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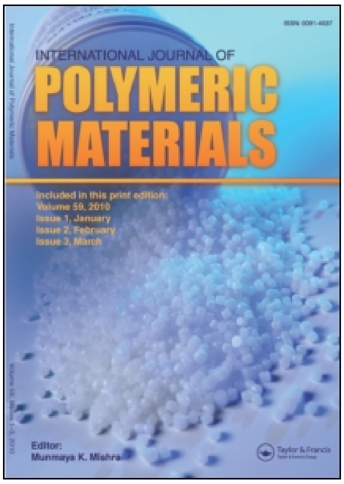

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Studies on Polymer Bound Antioxidants in NBR Vulcanizates

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The efficiency and permanence of polymer bound antioxidants like polyisobutylene bound paraphenylenediamine (PIB-PD) and chlorinated paraffin wax bound paraphenylene diamine (CPW–PD) in acrylonitrile–butadiene rubber (NBR) vulcanizates were studied. These polymer bound antioxidants were found to be less volatile and more resistant to solvent and oil extraction. The vulcanizates showed improved aging resistance in comparison to vulcanizates containing conventional antioxidant. The liquid polymer bound antioxidants reduce the amount of plasticizer required for compounding.

Keywords: acrylonitrile–butadiene rubber; aging resistance; solvent extraction and polymer bound antioxidants

INTRODUCTION

On account of their low cost, availability and oil resistance, nitrile rubbers (acrylonitrile butadiene rubbers) are widely used as oil seals, O–rings, gaskets and fuel and oil hose. Nitrile rubber based products, when in contact with mineral oil based hydraulic fluids, require protective antioxidants in order to retain their elastomeric properties for useful periods in service. But when they are subjected to continuous contact with hydraulic fluids at high temperature, the low molecular weight additives will be lost by extraction or volatilization [1, 2]. T.C.P. Lee et al. [3] conducted studies on network changes in nitrile rubber at elevated temperatures. Evaluation of compounding

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techniques for optimizing sealing performance of nitrile rubber vulcanizates was done by A.S. Farid [4].

Polymer bound antioxidants do not volatilize or get leached during service. Several methods of preparation of bound antioxidants were described by Scott et al. and others [5–12]. Most of the antioxidants prepared have unsaturated backbone. So during the process of vulcanization their backbone gets attached to the main chain of the polymer through sulfur crosslinking and it reduces its mobility. Studies were conducted to overcome this defect [13, 14]. This paper describes the use of novel polymer bound antioxidants like polyisobutylene bound paraphenylenediamine (PIB-PD) [13] and chlorinated paraffin wax bound paraphenylene diamine (CPW-PD) [14] in nitrile rubber. These bound antioxidants were compared with conventional vulkanox 4020 in filled NBR compounds.

EXPERIMENTAL

Materials

Acrylonitrile–butadiene rubber (NBR; N 553) was supplied by Apar Polymers Ltd., Gujarat, India. Compounding ingredients, ZnO, stearic acid, dioctylphthalate and carbon black (HAF, N 330) were commercial grade. Tetramethylthiuram disulfide (TMTD), Vulkanox 4020 (N-phenyl–N′(1,3 dimethylbutyl)–p-phenylenediamine) were rubber grade and supplied by Bayer India. Ltd. Mumbai. Methanol, acetone and toluene were of reagent grade and used as received. Transformer oil and engine oil were commercial grade.

The novel polymer bound antioxidants were prepared in the laboratory and their structure is shown in Table 1.

The optimum concentrations of polyisobutylene bound paraphenylenediamine (PIB-PD) and chlorinated paraffin wax bound paraphenylene diamine (CPW-PD) antioxidants in NBR getting maximum retention in properties were determined by varying the amount of antioxidants in a standard formulation from 1 to 10 phr (Table 2).

The optimum cure times, T_{90} min (the time required to reach 90% of the maximum torque), and scorch times (the time required to reach 10% of the maximum torque) of the compounds were determined on a Göttfert Elastograph Model 67.85 according to ASTM D 1648 (1981).

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

TABLE 1 Antioxidants Used

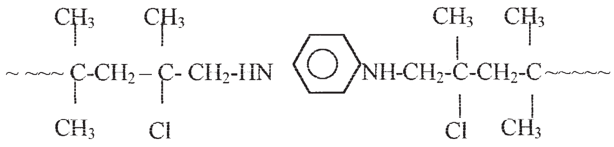
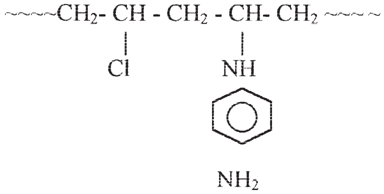
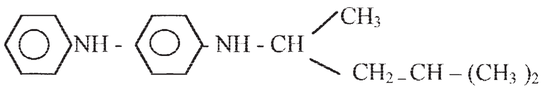
No.	Name	Formula
1.	Prepared antioxidants Polyisobutylene bound paraphenylenediamine (PIB-PD)	
2.	Chlorinated paraffin wax bound paraphenylene diamine (CPW-PD)	
3.	Conventional antioxidant Vulkanox 4020	

TABLE 2 Formulations for testing antioxidants

Sample	A	B	C	D	E	F	G	H	I	J	K	L
Acrylonitrile-butadiene rubber (NBR)	100	100	100	100	100	100	100	100	100	100	100	100
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Carbon black (HAF, N330)	40	40	40	40	40	40	40	40	40	40	40	40
Dioctylphthalate (DOP)	–	–	5.0	5.0	3.0	1.0	–	–	3.0	1.0	–	–
Mercaptobenzothiazole (MBTS)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Tetramethylthiuram disulphide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PIB-PD	8.0	–	–	–	2.0	4.0	6.0	10.0	–	–	–	–
CPW-PD	–	8.0	–	–	–	–	–	–	2.0	4.0	6.0	10.0
Vulkanox 4020	–	–	1.0	–	–	–	–	–	–	–	–	–

machine using a cross head speed of 500 mm/min according to ASTM D-412-80.

Tear resistance of the vulcanizates was evaluated as per ASTM D-624-81 using un-nicked 90° angled test specimens. The compression set of the samples was determined as per ASTM D-395 methods. The hardness (shore A) of the molded samples was tested using a Zwick 3115 hardness tester in accordance with ASTM D-2240. Flex resistance of the samples was tested using a Demattia flexing machine as per ASTM D-430-577. Resilience of the samples was determined by vertical rebound as per ASTM D 2632.

The aging resistance of the vulcanizates was studied by aging for 12, 24, 36 and 48 h at 100°C, then measuring the retention in tensile properties. Oil resistance of the NBR vulcanizates containing

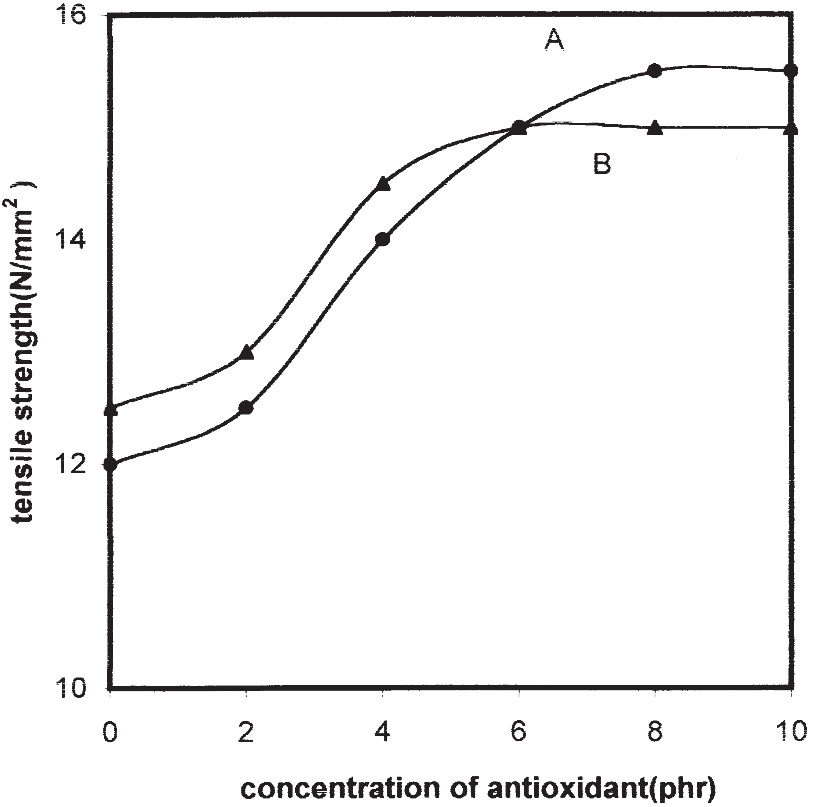


FIGURE 1 Variation in tensile strength after aging for 48 h with the concentration of antioxidants; (a) – PIB –PD, (b) – CPW–PD.

bound antioxidants was studied by keeping the samples in light oil and engine oil at room temp and also at 70°C for 24 h. The retention in tensile properties and tear strength were evaluated.

Solvent resistance of bound antioxidants was studied in methanol and acetone by keeping the vulcanizates in methanol and acetone for 48 h at room temperature. The retention of tensile properties of samples after methanol and acetone 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.

Crosslink density ($1/2M_c$ was determined using Flory Rehner equation.[15]

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

RESULTS AND DISCUSSION

Figure 1 shows the variation in tensile strength with concentration of antioxidant after aging the samples for 48 h at 100°C. Aging resistance

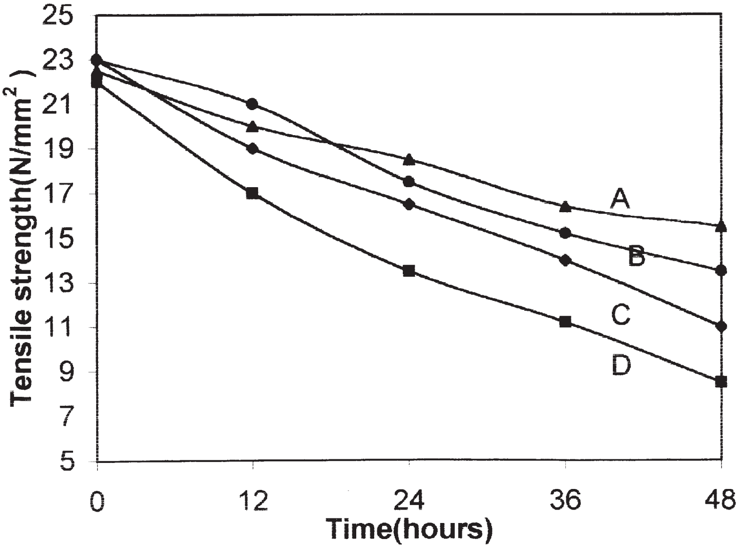


FIGURE 2 Variation in tensile strength of the vulcanizates before and after aging at 100°C. (a) – PIB–PD, (b) – CPW–PD, (c) – vulkanox 4020 and (d) – without antioxidant.

of NBR vulcanizates was enhanced by the addition of PIB-PD and CPW-PD, reaches a maximum and then levels off. The higher amount requirement of bound antioxidant compared to conventional antioxidant may be due to a lower amount of effective antioxidant in the bound product.

Figure 2 shows the tensile strength of the vulcanizates of compounds shown in Table 2 before and after aging. All the vulcanizates show fairly good resistance to aging at 100°C for 24 h but only compounds containing PIB-PD and CPW-PD show good resistance when the aging time is increased to 48 h, which shows the superiority of bound antioxidants over conventional antioxidant.

Figure 3 shows cure curves of the compounds given in Table 2. Cure time and scorch time are found to be reduced by the addition of PIB-PD and CPW-PD.

Figure 4 shows the tear strength of the above vulcanizates before and after aging. Retention in tear strength of the vulcanizates

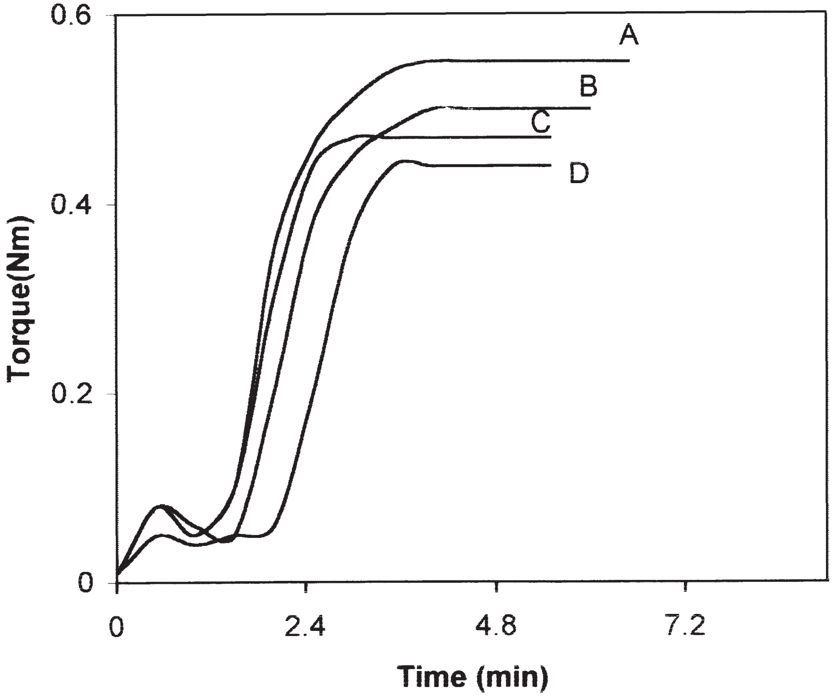


FIGURE 3 Cure cures of the compounds; (a) – PIB–PD, (b) – CPW–PD, (c) – vulkanox 4020 and (d) – without antioxidant.

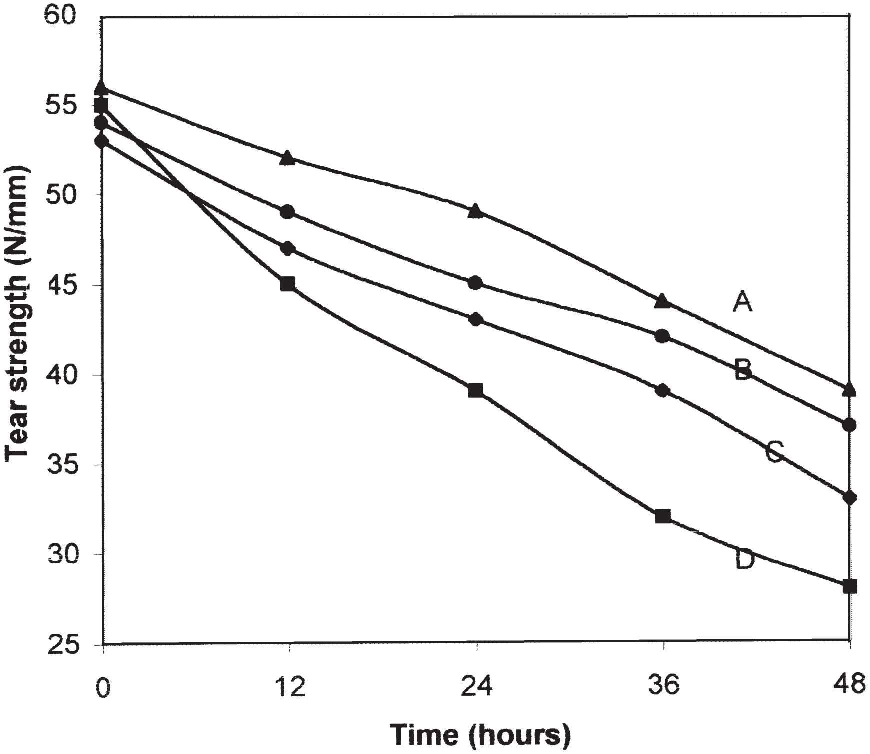


FIGURE 4 Variation in tear strength of the vulcanizates before and after aging at 100°C. (a) – PIB–PD, (b) – CPW–PD, (c) – vulkanox 4020, and (d) – without antioxidant.

containing PIB-PD and CPW-PD after aging are superior to vulcanizates containing vulkanox 4020.

Figure 5 shows the modulus of the vulcanizates before and after aging. The increase in modulus after aging may be due to increase in crosslink density.

Figure 6 shows the change in elongation at break of the vulcanizates before and after aging. The compounds containing PIB-PD and CPW-PD show better retention in elongation at break after aging. This again shows that polymer bound antioxidants can improve the aging resistance of NBR vulcanizates.

Figures 7 and 8 show 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

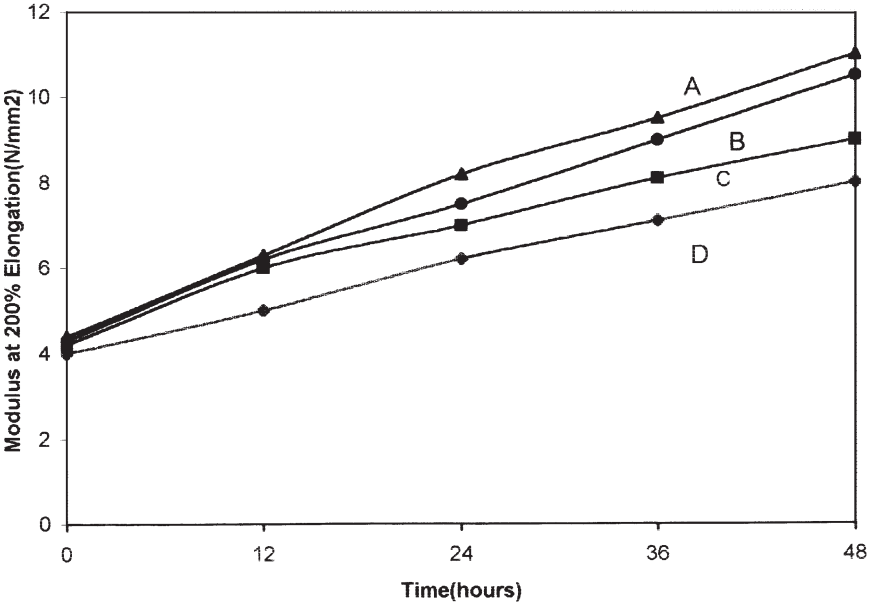


FIGURE 5 Variation in modulus of the vulcanizates before and after aging. (a) – PIB–PD, (b) – CPW–PD, (c) – vulkanox 4020, and (d) – without antioxidant.

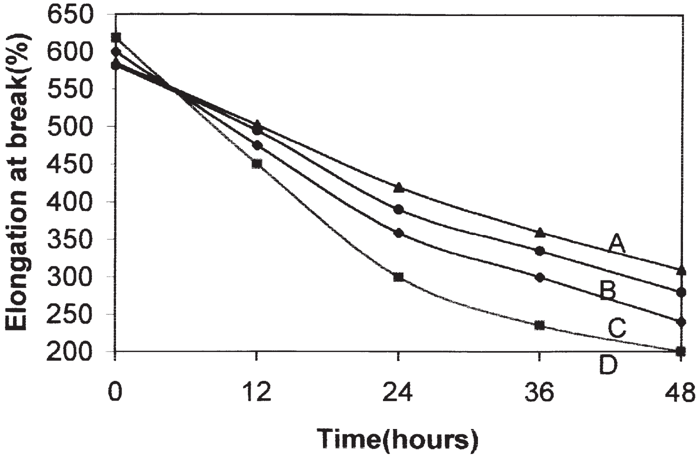


FIGURE 6 Variation in elongation at break of the vulcanizates before and after aging at 100°C. (a) – PIB–PD, (b) – CPW–PD, (c) – vulkanox 4020, and (d) – without antioxidant.

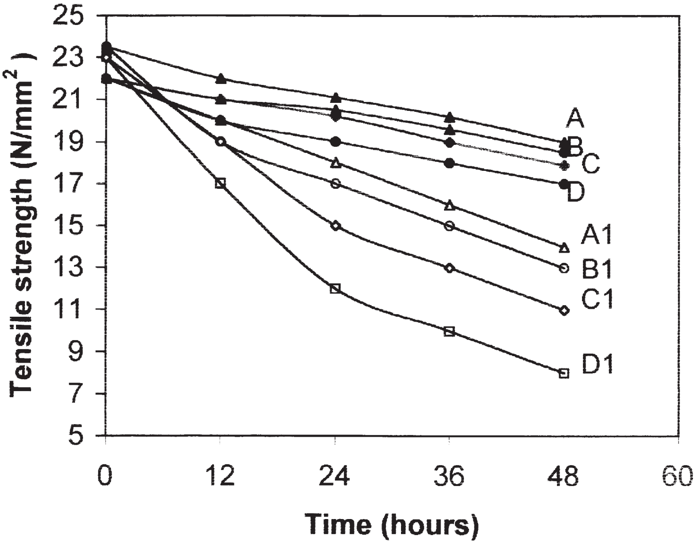


FIGURE 7 Variation in tensile strength of the vulcanizates before and after extraction in solvents followed by aging at 100°C. (a) in methanol, (A) – PIB–PD, (B) – CPW–PD, (C) – vulkanox 4020, and (D) – without antioxidant. (b) in acetone, (A^1) – PIB–PD, (B^1) – CPW–PD, (C^1) – vulkanox 4020, and (D^1) – without antioxidant.

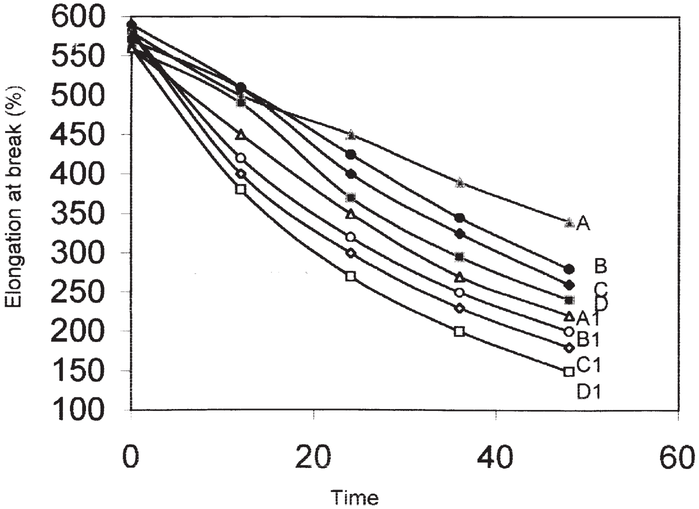


FIGURE 8 Variation in elongation at break of the vulcanizates before and after extraction in solvents followed by aging at 100°C. (a) in methanol, (A) – PIB–PD, (B) – CPW–PD, (C) – vulkanox 4020, and (D) – without antioxidant. (b) in acetone, (A^1) – PIB–PD, (B^1) – CPW–PD, (C^1) – vulkanox 4020 and (D^1) – without antioxidant.

TABLE 3 Properties of Vulcanizates

Properties	A (PIB-PD)	B (CPW-PD)	C (Pilflex-13)	D (WA)
Abrasion resistance (volume loss, cc/h)	2.396	2.411	2.523	3.105
Compression set (%)	16.5	16.8	17	17.9
Hardness (Shore A)	68	67	65	62
Flex resistance (k cycles)	95.542	93.462	83.147	52.816
Resilience (%)	29	28	27	25
Crosslink density (g mol/cc)	2.235×10^{-4}	2.118×10^{-4}	2.02×10^{-4}	1.879×10^{-4}

of vulcanizates containing PIB-PD and CPW-PD are probably due to lower extractability of the bound antioxidant by the solvents.

Table 3 shows the variation in abrasion resistance, compression set, hardness, flex resistance, resilience and crosslink density of the vulcanizates of the compounds in Table 2.

The abrasion resistance, compression set and crosslink densities of vulcanizates containing conventional and bound antioxidant are almost the same as shown in Table 3. These show that vulcanizates containing PIB-PD and CPW-PD are comparable with conventional antioxidant. The flex resistance shows vulcanizates containing PIB-PD and CPW-PD are superior to vulcanizate containing conventional antioxidant.

Table 4 shows the variation in tensile strength, elongation at break, modulus and tear strength of the vulcanizates (of the compound shown in Table 2) before and after extractingthe samples in transformer oil and engine oil at room temperature and 70°C.

Table 5 shows the variation in tensile strength, elongation at break, modulus and tear strength of the vulcanizates after extracting the samples in water at 70°C and 100°C followed by aging at 100°C for 48 hours. The retention in properties shown by the vulcanizates containing bound antioxidants are superior to those vulcanizates containing conventional antioxidants because PIB-PD and CPW-PD do not get extracted into hot water or boiling water.

CONCLUSIONS

1. The polymer bound antioxidants have much better resistance to volatility compared to conventional antioxidant.
2. The polymer bound antioxidants can improve the aging resistance of NBR vulcanizates.

TABLE 4 Properties of Oil Extraction at Room Temperature Followed by Aging for 48 h at 70°C

					Properties after extraction and aging for 48 h at 70°C							
	Properties before extraction				Transformer oil				Engine oil			
Property	A	B	C	D	A	B	C	D	A	B	C	D
Tensile strength (N/mm^2)	21.3	21.6	22.4	22	18.5	18	16.6	14.3	18.9	18	16	14.2
Elongation at break (%)	550	570	580	595	527	542	462	385	578	510	482	350
Modulus at 100% elongation (N/mm^2)	3.2	2.6	2.4	2.2	8.2	7.2	6.8	8.0	8.01	6.9	6.5	7.9
Tear strength (N/mm)	59.5	55	53	51	47	42	39	31	44.2	38	33	28.5

TABLE 5 Properties after Water Extraction at 70°C and 100°C Followed by Aging at 100°C for 48 h

	Extraction					
Property	Time	Temp	A (PIB-PD)	B (CPW-PD)	C -(Conv)	D (WA)
Tensile strength (N/mm^2)	0	27°C	22	22	23	22.5
Elongation at break(%)			550	570	580	595
Modulus at 100% elongation (N/mm^2)			3.2	2.7	2.5	2.2
Tear strength (N/mm)			59.5	55	53	51
Tensile strength (N/mm^2)	24 h	70°C	19.2	18	16	14
Elongation at break(%)			410	480	425	400
Modulus at 100% elongation (N/mm^2)			6.2	5.95	5.42	5.12
Tear strength (N/mm)			45	41	39	33
Tensile strength (N/mm^2)	10 h	100°C	18.3	17.1	14.5	10.8
Elongation at break(%)			282	261	205	198
Modulus at 100% elongation (N/mm^2)			6.85	6.25	5.6	5.32
Tear strength (N/mm)			42	40	32	25

3. The polymer bound antioxidant can reduce the amount of plasticizer required for compounding.
4. Water and oil resistance of the NBR vulcanizates could be improved by the use of polymer bound antioxidant.

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