

# Synthesis and Characterization of Chlorinated Paraffin Wax-Bound Paraphenylenediamine Antioxidant and Its Application in Natural Rubber

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**ABSTRACT:** *p*-Phenylenediamine was chemically attached to low molecular weight chlorinated paraffin wax. The polymer-bound *p*-phenylenediamine was characterized by vapor-phase osmometry (VPO), proton magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ), infrared spectroscopy (IR), and thermogravimetric analysis (TGA). The efficiency and permanence of the polymer-bound *p*-phenylenediamine as an antioxidant was compared with a conventional amine-type antioxidant in natural rubber vulcanizates. The vulcanizates showed improved aging resistance in comparison to vulcanizates containing a conventional antioxidant. The presence of liquid polymer-bound *p*-phenylenediamine also reduces the amount of the plasticizer required for compounding. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2183–2189, 2001

**Key words:** chlorinated paraffin wax; *p*-phenylenediamine; bound antioxidant; natural rubber aging resistance

## INTRODUCTION

Substituted *p*-phenylenediamines are used as a stabilizer for various rubber products for improving their aging resistance. They impart a better overall protection than does any phenolic antioxidant but are of limited use due to their discoloring and staining properties.

All aromatic amines are able to scavenge  $\text{RO}^\bullet$  and  $\text{RO}_2^\bullet$  radicals and, therefore, possess chain-breaking antioxidant properties. The general features of aromatic amines as chain-breaking antioxidants for polymers have been reviewed.<sup>1–6</sup> Also, aromatic amines have been reported to have the ability to scavenge  $\text{R}^\bullet$  in peroxide-cured natural rubber (NR).<sup>7</sup>

The unsaturation in diene-based elastomers accounts for their sensitivity not only to oxidation but also to ozone attack. Ozone causes surface cracking of stressed or flexed rubber vulcanizates as a result of the chain scission of rubber molecules. Rubbers having a high degree of unsaturation require protection with both physical and chemical antioxidants for static and dynamic exposure. Waxes which bloom to the rubber surface and form a film inert to ozone attack function as physical antioxidants. Good static protection is provided by waxes but protection under dynamic exposure is possible only with chemical antioxidants where the effect is generally to reduce the rate of crack growth.<sup>8–13</sup>

Several polymerizable antioxidants were discussed in the literature.<sup>14–22</sup> Attempts to form molecularly dispersed antioxidants by attachment to the polymer backbone in the presence of free radicals have led to interesting conclusions

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**Table I Formulations for Testing Rubber-Bound Antioxidant**

Ingredients	A	B	C	A'	E	F
NR (phr)	100	100	100	100	100	100
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
Mercaptobenzothiazole	0.6	0.6	0.6	0.6	0.6	0.6
Tetramethylthiuram disulfide	0.2	0.2	0.2	0.2	0.2	0.2
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5
Pilflex 13	—	1.0	—	—	—	—
CPW-PD	8.0	—	—	6.0	4.0	2.0

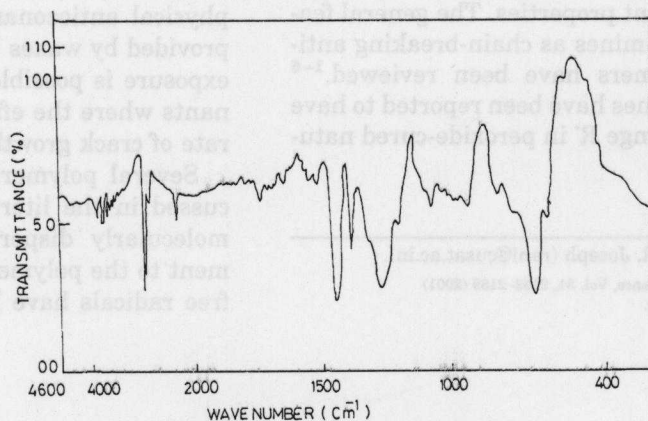
about their effectiveness both in the extent of binding and antioxidant effectiveness.<sup>20</sup> Antioxidants like styrenated phenol, diphenylamine, etc., bound to hydroxy-terminated liquid NR by a modified Friedel Crafts reaction, were also found to be effective in improving aging resistance. NR-bound diphenylamine antioxidants were reported by Avirah and Joseph.<sup>19</sup>

Most of the polymer-bound antioxidants prepared have an unsaturated backbone. So, during the process of vulcanization, their backbone becomes attached to the main chain through sulfur crosslinking and it loses its mobility still further.<sup>23</sup> A polyisobutylene-bound *p*-phenylenediamine antioxidant with a saturated backbone was found to be effective in improving aging resistance.<sup>24</sup> This article describes the chemical binding of *p*-phenylenediamine to chlorinated paraffin wax. This bound antioxidant was compared with conventional antioxidants in filled NR compounds.

## EXPERIMENTAL

### Materials

Chlorinated paraffin wax (CPW), with a 51.5% chlorine content and a viscosity of 15.9 poise, was supplied by KLJ Organic Ltd. (Gujarat, India). NR [(ISNR-5), Mooney viscosity ML(1+4) at 100°C = 82] was supplied by the Rubber Research Institute of India (Kottayam, India). Compounding ingredients—zinc oxide, stearic acid, aromatic oil, and carbon black (HAF N 330)—were of commercial grade. Mercaptobenzothiazole (MBT) and tetramethylthiuram disulfide (TMTD) were rubber grade supplied by Bayer India, Ltd. (Mumbai, India). Methanol, carbon tetrachloride, ether, toluene, dioxane, and triethylamine were of reagent grade and used as such. E. Merck India (Mumbai, India) supplied the *p*-phenylenediamine (PD) (Analar grade). Commercial antioxidants such as Pilflex-13 (substituted PD) was supplied by Poly Olefins Industries Ltd. (Mumbai, India).

**Figure 1** IR spectrum of CPW.

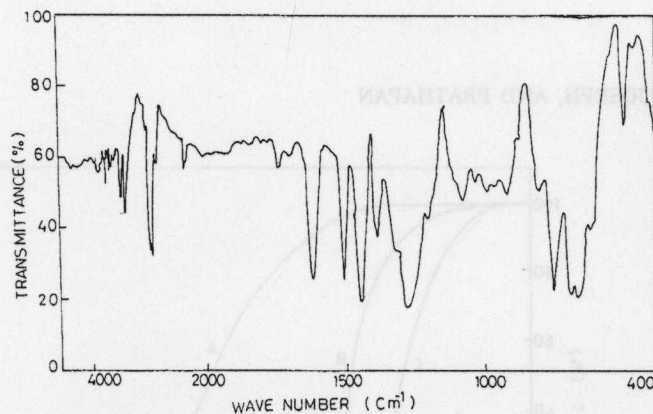


Figure 2 IR spectrum of CPW-PD.

### Preparation of CPW-bound PD

CPW and PD, each in a dioxane solution, were mixed at a 1:1 ratio. The reaction mixture was made basic by adding triethylamine to neutralize the HCl evolved during the condensation reaction. The reaction mixture was taken in a two-necked flask fitted with a water condenser and a thermometer. The mixture was heated at 100°C for 14 h. Dioxane 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.

### Analysis of Bound Antioxidant

Analysis of the bound antioxidant was carried out by using infrared spectroscopy (IR), proton mag-

netic resonance spectroscopy ( $^1\text{H-NMR}$ ), vapor-phase osmometry (VPO), and thermogravimetric analysis (TGA). IR spectra of the samples were taken on a Perkin-Elmer Model 377 IR spectrometer. The  $^1\text{H-NMR}$  spectra of the samples were recorded from a solution in  $\text{CCl}_4$  using a JEOL-JNM spectrometer.

TGA was carried out using a DuPont TG-DSC standard model in a nitrogen atmosphere at a heating rate of 10°C/min. The optimum concentration of the rubber-bound antioxidant for attaining the maximum retention in properties was determined by varying the amount of the antioxidant in the mix from 1 to 10 phr.

The chemically bound PD was added to the NR as per formulations given in Table I. The amount of the plasticizer can be reduced by the use of a liquid polymer-bound antioxidant as shown in Ta-

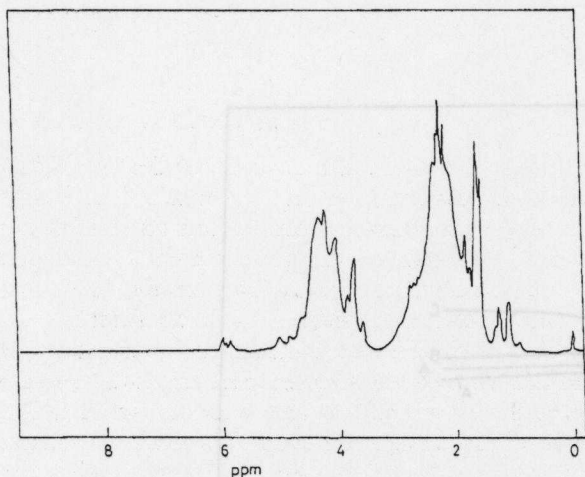


Figure 3  $^1\text{H-NMR}$  spectrum of CPW.

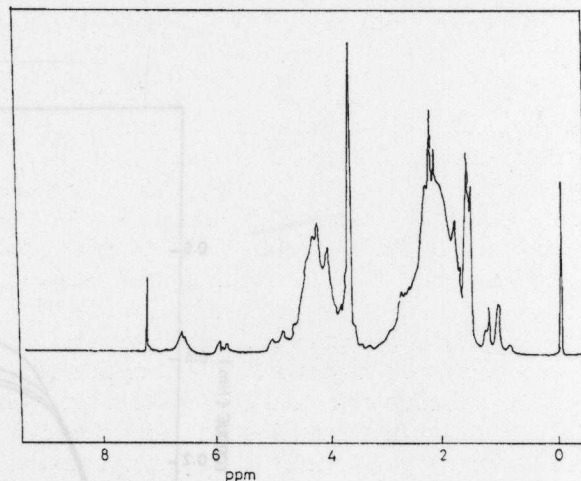


Figure 4  $^1\text{H-NMR}$  spectrum of CPW-PD.

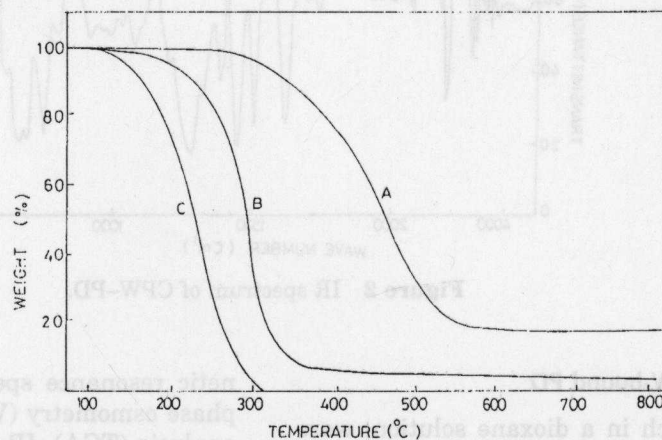


Figure 5 TGA of compounds: (A) CPW-PD; (B) CPW; (C) PD.

ble I. 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 molded in an electrically heated laboratory hydraulic press at 150°C to their optimum cure time and 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 according to ASTM D-412-80. The tear

resistance of the vulcanizates was evaluated as per ASTM D-2240. The retention in tensile and tear properties were evaluated after aging the samples at 100°C for 12, 24, 36, and 48 h. The compression set of the samples was determined as per ASTM D-39 methods.

A Goodrich flexometer conforming to ASTM D 623-67 Method A was used for measuring heat buildup. The test was carried out with a cylindrical sample of 2.5 cm in height and 1.9 cm in diameter. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and a load of 10.9 kg.

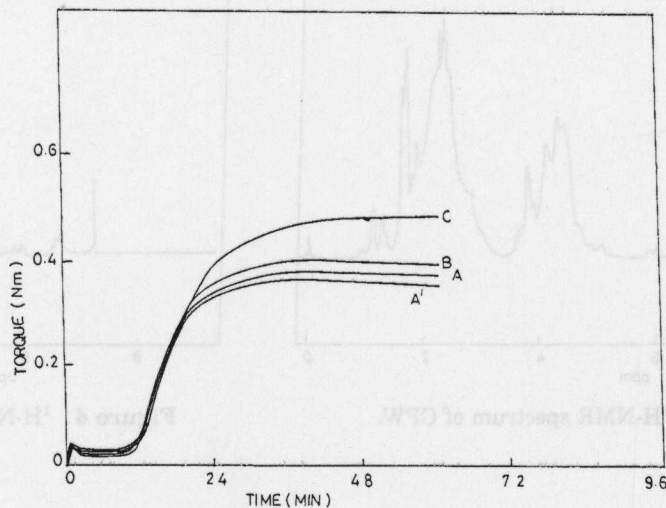
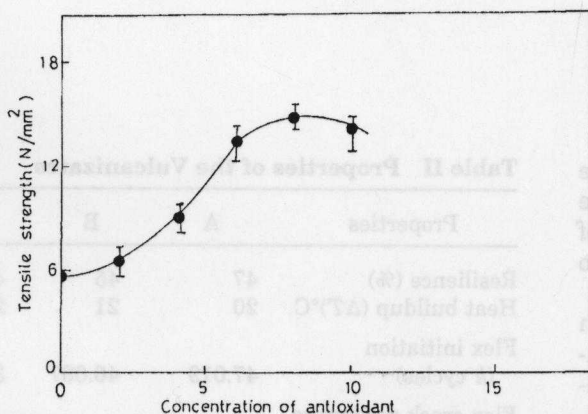
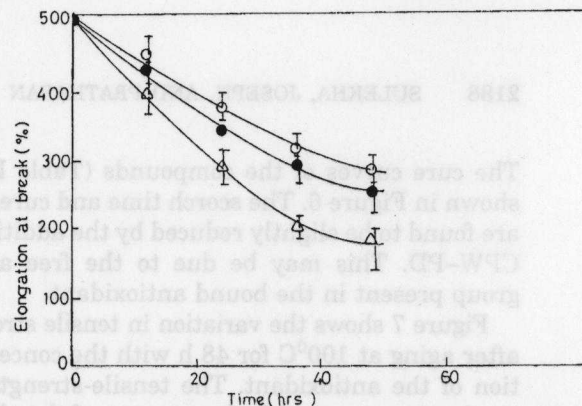


Figure 6 Cure curves of vulcanizates containing (A) CPW-PD, (B) pilflex-13, and (C) without antioxidant.



**Figure 7** Variation of tensile strength of the vulcanizates with the amount of antioxidant.

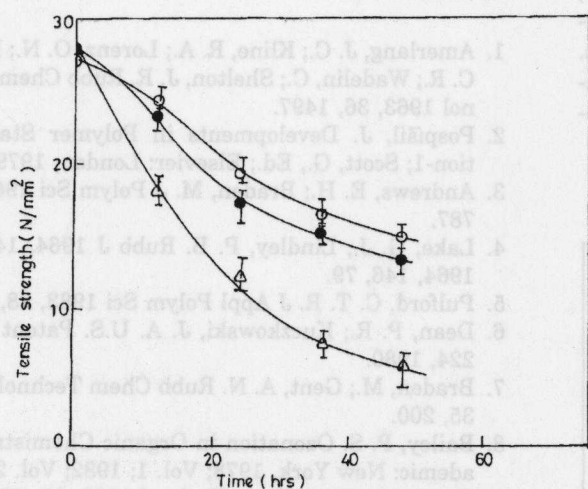


**Figure 9** Variation in tear strength of the vulcanizates before and after aging: (○) CPW-PD; (●) Piflex-13; (△) without antioxidant.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the IR spectra of CPW and CPW-PD. The IR spectrum of CPW-PD shows additional peaks at  $3400\text{ cm}^{-1}$  due to primary NH-stretching, at  $3387\text{ cm}^{-1}$  due to secondary NH-stretching, at  $1614.6\text{ cm}^{-1}$  due to NH-bending, and at  $1500\text{ cm}^{-1}$  corresponding to an aromatic ring in *p*-phenylenediamine.<sup>25</sup>

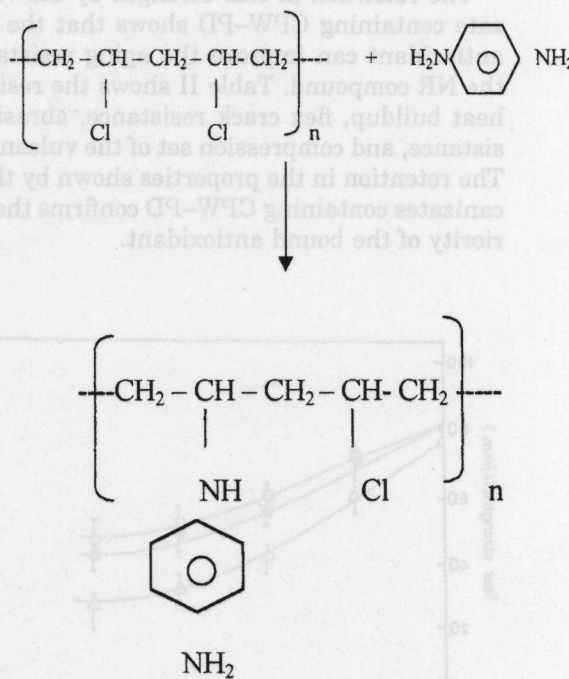
Figures 3 and 4 show the  $^1\text{H-NMR}$  spectra of CPW and CPW-PD. The  $^1\text{H-NMR}$  spectrum of CPW-PD shows additional peaks at 7.27 and 5.978  $\delta$  corresponding to an aromatic ring present in *p*-phenylenediamine. Note that the peak due to NH is masked by other peaks of the sample.



**Figure 8** Variation in tensile strength of the vulcanizates before and after aging at  $100^\circ\text{C}$ : (○) CPW-PD; (●) Piflex-13; (△) without antioxidant.

Figure 5 shows thermograms of PD, CPW, and CPW-PD. The low molecular weight PD volatilizes easily while rubber-bound PD is less volatile. This again confirms the chemical binding of PD onto CPW.

The molecular weights of the samples were determined by VPO. The molecular weights of CPW, CPW-PD, and PD were 530, 1050, and 110, respectively. This shows that CPW is bound to PD. From the above data, the binding reaction of CPW and *p*-phenylenediamine may be as shown below:



The cure curves of the compounds (Table I) are shown in Figure 6. The scorch time and cure time are found to be slightly reduced by the addition of CPW-PD. This may be due to the free amino group present in the bound antioxidant.

Figure 7 shows the variation in tensile strength after aging at 100°C for 48 h with the concentration of the antioxidant. The tensile-strength retention increases with the amount of the chemically bound antioxidant, reaches a maximum, and then levels off. The higher quantities of the bound antioxidant are due to a lower amount of the effective antioxidant in the bound product.

Figure 8 shows the variation in the tensile strength of the vulcanizates before and after aging. All the vulcanizates show fairly good resistance to aging at 100°C for 24 h. A vulcanizate containing CPW-PD is found to be better than is a vulcanizate containing pilflex 13 when the time of aging is increased to 48 h.

Figures 9 and 10 show changes in the elongation at break and tear strength of the vulcanizates before and after aging. The vulcanizate containing CPW-PD has better retention in the elongation at break after aging, which confirms the superiority of the bound antioxidant.

The retention in tear strength by the vulcanizate containing CPW-PD shows that the bound antioxidant can improve the aging resistance of the NR compound. Table II shows the resilience, heat buildup, flex crack resistance, abrasion resistance, and compression set of the vulcanizates. The retention in the properties shown by the vulcanizates containing CPW-PD confirms the superiority of the bound antioxidant.

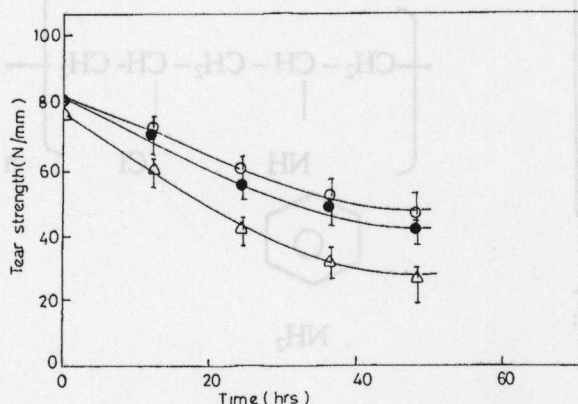


Figure 10 Variation in modulus of the vulcanizates before and after aging: (○) CPW-PD; (●) Pilflex-13; (△) without antioxidant.

Table II Properties of the Vulcanizates

Properties	A	B	C
Resilience (%)	47	45	45
Heat buildup ( $\Delta T$ )°C	20	21	22
Flex initiation ( <i>k</i> cycles)	47.019	46.087	34.933
Flex crack resistance ( <i>k</i> cycles)	180.697	103.942	80.697
Abrasion resistance (volume loss, cc/h)	3.5818	3.571	3.769
Compression set (%)	16.98	17.7	18

## CONCLUSIONS

PD can be chemically bound to CPW by a condensation reaction. The rubber-bound antioxidant has a much superior resistance to volatility compared to a conventional antioxidant. The bound antioxidant is found to have superior retention in the mechanical properties compared to a vulcanizate containing pilflex 13. The amount of the plasticizer in the compound can be reduced when a bound antioxidant is used.

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