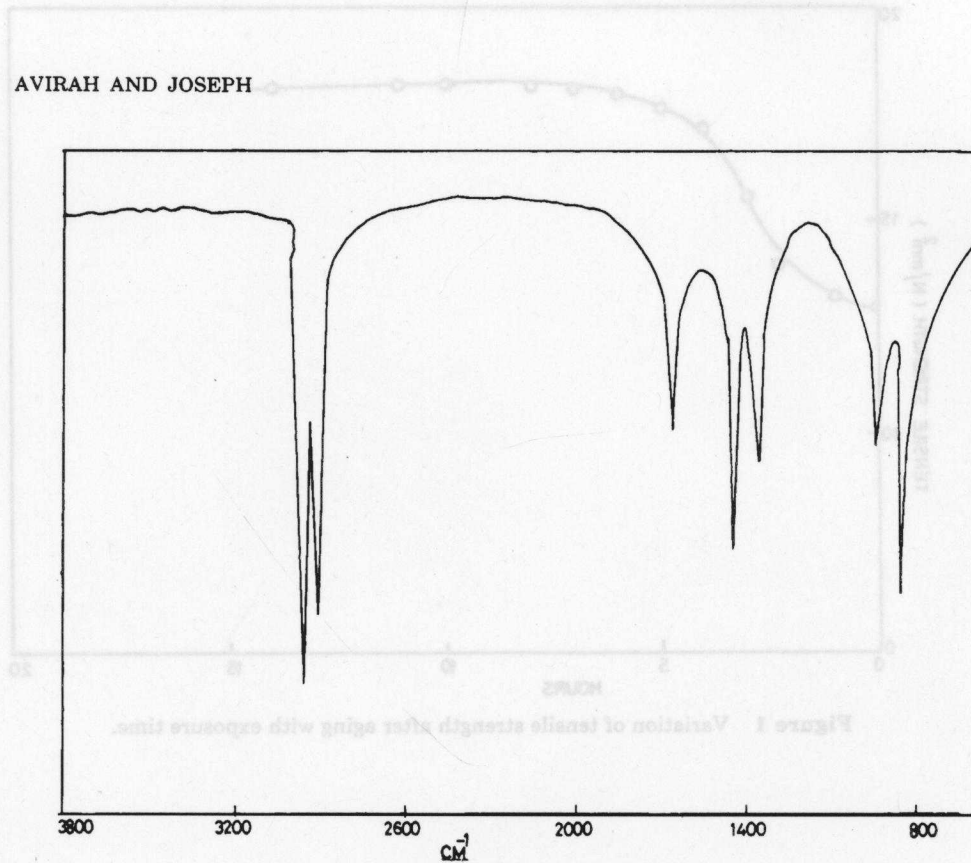


Figure 3 IR spectrum of NR.

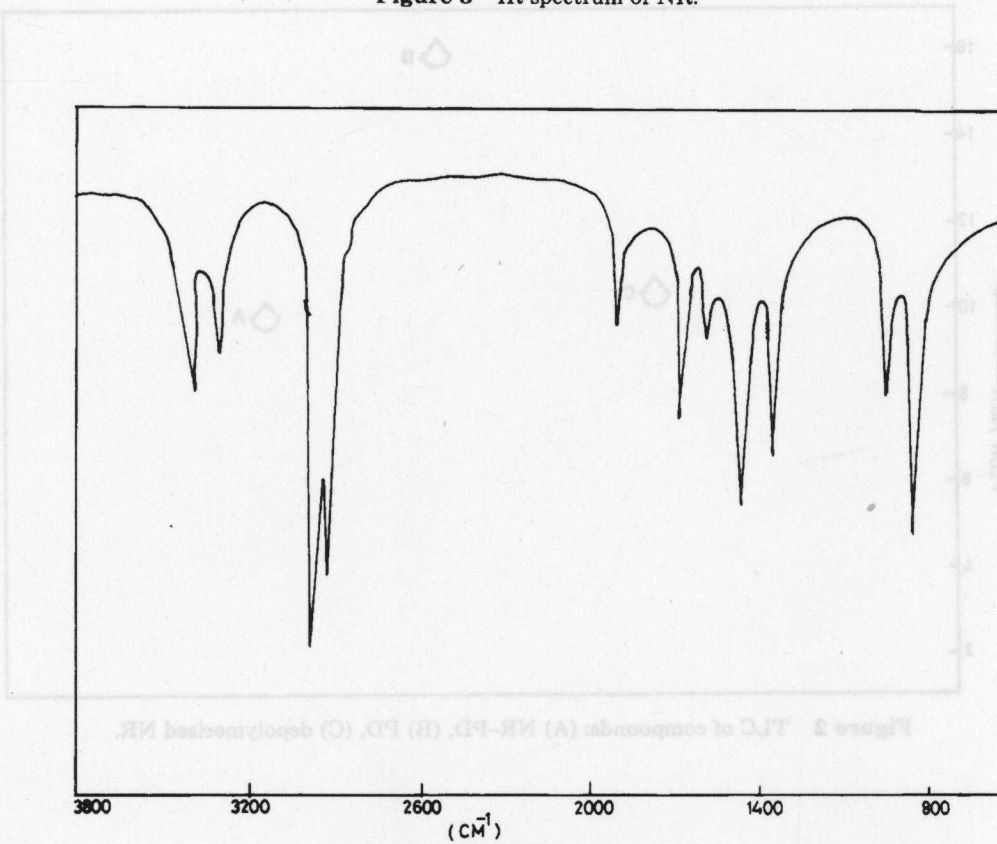


Figure 4 IR spectrum of NR-PD.

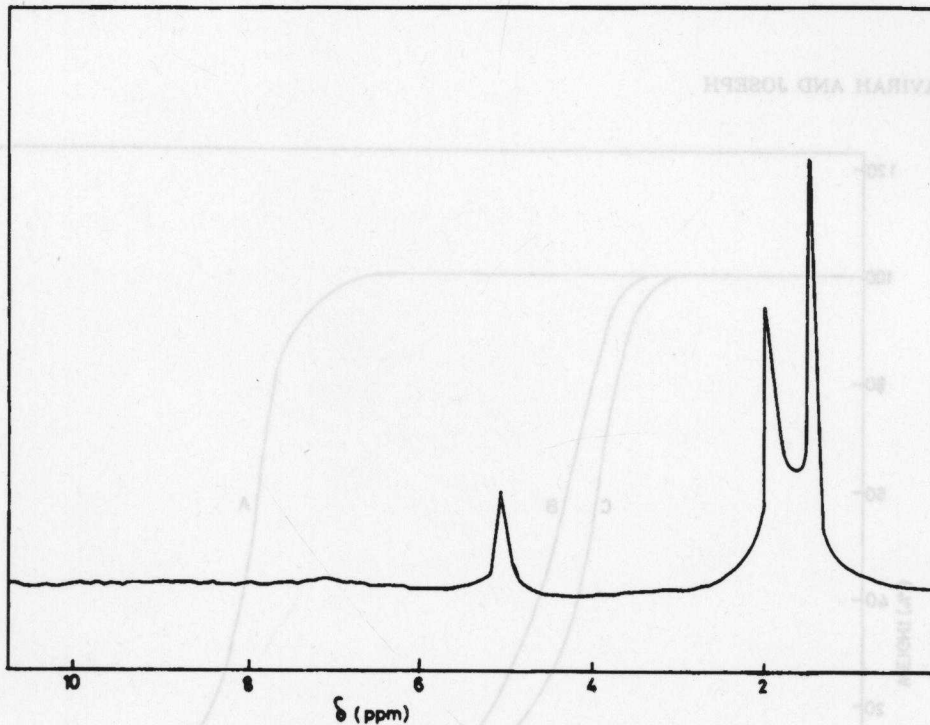


Figure 5 ¹H-NMR spectrum of depolymerized NR.

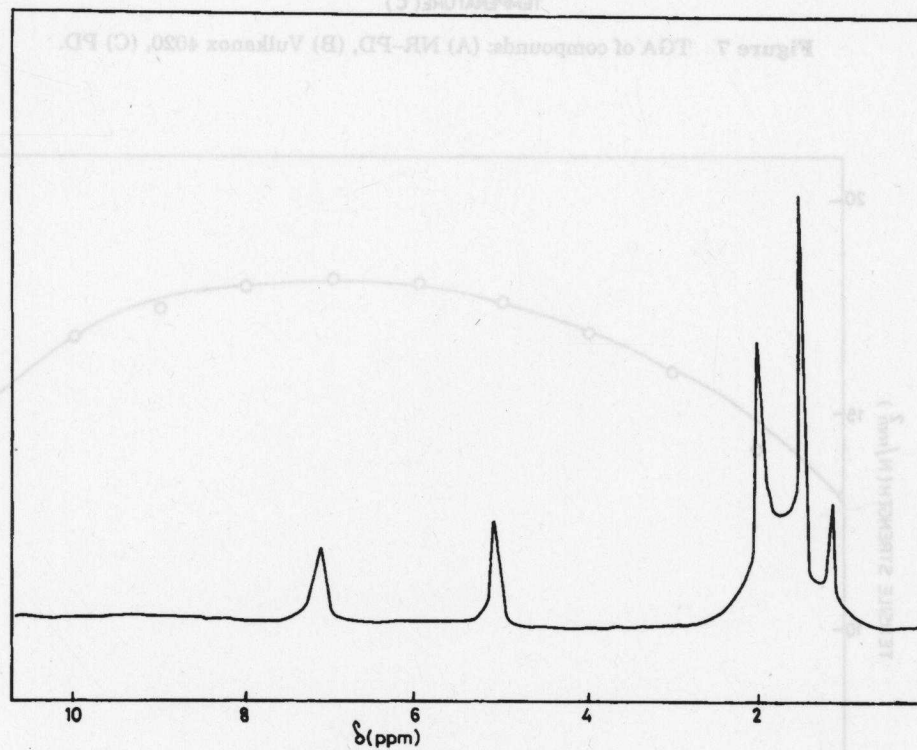


Figure 6 ¹H-NMR spectrum of NR-PD.

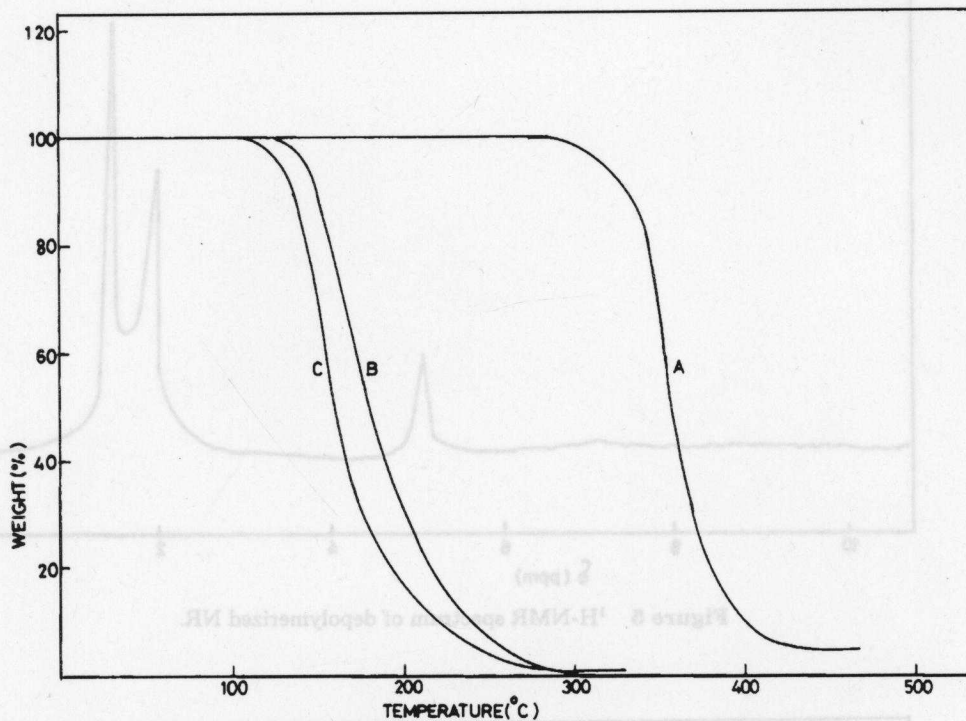


Figure 7 TGA of compounds: (A) NR-PD, (B) Vulkanox 4020, (C) PD.

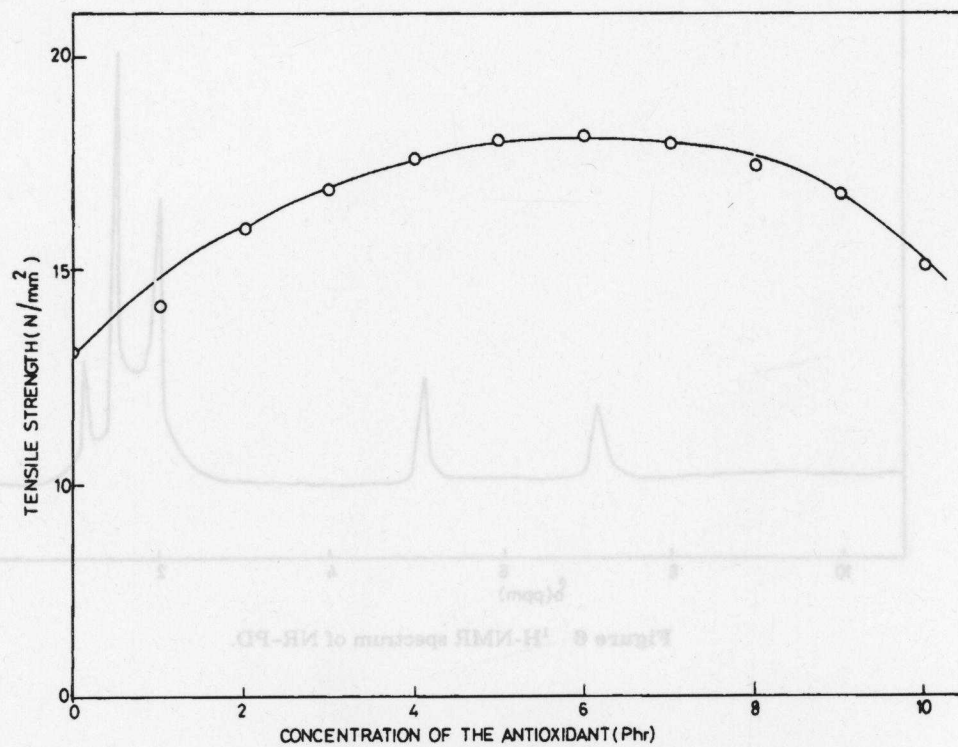


Figure 8 Variation of tensile strength after aging with concentration of antioxidant.

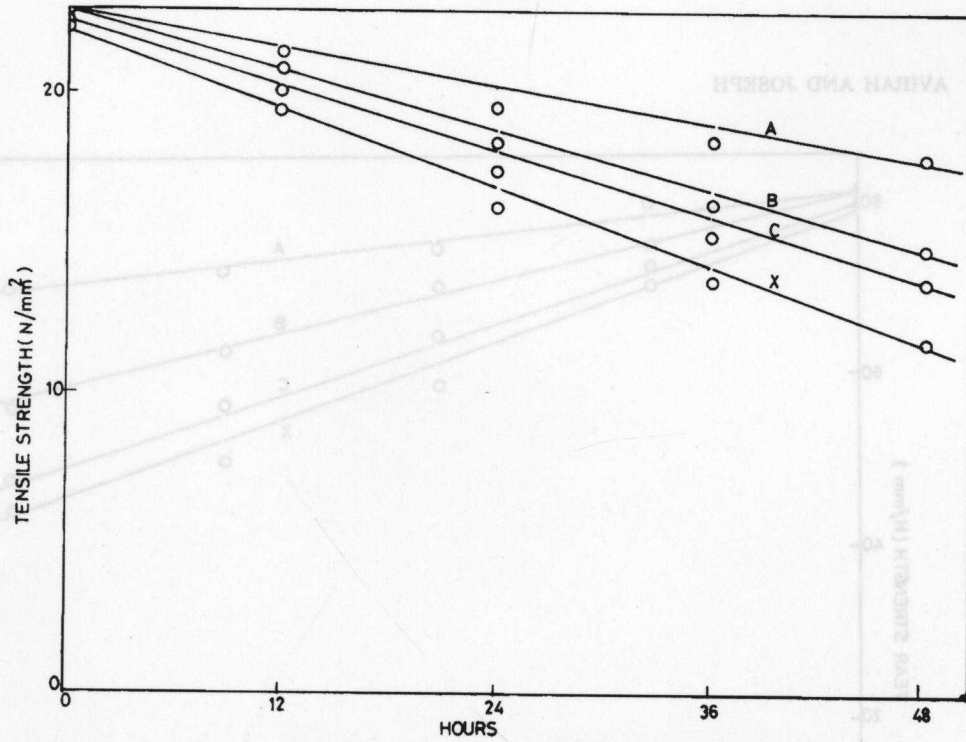


Figure 9 Variation of tensile strength of the vulcanizates before and after aging: (A) NR-PD, (B) Vulkanox 4020, (C) Vulkanox HS, (X) without antioxidant.

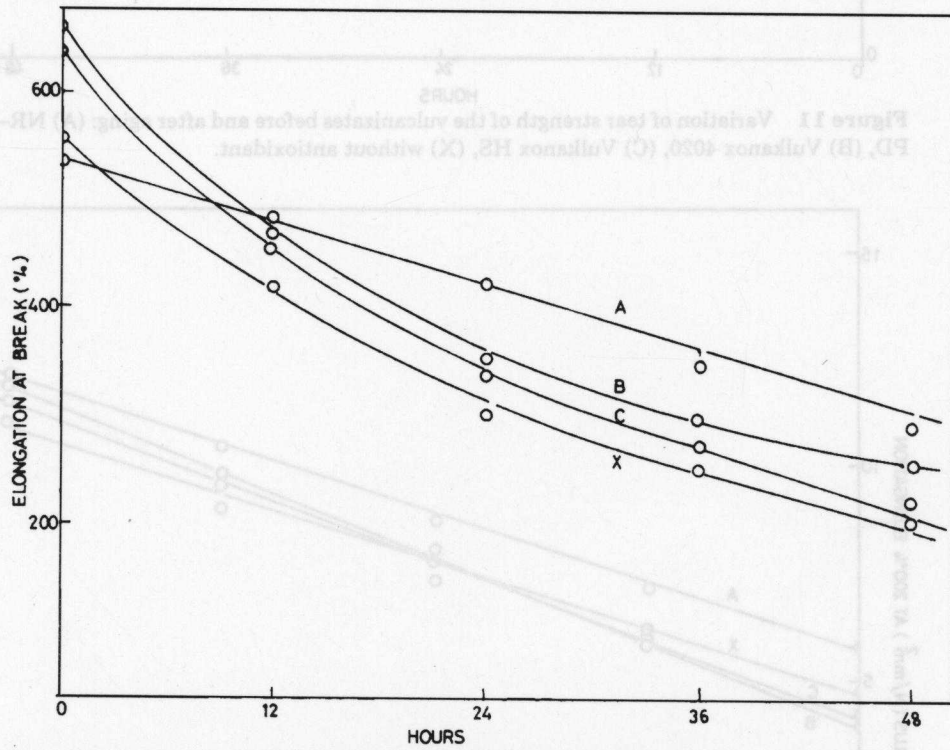


Figure 10 Variation of elongation at break of the vulcanizates before and after aging: (A) NR-PD, (B) Vulkanox 4020, (C) Vulkanox HS, (X) without antioxidant.

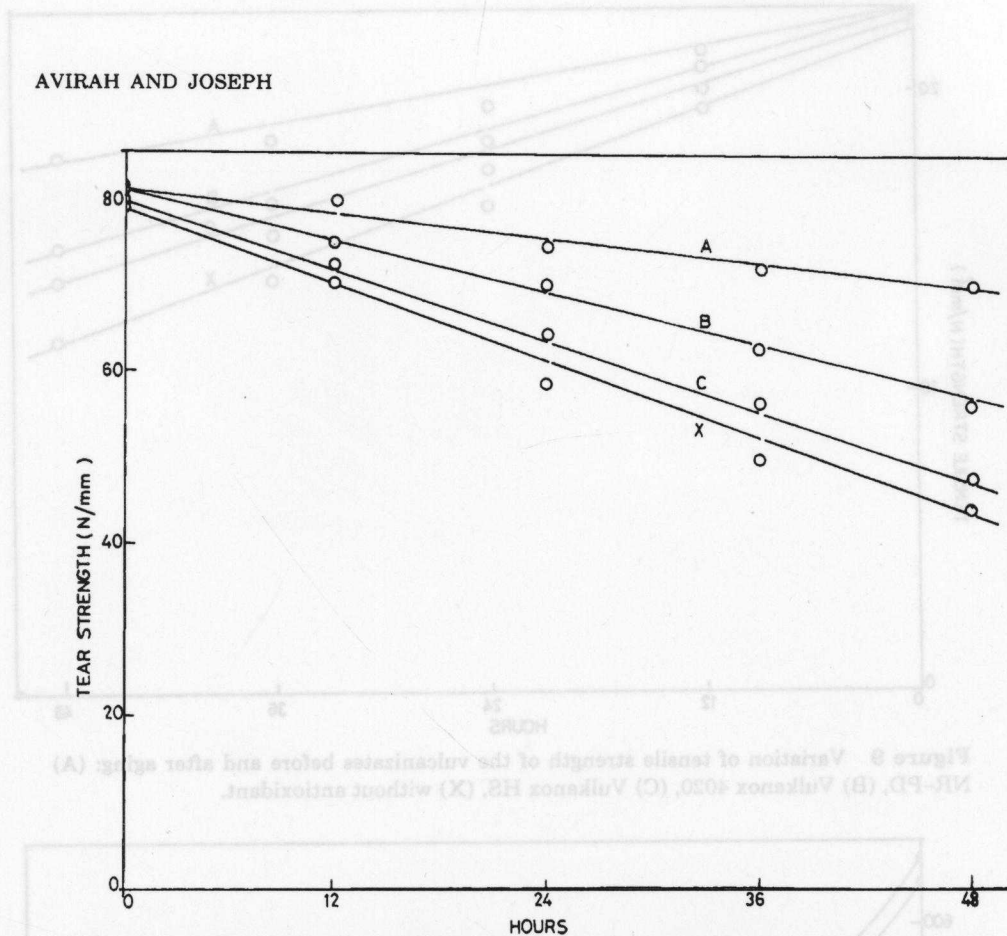


Figure 11 Variation of tear strength of the vulcanizates before and after aging: (A) NR-PD, (B) Vulkanox 4020, (C) Vulkanox HS, (X) without antioxidant.

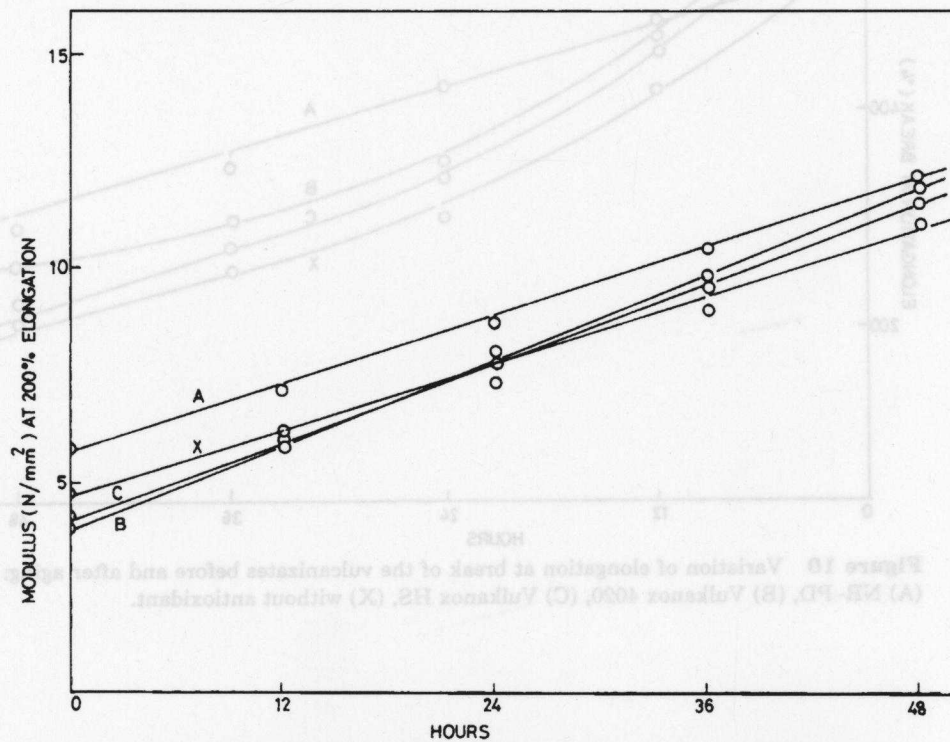


Figure 12 Variation of modulus of the vulcanizates before and after aging: (A) NR-PD, (B) Vulkanox 4020, (C) Vulkanox HS, (X) without antioxidant.

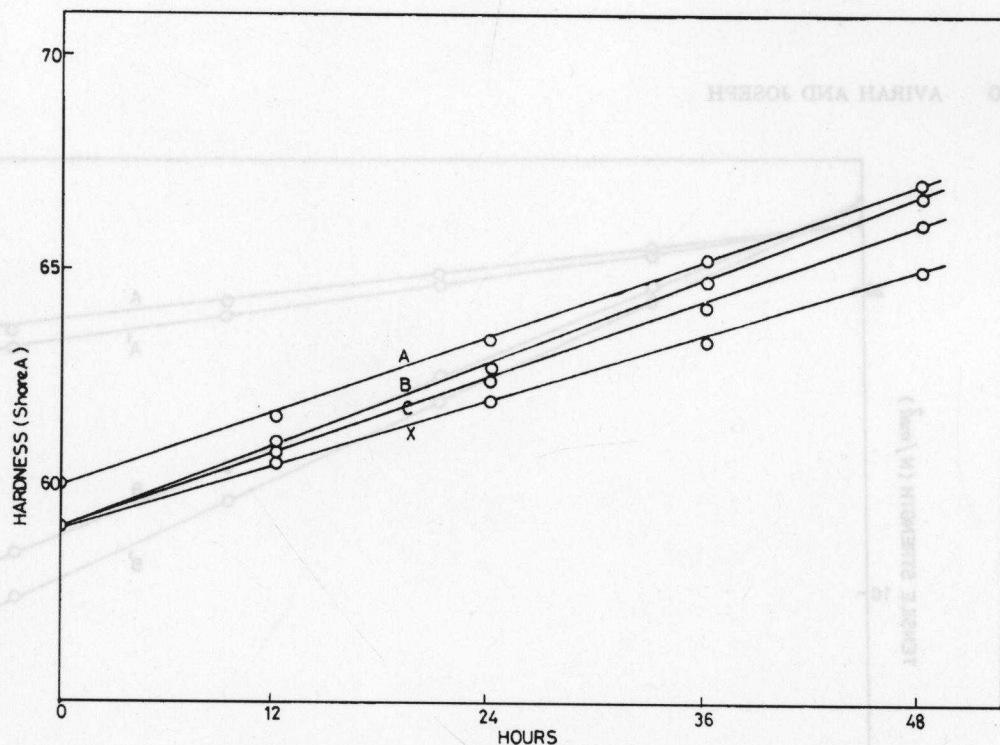


Figure 13 Variation of hardness of the vulcanizates before and after aging: (A) NR-PD, (B) Vulkanox 4020, (C) Vulkanox HS, (X) without antioxidant.

The optimum concentration of the rubber bound antioxidant for attaining maximum retention in properties was determined by varying the amount of antioxidant in the mix from 1 to 10 phr.

The chemically bound *para*-phenylenediamine was added in NBR as per formulations given in Table I. The optimum cure times (time to reach x90% of the maximum torque) and scorch times (time to reach 10% of the maximum torque) of the compounds were determined on a Göttfert Elastograph Model 67.85 according to ASTM D-1646.

Rubber compounds were molded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression molded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick Universal Testing Machine Model 1445 using a crosshead speed of 500 mm/min per ASTM D-412-80. Tear resistance of the vulcanizates was evaluated with ASTM D-624-81 using unnicked 90° angled test specimens. The hardness (shore A) of the molded samples was tested using a Zwick 3115 hardness tester in accordance with ASTM D-2240. The compression set

of the samples was calculated with ASTM D-395 methods. Rebound resilience of the vulcanizates was evaluated using a Dunlop tripsometer (BS 903, part 22, 1950). Flex resistance of the samples was tested using a Demattia flexing machine (ASTM D-430-577). Retention in tensile properties and tear strength were evaluated after aging the samples at 100°C for 12, 24, 36, and 48 h. Retention in compression set, heat buildup, resilience, and flex crack resistance were evaluated after aging the samples at 100°C for 48 h.

Oil resistance of the NBR vulcanizates containing bound antioxidants was studied by keeping the samples in light oil, gear oil, transformer oil, or engine oil at room temperature and also at 70°C for 24 h. The retention in tensile properties and tear strength were evaluated. Solvent resistance of the bound antioxidant was studied in methanol and acetone by keeping the vulcanizates in methanol and acetone for 48 h at room temperature. The retention in tensile properties of the samples after acetone and methanol extraction was evaluated after aging the extracted samples at 100°C for 12, 24, 36, and 48 h. Water resistance of the samples was studied by keeping the samples in water at 70°C for 24 h and also in boiling water for 10 h. Retention in ten-

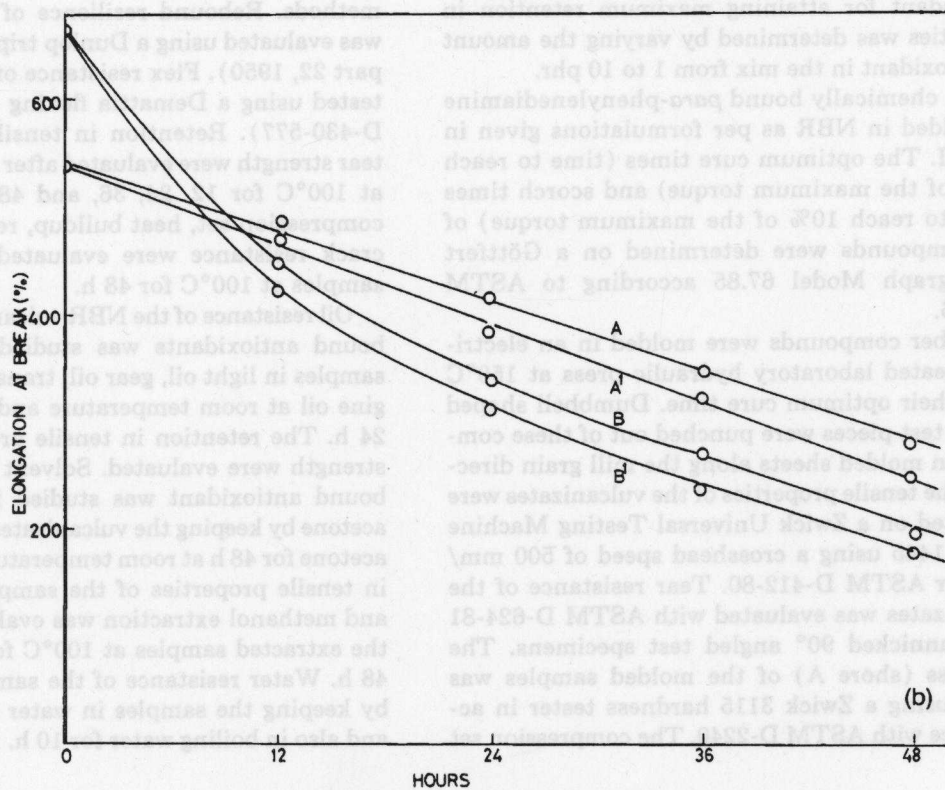
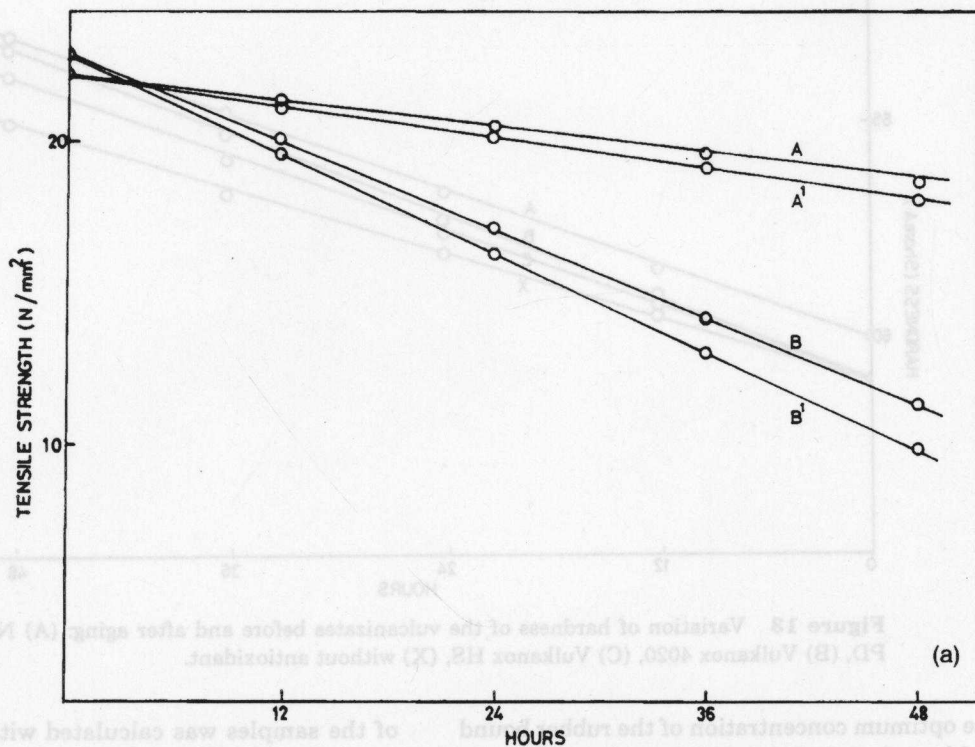


Figure 14 Variation of (a) tensile strength and (b) elongation at break of the vulcanizates before and after aging after extraction: (A) NR-PD and (B) Vulkanox 4020 in methanol; (A') NR-PD and (B') Vulkanox 4020 in acetone.

Table II Properties after Oil Extraction at Room Temperature and 70°C

Property	Type of Oil									
	Extraction		Light		Gear		Transformer		Engine	
	Time	Temp.	A	B	A	B	A	B	A	B
Tensile strength (N/mm ²)			21.23	22.59	21.23	22.29	21.23	22.59	21.23	22.59
Elongation at break (%)	0	27°C	535.43	699.03	535.43	699.03	535.43	699.03	535.43	699.03
Modulus at 200% elongation (N/mm ²)			5.86	3.96	5.86	3.96	5.86	3.96	5.86	3.96
Tear strength (N/mm)			80.00	79.00	80.00	79.00	80.00	79.00	80.00	79.00
Tensile strength (N/mm ²)			20.18	22.43	21.12	22.20	20.18	17.79	21.10	21.27
Elongation at break (%)	48 h	27°C	506.76	660.52	525.16	656.30	511.17	675.53	517.12	641.76
Modulus at 200% elongation (N/mm ²)			6.27	4.49	6.50	4.32	6.29	3.84	6.46	4.51
Tear strength (N/mm)			61.98	58.12	60.74	59.11	51.02	40.80	61.50	48.42
Tensile strength (N/mm ²)			18.72	16.68	17.61	16.24	17.63	12.38	17.61	16.24
Elongation at break (%)	24 h	70°C	463.15	399.26	484.86	312.15	444.50	360.98	502.48	312.15
Modulus at 200% elongation (N/mm ²)			6.97	6.41	6.80	6.79	6.93	6.45	6.53	6.99
Tear strength (N/mm)			59.89	46.97	58.81	45.41	49.89	36.90	46.87	39.00

sile properties, tear strength, and hardness after water extraction were evaluated by aging the samples at 100°C for 12, 24, 36, and 48 h. Swelling in oil of the vulcanizates containing bound antioxidants was studied by keeping a known weight of the sample in transformer oil or gear oil for 48 h at room temperature and then measuring the increase in weight.

RESULTS AND DISCUSSION

Figure 1 shows the variation in tensile strength after 48-h aging at 100°C with exposure time in the presence of and absence of PD. Aging resistance of NBR vulcanizate was enhanced by the addition of depolymerized rubber, irradiated in the presence of PD. The retention in tensile strength was found to

Table III Properties after Water Extraction at 70 and 100°C Followed by Aging at 100°C for 48 h

Property	Extraction					
	Time	Temp.	A	B	C	X
Tensile strength (N/mm ²)			21.23	22.59	22.74	22.00
Elongation at break (%)			535.43	699.03	651.00	556.51
Modulus at 100% elongation (N/mm ²)	0	27°C	3.00	2.14	2.21	2.48
Tear strength (N/mm)			80.00	79.00	78.00	77.00
Hardness (shore A)			60	59	59	59
Tensile strength (N/mm ²)			19.57	15.84	14.79	13.11
Elongation at break (%)			286.50	248.46	214.14	211.47
Modulus at 100% elongation (N/mm ²)	24 h	70°C	5.66	5.07	5.01	5.02
Tear strength (N/mm)			69.41	52.12	45.84	41.84
Hardness (shore A)			65	64	65	64
Tensile strength (N/mm ²)			18.27	14.26	12.18	11.10
Elongation at break (%)			265.50	197.22	149.35	201.00
Modulus at 100% elongation (N/mm ²)	10 h	100°C	5.85	6.21	6.99	5.08
Tear strength (N/mm)			65.01	49.66	43.67	36.54
Hardness (shore A)			65	66	65	65

Table IV Percent Weight Increase in Oil

Type of Oil	A	B
Transformer	5.01	4.81
Gear	0.33	0.37

increase first, reached a maximum, and then leveled off at an exposure time of 6 h. This shows that after an optimum time of exposure, all the PD molecules are attached to the depolymerized rubber. And aging resistance of NBR vulcanizates does not show much improvement by the addition of depolymerized rubber.

Figure 2 shows the TLC of PD, depolymerized NR (UV irradiated for an equivalent time), and PD bound to depolymerized NR. NR was not colored by a nitrous acid/resorcinol system, but NR-PD and PD were colored. The R_f value of NR-PD was found to be almost equal to that of depolymerized NR. This shows that PD is chemically attached to depolymerized NR during UV irradiation.

The viscosity average molecular weight (\bar{M}_v) of NR and NR-PD were found to be 706,496 and 2,800, respectively.

Figures 3 and 4 show the IR spectra of depolymerized NR and NR-PD. The IR spectrum of NR shows peaks at 3000 and 2980 cm^{-1} corresponding to aliphatic $\text{C}-\text{H}$, at 1665 cm^{-1} due to $\text{C}=\text{C}$, at 1450 and 1375 cm^{-1} due to $-\text{CH}_3$, and at 835 cm^{-1} due to $-\text{C}(\text{CH}_3)=\text{CH}-$. The IR spectrum of NR-PD shows additional peaks at 3400 cm^{-1} (N-H stretching primary), 3310 cm^{-1} (N-H stretching, secondary), 1590 cm^{-1} (N-H bending), 1350 cm^{-1} (C-N vibration), and 1500 cm^{-1} corresponding to the aromatic ring in PD.⁷ This indicates that the PD was chemically bound onto the depolymerized NR during UV irradiation.

Figure 5 shows the $^1\text{H-NMR}$ spectrum of depolymerized NR. There are peaks at $\delta = 5.1$ ($-\text{C}=\text{C}$), $\delta = 1.2$ ($-\text{CH}_2$), and $\delta = 1.65$ ppm ($-\text{CH}_3$). Figure 6 shows the $^1\text{H-NMR}$ spectrum of NR-PD, which shows additional peaks at $\delta = 1.98$ and $\delta = 7.1$ ppm corresponding to the amino group and the aromatic ring present in PD. This again indicates that the PD is chemically bound to the depolymerized NR.

A free radical mechanism has been suggested for the photodegradation of NR.⁸ The presence of a $-\text{CH}_3$ group attached to the ethylenic carbon atom in polyisoprene tends to reduce the $-\text{C}-\text{H}$ dissociation energy by hyperconjugation facilitating substitution at the α -methylene carbon atom.⁹ In

photochemical degradation, the photons remove the $-\text{C}-\text{H}$ proton giving rise to macroradicals.¹⁰ This is evidenced by the fact that there is no change observed in the absorption band of the isoprene unit,

$$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array} \quad (835 \text{ cm}^{-1})$$
 in the IR spectrum (Fig. 4). Based on the photooxidation of PD, and from the mechanism of degradation of NR, the following mechanism can be suggested for the attachment of PD onto depolymerized NR.^{8,11,12}

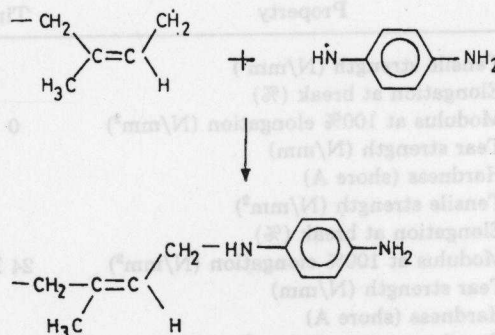
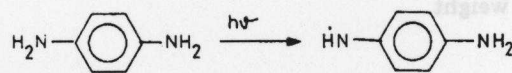
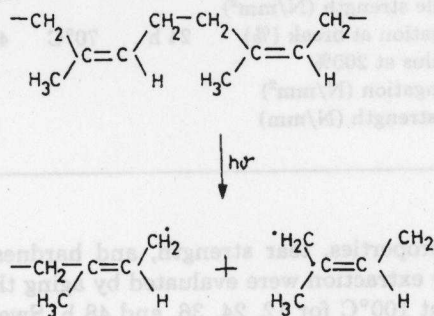


Figure 7 shows the thermograms of PD, Vulkanox 4020, and NR-PD. Low molecular weight antioxidants volatilize easily while rubber bound PD (NR-PD) is less volatile. This again confirms the chemical bonding between depolymerized NR and PD.

Figure 8 shows the variation in tensile strength on aging with concentration of bound antioxidant. The tensile strength retention is found to increase with the amount of chemically bound antioxidant,

Table V Variations in Properties Before and After Aging

Sample	A	B
Resilience (%)	59	48.61
Heat buildup ($\Delta T^{\circ}\text{C}$)	23	25.6
Flex crack resistance (<i>k</i> cycles)	525.0	223
Compression set (%)	16.84	17.93
After aging at 100°C for 48 h		
Resilience (%)	45.54	36.54
Heat buildup ($\Delta T^{\circ}\text{C}$)	40.71	49.50
Flex crack resistance (<i>k</i> cycles)	390.72	120.75
Compression set (%)	15.94	18.83

reaches a maximum, and then decreases. The decrease in tensile strength retention after an optimum level may be due to the incompatibility of bound antioxidant with NBR. The higher amount requirement of bound antioxidant may be due to a lower amount of effective antioxidant in the bound product, because $^1\text{H-NMR}$ calculations show that less than 1 g of antioxidant is present in 5 g of bound product.

Figure 9 shows the tensile strength of the vulcanizates of the compounds shown in Table I before and after aging. All the vulcanizates show fairly good resistance to aging at 100°C for 24 h, but compounds containing NR-PD alone show good aging resistance when aging time is increased to 48 h, which shows the superiority of bound antioxidant over conventional antioxidant.

Figure 10 shows the change in elongation at break of the vulcanizates before and after aging. The compound containing the bound antioxidant shows lower elongation at break. This may be due to the lower amount of dioctylphthalate in the compound and the higher total crosslink density of the vulcanizate. The compound containing NR-PD shows better retention in elongation at break after aging. This again shows that the bound antioxidant can improve the aging resistance of NBR compounds.

Figure 11 shows the variation in tear strength of the vulcanizates before and after aging, which further confirms the superiority of the bound antioxidant.

Figure 12 shows the variation in modulus (at 200% elongation) of the vulcanizates before and after aging. The increase in modulus may be attributed to the postcuring of NBR.

Figure 13 shows the variation in hardness of the vulcanizates before and after aging. The increase in hardness may be due to the increase in the total crosslink density.

Figure 14 shows the variation in tensile strength and elongation at break of the vulcanizates before and after aging, after extracting the samples in acetone and methanol. The retention in properties by the vulcanizates containing NR-PD are superior due to lower extractibility of the bound antioxidant by acetone and methanol.

Table I shows the cure characteristics of the vulcanizates. The compound containing NR-PD shows less cure time and scorch time. This may be attributed to the presence of a free amino group in the bound product.

Table II shows the variation in tensile strength, elongation at break, modulus, and tear strength of the vulcanizates (of the compound shown in Table I) before and after extracting the samples in transformer oil, gear oil, light oil, or engine oil at room temperature and 70°C. Tensile strength, elongation at break, and modulus of the vulcanizates are comparable after room temperature oil extraction. The tear strength is found to be superior for the vulcanizates containing NR-PD. This may be due to the lower extractibility of the bound antioxidants by oils. The superiority of the vulcanizate containing NR-PD is more pronounced after oil extraction at 70°C than at 25°C. The tensile properties and tear resistance were found to be better for the vulcanizate containing NR-PD. This shows that the extractibility of conventional antioxidant and dioctylphthalate is more pronounced at 70°C than at 25°C.

Table III shows the variation in tensile strength, elongation at break, hardness, modulus, and tear strength of the vulcanizates before and after aging, after extracting the samples in water at 70 and 100°C. More than 25% of the conventional antioxidant was leached out during boiling water extraction. The IR spectra of the dried water extract also confirms this (not shown). Water extract from vulcanizates containing conventional antioxidant shows the peak at 3400 cm^{-1} corresponding to the amino group, but NR-PD does not get extracted in boiling water. The retention in properties shown by the vulcanizates containing NR-PD are superior to those vulcanizates containing conventional antioxidants because NR-PD does not get extracted in hot water or boiling water.

Table IV shows the percentage increase in weight in transformer oil and gear oil. The lower increase in weight of the vulcanizates containing conventional antioxidant in transformer oil may be due to the leaching of the antioxidant and plasticizer; the compound containing NR-PD as antioxidant contains only a lower amount of plasticizer and the antioxidant gets attached to NBR during vulcaniza-

tion. The percentage increase in weight of the vulcanizates in gear oil is more or less the same. This may be due to the lower extractibility of the antioxidants and plasticizer in gear oil as evidenced by the mechanical property retention shown in Table II.

Table V shows the variation in resilience, heat buildup, flex crack resistance, and compression set of the vulcanizates of the compounds in Table I before and after aging. Resilience and heat buildup values of the NBR vulcanizates containing bound antioxidant are better than for the one containing conventional antioxidant. This may be due to the NR part in the bound antioxidant. The better retention in properties after aging shown by the compounds containing bound antioxidant may be due to the lower volatility of the bound antioxidant during aging.

CONCLUSION

1. PD can be chemically attached to depolymerized NR by photochemical reaction.
2. The rubber bound antioxidant has much superior resistance to volatility and extractibility compared to conventional antioxidants.
3. This rubber bound antioxidant could reduce heat buildup and improve resilience and aging resistance of the NBR vulcanizates.
4. Water and oil resistance of the NBR vulcanizates could be improved by the use of rubber bound product.
5. The rubber bound antioxidant can reduce the amount of plasticizer required for compounding.

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