PREPARATION, CHARACTERISATION AND USE OF
NOVEL PHENOLIC TYPE ANTIOXIDANTS

Introduction

The trend towards the use of rubbers in aggressive atmosphere has led to a
search for methods of producing non-extractable antioxidants. Phenol was one of
the earlier materials used to retard the oxidation of rubber. Alkylated phenols were
found to be more effective, less toxic and less volatile. Higher molecular weight
non-staining antioxidants by alkylating phenols were reported.\textsuperscript{1,2} A wide variety of
substituted phenols have been synthesised and evaluated as antioxidants during
last 70 years. The patent literature represents one of the best sources of
information on the current direction of research in the area of polymer stabilisation.
Two books deal exclusively with the United states patent literature on antioxidants
during the period of 1972 to 1979.\textsuperscript{3,4} For rubber applications, cost as well as low
volatility and compatibility with the polymer are important and most of the research
effort deals with the alkylation of phenols. Spach\textsuperscript{\textregistered} found that the reaction of p-
cresol and dicyclopentadiene, when tertiary butylated in the ortho positions of the
terminal phenol is an effective antioxidant. Goto\textsuperscript{5} discovered that the three isomers of dicyclopentyl-p-cresol (2,6-, 2,5-, 3,5-) obtained by reacting cyclopentene with p-cresol, were as effective as BHT in retaining physical properties of NR vulcanizes when aged 3 days at 100°C. Scott and co-workers have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position, can react with natural rubber in the presence of oxidising free radicals to yield polymer-bound antioxidants.\textsuperscript{6,7} De Jonge and Hope\textsuperscript{9} described the development of a novel type of antioxidant based on 2,6-diphenylphenol. These antioxidants display novel regenerative characteristics in the presence of thiodipropionate esters and lead to maintenance of the antioxidant concentration during processing and oxidation. Antioxidants like styrenated phenol bound to hydroxyl-terminated liquid natural rubber by modified Friedel-Crafts reaction were also found to be effective in improving ageing resistance.\textsuperscript{10}

This chapter describes the chemical binding of phenol to polyisobutylene and stearic acid respectively. These bound-antioxidants were compared with conventional antioxidants like styrenated phenol and 2,6 di-t-butyl p-cresol in filled natural rubber.

PART I
5.1 Preparation and Characterisation of Polyisobutylene-Bound Phenol and its use in NR Vulcanizes.

5.1.1 Experimental

\textit{a) Materials used}

Phenol, chlorinated polyisobutylene, anhydrous AlCl$_3$, o-xylene, fused calcium chloride and methanol.

\textit{b) Preparation of polyisobutylene-bound phenol}

The chlorinated polyisobutylene (PIB-Cl) is prepared by the method described in chapter 3. The phenol was alkylated using modified Friedel-Crafts
alkylation reaction. 0.1 mol of PIB-Cl, 0.2 mol of phenol, 0.4 mol catalyst (anhydrous aluminium chloride and 60 mol of solvent (o-xylene) were introduced into a two-necked flask fitted with a thermometer and soxhlet extraction unit which was packed with fused CaCl₂. The reaction mixture was heated for 14h. When the reaction was complete, the reaction mixture was neutralized with sodium carbonate and washed several times with water to remove the catalyst. The contents of the vessel were poured into excess methanol with stirring to precipitate the liquid phenol-bound polyisobutylene (PIB-Ph). It was separated using a separating funnel, washed and dried in a vacuum oven. The polyisobutylene bound phenol was obtained in the form of a viscous liquid.

c) Analysis of bound antioxidant

Analysis of bound antioxidant was carried out by using infrared spectroscopy (IR), proton magnetic resonance spectroscopy (¹H-NMR) and Thermo gravimetric analysis (TGA).

IR spectra of the samples 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 in nitrogen atmosphere at a heating rate of 10°C/min. The optimum concentration of the rubber bound antioxidant for attaining maximum retention in properties was determined by varying the amount of the antioxidant in the mix from 1 to 10 phr.

The polyisobutylene-bound phenol antioxidant was added in NR as per formulations given in table 5.1.

The amount of the plasticiser can be reduced by the use of liquid polymer-bound antioxidant as shown in table 5.1. The optimum cure times (time to reach 90 % of the maximum torque) of compounds were determined on a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981).
Table 5.1 Formulations for testing PIB-Ph antioxidant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>2,6 di-t-butyl p-cresol</td>
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</tr>
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<td>-</td>
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<td>4.0</td>
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</table>

Rubber compounds were moulded 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 moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick Universal Testing machine using a cross head speed of 500mm /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. Retention in tensile and tear properties were evaluated after ageing the samples at 100°C for 12, 24, 36 and 48hrs. The compression set of the samples was determined as per ASTM D-395 method B (1982). The abrasion resistance of the samples was tested using DIN Abrader.

Results and discussion

Figs. 5.1 shows the IR spectra of polyisobutylene (PIB), polyisobutylene-bound phenol (PIB-Ph) respectively. The IR spectra of PIB shows peaks at 2950 cm\(^{-1}\) corresponding to aliphatic - CH stretching, at 1480 cm\(^{-1}\) due to - CH bending, 1650 cm\(^{-1}\) corresponds to C=C.
The IR spectra of PIB-Ph shows additional peaks at 3500 cm\(^{-1}\) due to the presence of -OH stretching, 3000 cm\(^{-1}\) corresponding to aliphatic -CH stretching, 1600 cm\(^{-1}\) corresponds to aromatic ring and 780 cm\(^{-1}\) due to the presence of C-Cl stretching.\(^{11}\) This confirms the chemical binding of phenol to polyisobutylene.

Fig. 5.2 shows the \(^1\)HNMR spectra of PIB and PIB- Ph respectively. PIB shows peaks at \(\delta=1.22\) (\(-\text{CH}_2\)) and \(\delta=1.6\) ppm (\(-\text{CH}_3\)) while PIB-Ph shows additional peaks at \(\delta=7.2\) and \(\delta=6.8\) ppm corresponding to aromatic ring and -OH group in polymeric association respectively present in PIB-Ph. This again confirms the chemical binding of phenol to PIB.
Fig. 5.3 shows the thermograms of Phenol, PIB, and PIB-Ph. The low molecular weight phenol volatilises easily while polymer-bound phenols are less volatile. This again confirms the chemical bonding of phenol to PIB.
From the above data the binding of phenol and PIB may be represented as follows:

\[
\begin{align*}
\text{CH}_3 \quad \text{CH}_2 \\
\text{CH}_3 \quad \text{CH}_3
\end{align*}
\xrightarrow{\text{Cl}_2} 
\begin{align*}
\text{CH}_3 \quad \text{Cl} \\
\text{CH}_3 \quad \text{CH}_3
\end{align*}
\begin{align*}
\text{CH}_3 \quad \text{Cl} \\
\text{CH}_3 \quad \text{CH}_3
\end{align*}
\begin{align*}
\text{C-CH}_2\text{C-CH}_2\text{OH} \\
\text{CH}_3 \quad \text{CH}_3
\end{align*}

Scheme 5.1

The Fig.5.4 shows the variation in tensile strength with concentration of the compounds given in the Table5.1, after ageing at 100°C for 48hrs. The retention in properties is found to increase with the amount of the bound antioxidant, reach a
maximum and then levels off. The higher requirement of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the rubber bound product.

Fig. 5.4 Variation in tensile strength with the concentration of PIB-Ph after ageing at 100°C for 48h.

Fig. 5.5 Tensile strength Vs time of ageing at 100°C, A- PIB-Ph, B- styrenated phenol C-2,6 di-t butyl p-cresol, D- without antioxidant.
Fig. 5.6 Elongation at break of NR vulcanizates with time of ageing at 100°C, A- PIB-Ph, B- styrenated phenol C-2, 6 di-t butyl p-cresol, D- without antioxidant.

Fig. 5.5 shows the variation in tensile strength with ageing. All the vulcanizates show fairly good resistance to ageing at 100°C after 12hrs. The vulcanizates containing PIB-Ph show good resistance when the ageing time is increased to 48hrs, which shows the superiority of bound antioxidant over conventional antioxidant.

Fig. 5.6 shows the change in elongation at break of the vulcanizates time of ageing. The compound containing PIB-Ph shows better retention in elongation at break after ageing than compounds containing conventional antioxidants like styrenated phenol and 2,6 di-t butyl p-cresol.

This again shows that bound antioxidant can improve the ageing resistance of NR compound.

<table>
<thead>
<tr>
<th>Table 5.2 Properties of vulcanizates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>Abrasion resistance (volume loss, cc/h)</td>
</tr>
<tr>
<td>Compression set (%)</td>
</tr>
</tbody>
</table>
Chapter 5

The table 5.2 shows the abrasion resistance and compression set of the vulcanizates containing PIB-Ph, SP and WA. The values show marginal decrease in comparison with the control mix.

PART II

5.2 Preparation and characterisation of 4-octadecyl phenol and its use in NR vulcanizates.

5.2.1 Experimental

a) Materials

Stearic acid, thionyl chloride, carbon disulphide, anhydrous aluminium chloride, zinc dust and concentrated HCl.

b) Preparation of alkylated phenol using stearic acid.

0.1mol of stearic acid (SA) was weighed and dissolved in CS₂ and to it 0.1mol SOCl₂ was added drop wise and the reaction mixture was cooled in an ice bath. The reaction mixture is then heated gently under reflux for 2h. The acid chloride formed was separated and used for conducting Friedel Craft's acylation. 0.1mol of phenol was dissolved in CS₂ and mixed with 0.1 mol of anhydrous aluminium chloride catalyst. It is cooled using an ice bath and acid chloride dissolved in CS₂ was added drop wise to the reaction mixture, swirling the mixture during addition. After addition is complete removed from the ice bath and allowed to stand at room temperature for 30 minutes. Swirl the reaction mixture frequently during this period. Then the reaction mixture was heated on a hot plate with magnetic stirring for 5h. When the action was complete, the acetylated phenol was separated and reduced using zinc dust and HCl. The phenol bound stearic acid (SA-Ph) was separated washed and dried.

5.2.2 Analysis of bound antioxidant

Analysis of bound antioxidant was carried out by using thin layer chromatography (TLC), infrared spectroscopy (IR) and Thermogravimetric analysis (TGA).

The optimum concentration of the 4-octadecyl phenol antioxidant for attaining maximum retention in properties was determined by varying the amount
of the antioxidant in the mix from 1 to 10 phr. The antioxidant was added in NR as per formulations given in table 5.3. The optimum cure times (time to reach 90 % of the maximum torque) of compounds were determined on a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981).

5.2.3 Results and Discussion

The Fig. 5.7 shows the TLC of phenol, stearic acid (SA) and phenol bound stearic acid (SA-Ph). The TLC plate was spotted with the sample and it was kept in iodine chamber for colour development. The Rf values of the phenol, styrenated phenol (SP) and phenol bound stearic acid (SA-Ph) indicate the chemical binding of phenol and stearic acid.

![TLC graph](image-url)

**Fig.5.7 TLC of A- Phenol, B- Stearic acid C- SA-Ph**
Fig. 5.8 IR. spectrum of stearic acid

Fig. 5.9 IR. spectrum of SAPh
Novel Phenolic Type Antioxidants

Fig. 5.10 TGA of phenol, stearic acid and phenol bound stearic acid

The Fig. 5.8 & 5.9 shows the IR spectra SA and SA-Ph. The IR spectrum of stearic acid shows distinct peak of -C=O at 1709 cm\(^{-1}\). IR Spectrum of SA-Ph shows peak at 3500 cm\(^{-1}\) due to -OH stretching, 3000 cm\(^{-1}\) corresponding to aliphatic -CH and peak at 1550 cm\(^{-1}\) due to the presence of aromatic ring. The disappearance of the peak at 1709 cm\(^{-1}\) confirms the absence of carbonyl group in the compound. This indicates the reduction of the carbonyl group. These data confirm the binding of phenol to stearic acid.

The Fig. 5.10 shows the thermograms of phenol, stearic acid and phenol bound stearic acid. The higher TGA values of SA-Ph confirm the binding of phenol and stearic acid and the reduction of the carbonyl group.
Thus the formation of SA-Ph can be represented as follows:

\[ \text{C}_{17}\text{H}_{35}\text{COOH} + \text{SOCl}_2 \rightarrow \text{C}_{17}\text{H}_{35}\text{COCl} + \text{SO}_2 + \text{HCl} \quad (1) \]

\[ \text{C}_{17}\text{H}_{35}\text{COCl} + \text{An.AlCl}_3 \rightarrow \text{C}_{17}\text{H}_{35}\text{CO} - \text{OH} \quad (2) \]

\[ \text{C}_{17}\text{H}_{35}\text{CO} - \text{OH} \rightarrow \text{Zn} / \text{HCl} \rightarrow \text{C}_{17}\text{H}_{38}\text{CH}_2 - \text{OH} \quad (3) \]

**Scheme 5.2**

**Table 5.3** Formulations for testing SA-Ph antioxidant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
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The Fig. 5.11 shows the variation in tensile strength after ageing at 100°C, for 48h after the addition of varying amounts of SA-Ph to NR vulcanizates. The retention in properties is found to increase with the amount of the bound antioxidant, reach a maximum and levels off. The higher requirement of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the bound product.

![Graph](image_url)

**Fig. 5.11 Variation in tensile strength with the concentration of SA-Ph after ageing at 100°C for 48h.**

![Graph](image_url)

**Fig. 5.12 Variation of tensile strength with ageing, A- SA-Ph, B- styrenated phenol C-2,6 di-t butyl p-cresol, D- without antioxidant.**
Fig. 5.12 Elongation at break of NR vulcanizates time of ageing A- PIB-Ph, B-styrenated phenol C-2,6 di-t butyl p-cresol, D- without antioxidant

Fig. 5.12 shows the tensile strength of the vulcanizates of compounds shown in Table 5.2 with time of ageing. All the vulcanizates show fairly good resistance to ageing at 100°C after 12h. The vulcanizates containing SA-Ph show good resistance when the ageing time is increased to 48h, which shows the superiority of bound antioxidant over conventional antioxidant.

Fig. 5.13 shows the change in elongation at break of the vulcanizates with time of ageing. The compound containing SA-Ph shows better retention in elongation at break after ageing while conventional antioxidants shows slightly less retention in elongation at break after ageing. This again shows that bound antioxidant can improve the ageing resistance of NR vulcanizate.

Table 5.4 Properties of vulcanizates.

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<thead>
<tr>
<th>Properties</th>
<th>A (SA-Ph)</th>
<th>B (SP)</th>
<th>C (WA)</th>
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<td>3.68</td>
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The Table 5.4 shows that the abrasion resistance and compression set values of vulcanizates containing bound-antioxidant and conventional antioxidants are more or less same. So SA-Ph is comparable with conventional antioxidant.

Conclusions

1. Phenol was chemically attached to low molecular weight chlorinated polyisobutylene by Friedel Craft's alkylation reaction.

2. The bound antioxidant can improve the ageing resistance of NR vulcanizates. The liquid polyisobutylene-bound phenol can reduce the amount of plasticiser required for compounding.

3. Phenol was chemically attached to stearic acid by a series of reactions (halogenation, Friedel Crafts acylation and Clemmenson reduction).

4. 4-octadecyl phenol can also improve the ageing resistance of NR vulcanizates.
References

1. Steinberg (to Geigy Chemical Corp.) Canadian 785,322(1968).