

# New Oligomer-Bound Antioxidants in Natural Rubber/Polybutadiene Rubber and Natural Rubber/Styrene–Butadiene Rubber Blends

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**ABSTRACT:** New paraphenylene diamine antioxidants were prepared. The efficiency and permanence of these oligomer-bound paraphenylene diamines were compared with those of conventional amine-type antioxidants in elastomer blends such as natural rubber/styrene–butadiene rubber and natural rubber/polybutadiene rubber. These oligomer-bound antioxidants showed improved aging resistance and

ozone resistance in comparison with the blends containing conventional antioxidants. The liquid oligomer-bound paraphenylene diamine could replace the plasticizer required for compounding. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 437–443, 2004

**Key words:** ageing; antioxidants; blends; oligomers

## INTRODUCTION

Elastomer blends are very important to the rubber industry. Almost all industrial rubber products are made of rubber blends. The largest use of elastomer blends is in the production of tires. For car tire treads, styrene–butadiene rubber (SBR) is preferred because of its good wet grip property, but it has the disadvantage of heat buildup. In large tires such as those of trucks, for which heat buildup must be minimized, natural rubber (NR) or blends of NR with polybutadiene rubber (BR) are used.

Corish<sup>1</sup> reviewed different aspects of elastomer blends. Glanville et al.<sup>2</sup> showed that the state of degradation of NR is reduced in blends with BR. Blow and Loo<sup>3</sup> studied the effects of the curing temperature on the technical properties of different blends consisting of NR, SBR, and BR. Bhowmick and De<sup>4</sup> studied the effects of the curing temperature and curing systems on the technical properties, polymer–filler interactions, and network structures of NR/BR, NR/SBR, and NR/BR/SBR blends.

Even though blends are superior to individual rubbers in their properties, their degradation cannot be effectively controlled with conventional antioxidants because of the volatility and leachability of conventional antioxidants. During recent years, there has

been a gradually increasing demand from tire manufacturers for chemicals that will protect rubber vulcanizates from oxidative degradation, and a search for new and improved types of antioxidants is ongoing. One of the main drawbacks of conventional antioxidants is their high volatility. This has led to a search for a new class of antioxidants with higher molecular weights, that is, polymer-bound antioxidants.

Polymer-bound antioxidants have been synthesized to overcome a serious disadvantage of conventional antioxidants: their disappearance from rubber vulcanizates during service due to volatility and extractability. This disappearance has been shown to have an adverse effect on aging.<sup>5–7</sup> Over the past several decades, numerous articles and reviews have appeared describing the benefits and various techniques of chemically incorporating antioxidants into polymeric substrates.<sup>8–13</sup> The preparation and characterization of new oligomer-bound antioxidants [polyisobutylene-bound paraphenylene diamine (PIB-PD) and chlorinated-paraffin-wax-bound paraphenylene diamine (CPW-PD)] with saturated backbones were reported in our earlier articles.<sup>14,15</sup> A brief description of the efficiency of these antioxidants in elastomer blends, in comparison with blends containing Accinox TQ (polymerized 1,2-dihydro-2,2,4-trimethyl quinoline), was reported.<sup>16</sup> In this study, we evaluated the efficiency of these antioxidants in elastomer blends, such as NR/SBR and NR/BR, by comparing their mechanical properties and ozone resistance with those of their counterparts containing a paraphenylene diamine

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TABLE I  
Structures of the New Antioxidants

No.	Name	Formula
1	PIB-PD	
2	CPW-PD	

(PD) conventional antioxidant, Vulkanox 4020 [*N*-(1,3-dimethyl butyl)-*N'*-phenyl-*p*-phenylenediamine].

## EXPERIMENTAL

### Materials

NR {ISNR-5; Mooney viscosity [ML (1+4) at 100°C] = 82} was supplied by the Rubber Research Institute (India, Kottayam). BR {Mooney viscosity [ML (1+4) at 100°C] = 45} was supplied by Indian Petrochemicals Corp., Ltd. (Baroda, India). Styrene-butadiene rubber (SBR; 1502), from Japanese Synthetic Rubber Co., Ltd., was supplied by Sreevidhya Enterprises, Ltd. (Mumbai, India) and had a Mooney viscosity [ML (1+4) at 100°C] of 45. Polyisobutylene (PIB) with a molecular weight of 934 was supplied by Cochin Refineries (Balmer Lawrie, Ltd., Ambalamugal, India). Chlorinated paraffin wax (CPW; 51.5% chlorine) with a viscosity of 15.9 P was supplied by KLJ Organic, Ltd. (Gujarat, India). The compounding ingredients, zinc oxide, stearic acid, and carbon black (HAF; N 330) were commercial-grade. Benzthiazyl 2-sulfenmorpholide (MOZ), tetramethylthiuram disulfide (TMTD), and Vulkanox 4020 [*N*-(1,3-dimethyl butyl)-*N'*-phenyl-*p*-phenylenediamine] were rubber-grade and were supplied by Bayer India (Mumbai, Ltd.). Methanol, dioxan, triethylamine, acetone, and toluene were reagent-grade and were used as such.

### Preparation of PIB-PD<sup>14</sup>

PIB was dissolved in CCl<sub>4</sub> (50% solution), and pure dry chlorine gas was passed through it for 5 h. The resulting solution was poured into water at 80°C, and

excess chlorine and CCl<sub>4</sub> were removed. The chlorinated sample was dissolved in toluene and reprecipitated with methanol. The sample was dried in a vacuum oven.

The chlorinated sample was dissolved in dioxan and mixed with PD dissolved in dioxan in a ratio of 2:1. The reaction mixture was made alkaline to neutralize the HCl that evolved during the condensation reaction with the addition of triethylamine. The reaction mixture was placed in a two-necked flask fitted with a water condenser and a thermometer. The mixture was kept at 100°C for 48 h. Dioxan and triethylamine were distilled off, and the mixture was washed with methanol a number of times to remove the unreacted PD. The resulting mixture was reprecipitated with a toluene/methanol (1:1 v/v) mixture, and the product was dried in a vacuum oven.

### Preparation of CPW-PD<sup>15</sup>

CPW and PD, each in a dioxan solution, were mixed in a 1:1 ratio. The reaction mixture was made basic with the addition of triethylamine to neutralize the HCl that evolved during the condensation reaction. The reaction mixture was placed in a two-necked flask fitted with a water condenser and a thermometer. The mixture was heated at 100°C for 14 h. Dioxan and triethylamine were distilled off, and the mixture was washed with water a number of times to remove the unreacted PD. The resulting mixture was reprecipitated and dried in a vacuum oven.

The structures of the new antioxidants used for this study are given in Table I.

TABLE II  
Formulations of the Blends

	Sample							
	A	B	C	D	A <sub>1</sub>	B <sub>1</sub>	C <sub>1</sub>	D <sub>1</sub>
NR	70	70	70	70	70	70	70	70
SBR	30	30	30	30	—	—	—	—
BR	—	—	—	—	30	30	30	30
Zinc oxide	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
HAF (N330)	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0
Aromatic oil	—	—	7.5	7.5	—	—	7.5	7.5
MOZ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Vulkanox 4020	—	—	1.0	—	—	—	1.0	—
PIB-PD	6.0	—	—	—	6.0	—	—	—
CPW-PD	—	6.0	—	—	—	6.0	—	—

The optimum concentrations of the antioxidants for maximum retention of the properties were determined through variations in the amount of each antioxidant in a standard formulation from 1 to 10 phr (Table II). The optimum concentrations of PIB-PD and CPW-PD were determined.

PIB-PD and CPW-PD were added to NR/BR and NR/SBR blends according to the formulation given in Table II. The liquid rubber-bound antioxidants could replace aromatic oil.

The optimum cure times (the times to reach 90% of the maximum torque) of the compounds were determined on a Göttfert model 67.85 elastograph (Buchen, Germany) according to ASTM D 1646 (1981).

The 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 (Germany) at a cross-head speed of 500 mm/min according to ASTM D 412-80 method A. The tear resistance of the vulcanizates was evaluated according to ASTM D 624-81 with unnicked 90° angle test specimens.

The aging resistance of the vulcanizates was studied via aging for 24, 48, and 72 h at 100°C and the subsequent measurement of the retention of the tensile properties. The compression set of the samples was determined according to ASTM D 395 method B (1982). The hardness (Shore A) of the molded samples was tested with a Zwick 3115 hardness tester in agreement with ASTM D 2240. The flex resistance of the samples was tested with a Demattia flexing machine (Prolific, Delhi, India) according to ASTM D 813-95. The abrasion resistance was measured with a DIN abrader according to DIN 53516.

The crosslink density ( $1/2M_c$ , where  $M_c$  is the number-average molecular weight of the rubber chains between crosslinks) was determined with an equilibrium swelling method with toluene as a solvent. Samples (0.2 g) approximately 1 cm in diameter and 0.2 cm thick were punched out from the central portion of the blend. These were allowed to swell in toluene for 24 h. The swollen samples were taken out of the solvent and dried in a vacuum oven, and then they were weighed again. The volume fraction of rubber ( $V_r$ ) in the swollen network was then calculated by the method reported by Ellis and Welding<sup>17</sup> with the following equation:

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}} \quad (1)$$

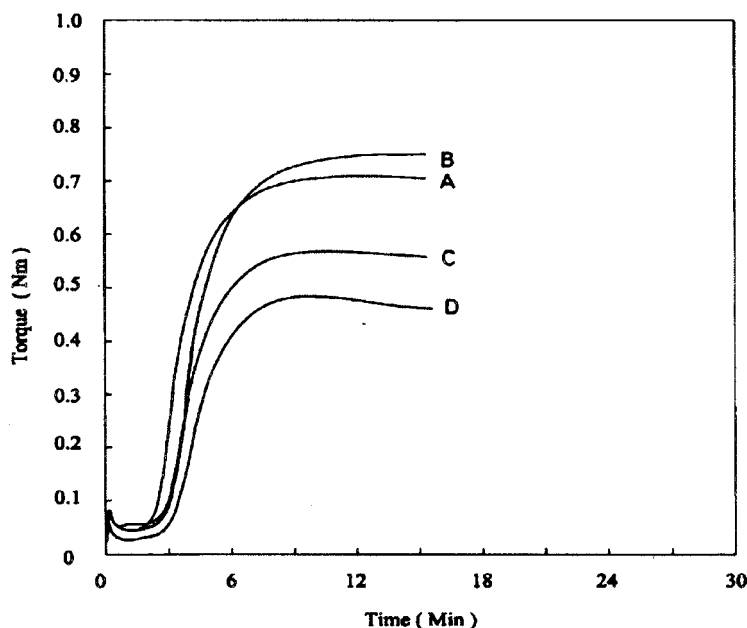
where  $T$  is the weight of the test specimen,  $D$  is the deswollen weight of the test specimen,  $F$  is the weight fraction of insoluble components,  $A_0$  is the weight of the absorbed solvent corrected for the swelling increment,  $\rho_r$  is the density of rubber, and  $\rho_s$  is the density of the solvent.

For blends containing HAF, the previously obtained value of  $V_r$  was converted into  $V_{r0}$  with the following equation derived by Porter:<sup>18</sup>

$$\frac{V_{r0}}{V_r} = 0.56 \times e^{-z} + 0.44 \quad (2)$$

where  $z$  is the weight fraction of the filler. The crosslink density  $1/2M_c$  was determined from  $V_{r0}$  with the Flory–Rehner equation:<sup>19</sup>

$$1/2M_c = - \frac{[\ln(1 - V_{r0} + V_{r0} + \chi V_{r0}^2)]}{2\rho_r V_s (V_{r0})^{1/3}} \quad (3)$$



**Figure 1** Cure curves of NR/BR blends: (A) with PIB-PD, (B) with CPW-PD, (C) with Vulkanox 4020, and (D) without an antioxidant.

where  $\rho_r$  is the density of NR ( $0.94 \text{ g cm}^{-3}$ ),  $V_s$  is the molar volume of the solvent [ $V_s$  (toluene) =  $106.2 \text{ cm}^{-3} \text{ mol}^{-1}$ ], and  $\chi$  is the parameter characteristic of the interaction between the blend and solvent ( $\chi$  of NR/BR and NR/SBR blends was found to vary linearly with their composition).  $V_{r0}$  is the volume fraction of rubber in the swollen network.

Ozone aging studies under static conditions were conducted according to ASTM D 518 method B in a Mast model 700-1 ozone test chamber at  $40^\circ\text{C}$ . The ozone concentration in the chamber was adjusted to 50 parts per hundred million. Photographs were taken with a Carl Zeiss Stemi 2000C optical microscope (Germany) with a magnification of  $2.5\times$ .

## RESULTS AND DISCUSSION

Figure 1 shows the cure curves of the NR/BR blends (A–D in Table II). The cure time and scorch time are reduced by the addition of PIB-PD and CPW-PD. This may be due to the accelerating effect of the amino group present in the liquid oligomer-bound antioxidant.

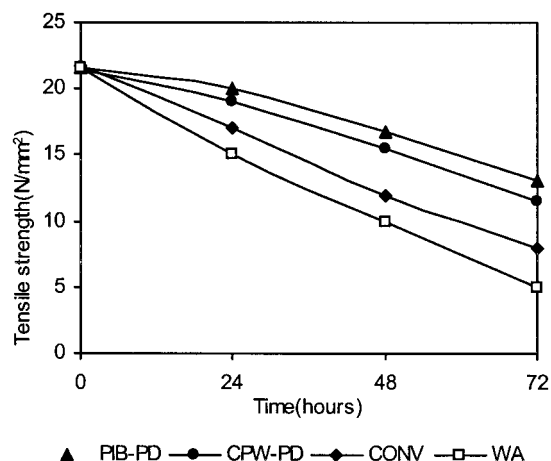
Figure 2 shows the tensile strength of the NR/BR blends with the time of aging at  $100^\circ\text{C}$ . The NR/BR blends containing PIB-PD and CPW-PD show fairly good resistance to aging at  $100^\circ\text{C}$  in comparison with those with a conventional antioxidant and without an antioxidant. This shows that the bound antioxidants are efficient in polymer blends.

Figure 3 shows the change in the elongation at break of the NR/BR blends before and after aging. The

blends containing PIB-PD and CPW-PD show better retention of the elongation at break after aging for 72 h at  $100^\circ\text{C}$ . Polymer-bound antioxidants can improve the aging resistance of blends. This may be due to the lower volatility of the bound antioxidant in comparison with the conventional antioxidant.

Figure 4 shows the tear strength of NR/BR blends before and after aging. The retention of the tear strength of the blends containing PIB-PD and CPW-PD after aging is better than that of the blends containing Vulkanox 4020.

Figure 5 shows cure curves of NR/SBR blends ( $A_1$ – $D_1$  in Table II). The cure time and scorch time are reduced by the addition of PIB-PD and CPW-PD.



**Figure 2** Variation in the tensile strength of NR/BR blends with the time of aging at  $100^\circ\text{C}$ .

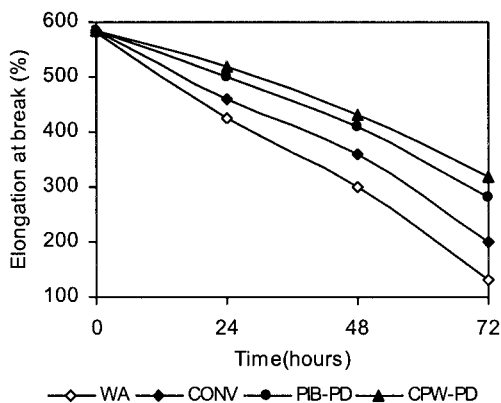


Figure 3 Change in the elongation at break of NR/BR blends with the time of aging at 100°C.

Figure 6 shows the tensile strength of the NR/SBR blends (A<sub>1</sub>–D<sub>1</sub> in Table II) with the time of aging. The blends containing PIB-PD and CPW-PD show fairly good resistance to aging at 100°C in comparison with those with a conventional antioxidant and without an antioxidant.

Figure 7 shows the tear strength of the aforementioned blends with the time of aging. The retention of the tear strength of the blends containing PIB-PD and CPW-PD after aging is better than that of the blends containing Vulkanox 4020.

Figure 8 shows the elongation at break of NR/SBR blends with the time of aging at 100°C. Here the same trend can be observed that was found for NR/BR.

Figures 9 and 10 represent photographs of NR/BR and NR/SBR blends after 19 h in an ozone chamber. The photographs clearly show that blends without antioxidants develop severe cracks [Figs. 9(a), 10(a)], and blends with conventional antioxidant show lesser

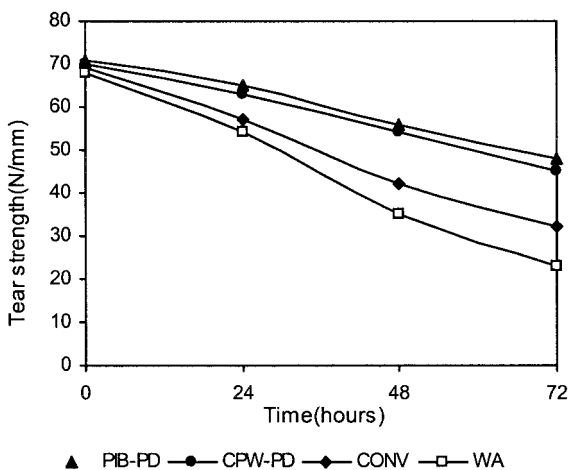


Figure 4 Variation in the tear strength of NR/BR blends with the time of aging at 100°C.

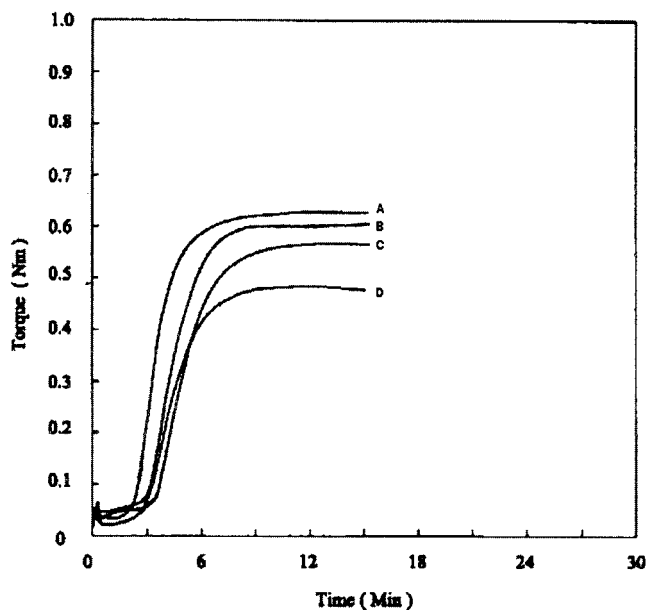


Figure 5 Cure curves of NR/SBR blends: (A) with PIB-PD, (B) with CPW-PD, (C) with Vulkanox 4020, and (D) without an antioxidant.

cracks [Figs. 9(b), 10(b)]; the least significant cracks can be observed for samples containing bound antioxidants [Figs. 9(c, d); 10(c, d)].

The greater resistance to ozone aging for polymers containing bound antioxidants may be due to their appreciably higher molecular weight, which makes them less volatile. The saturated backbone further prevents them from becoming chemically attached to the polymer backbone, which helps them to move toward the surface and act as good barriers for ozone attack. When the efficiency of the bound antioxidants CPW-PD and PIB-PD is compared, we can observe that the former imparts higher resistance. This may be due to

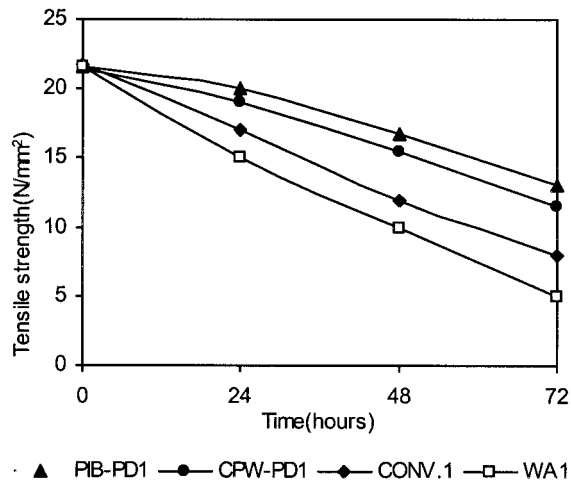
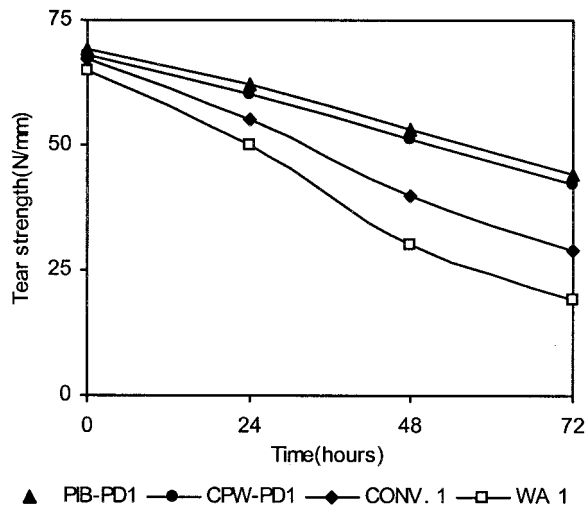


Figure 6 Variation in the tensile strength of NR/SBR blends with the time of aging at 100°C.



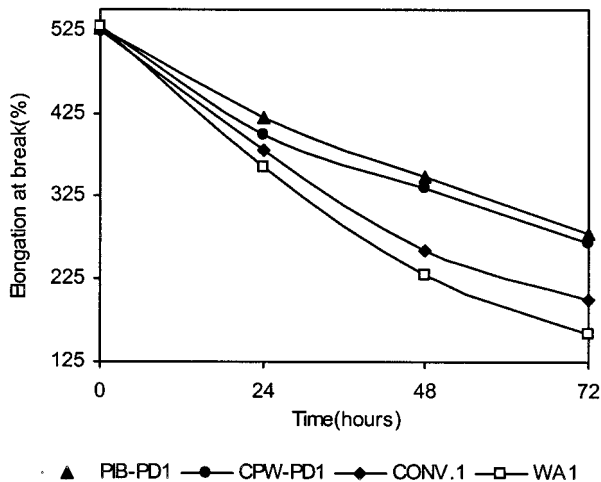


**Figure 7** Variation in the tear strength of NR/BR blends before and after aging at 100°C.

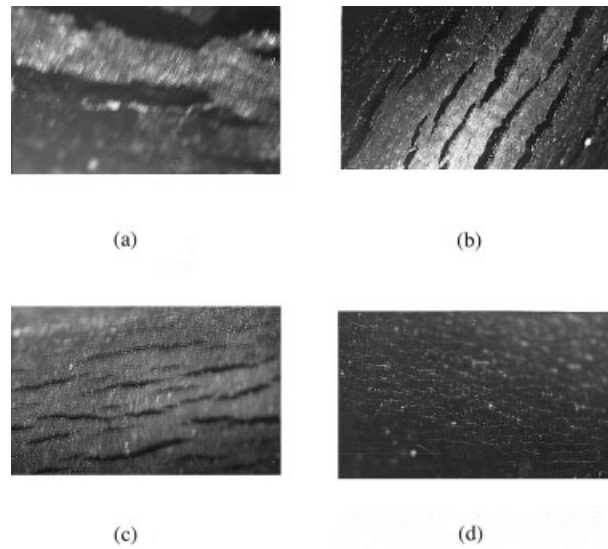
its lower molecular weight, which helps with the blooming and formation of a protective film on the surface of the vulcanizate, preventing direct contact with the atmosphere.

Table III shows the variations of the abrasion resistance, compression set, hardness, resilience, crosslink density, and ozone aging resistance of NR/BR and NR/SBR blends with the bound antioxidants and Vulkanox 4020 and without antioxidant.

The abrasion resistance and compression set of the blends containing conventional and bound antioxidants are almost the same, as shown in Table III. This shows that these properties are not affected by the addition of oligomer-bound antioxidants. The ozone aging studies show that blends containing PIB-PD and CPW-PD have greater resistance to aging than blends containing conventional antioxidants. This again sup-



**Figure 8** Variation in the elongation at break of NR/SBR blends before and after aging at 100°C.

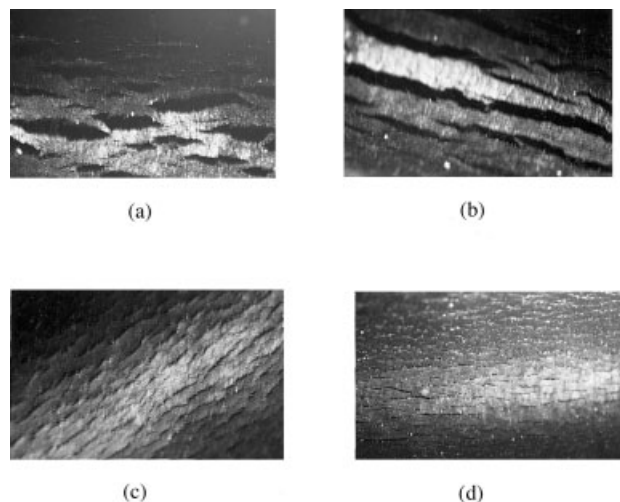


**Figure 9** Ozone crack growth of NR/BR blends after 19 h: (a) without an antioxidant, (b) with Vulkanox 4020, (c) with PIB-PD, and (d) with CPW-PD.

ports the superiority of the oligomer-bound antioxidants over conventional antioxidants. Both PIB-PD and CPW-PD have a saturated backbone, and their mobility is not lost during vulcanization; therefore, they have superior ozone resistance. The higher molecular weights also reduce their volatility in comparison with conventional antioxidants.

## CONCLUSIONS

The elastomer blends containing oligomer-bound antioxidants show greater aging resistance than those containing Vulkanox 4020. These antioxidants can re-



**Figure 10** Ozone crack growth of NR/SBR blends after 19 h: (a) without an antioxidant, (b) with Vulkanox 4020, (c) with PIB-PD, and (d) with CPW-PD.

TABLE III  
Properties of the Blends

Property	A (PIB-PD)		B (CPW-PD)		C (Vulkanox 4020)		D (WA)	
	NR/BR	NR/SBR	NR/BR	NR/SBR	NR/BR	NR/SBR	NR/BR	NR/SBR
Abrasion resistance (volume loss, cc/h)	2.6	3.1	2.6	3.1	2.8	3.3	2.9	3.5
Compression set (%)	19.4	21	18.8	20.4	21.1	23	21.7	23.1
Hardness (Shore A)	74	60	73	59	72	54	70	53
Tear strength (N/mm)	70	69	69	64	68	63	67	62
Ozone resistance (crack initiation, h)	7	8	8	9	4	5	3	3.5
Resilience (%)	58	50	59	51	57	48	58	48
Crosslink density $\times 10^{-5}$ (g mol/cc)	22.3	8.26	21.1	8	20.2	7.5	18.7	7

place the plasticizers required for compounding without affecting the physical properties. Ozone aging can be prevented to a greater extent by the use of these antioxidants.

## References

1. Corish, P. J. *Rubber Chem Technol* 1974, 47, 481.
2. Glanville, L. M.; Milner, P. W. *Plast Age* 1957, 48, 1059.
3. Blow, C. M.; Loo, C. T. *J Inst Rubber Ind* 1973, 7, 205.
4. Bhowmick, A. K.; De, S. K. *Rubber Chem Technol* 1980, 53, 960.
5. Angert, L. G.; Zenchenko, A. L.; Kuzminskii, A. S. *Rubber Chem Technol* 1961, 34, 807.
6. Spacht, R. B.; Hollingshead, W. S.; Bullard, H. L.; Wills, D. C. *Rubber Chem Technol* 1964, 37, 210.
7. Lewis, J. E.; Deviney, M. L., Jr.; Whittington, L. E. *Rubber Chem Technol* 1969, 42, 892.
8. Dunn, J. R. *Rubber Chem Technol* 1974, 47, 960.
9. Kuczkowski, J. A.; Gillick, J. G. *Rubber Chem Technol* 1984, 57, 621.
10. Al-Mehadawe, M. S.; Stuckey, J. E. *Rubber Chem Technol* 1989, 62, 13.
11. Avirah, S.; Joseph, R. *Angew Macromol Chem* 1991, 193, 1.
12. Avirah, S.; Joseph, R. *Polym Degrad Stab* 1994, 46, 251.
13. Avirah, S.; Joseph, R. *J Appl Polym Sci* 1995, 57, 1511.
14. Sulekha, P. B.; Joseph, R.; George, K. E. *Polym Degrad Stab* 1999, 63, 225.
15. Sulekha, P. B.; Joseph, R.; Prathapan, S. *J Appl Polym Sci* 2001, 81, 2183.
16. Sulekha, P. B.; Rani, J.; Madhusoodanan, K. N.; Thomas, K. T. *Polym Degrad Stab* 2002, 77, 403.
17. Ellis, B.; Welding, G. N. *Techniques of Polymer Science; Society of Chemistry and Industry: London, 1972, p 3240.*
18. Porter, M. *Rubber Chem Technol* 1967, 40, 866.
19. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 512.