Chapter 3

PREPARATION AND CHARACTERISATION OF
AMINE TYPE POLYMER-BOUND ANTIOXIDANTS

Introduction

Both natural and synthetic rubber requires effective antioxidants or protective agents in inhibiting oxidative degradation of rubber by atmospheric oxygen. The serious disadvantages of conventional antioxidants are their volatility and extractability in water and other solvents. The removal of antioxidants from the rubber during service has an adverse effect on the useful life of the products.1 One method to overcome this problem is the use of polymer-bound antioxidants. There are two basic approaches to obtain polymeric antioxidants. One is to copolymerise various monomers having antioxidant moiety with elastomeric monomers and the other is by the direct combination of the conventional antioxidant with modified elastomers.2,3 The large size of the resulting polymer-bound antioxidants makes them highly resistant to volatilisation and extraction.4
Polymerisable monomeric antioxidants were described by Tamura and coworkers.\textsuperscript{5,6} The reaction of chloroprene (CR) w-type with amines producing polymer bound antioxidants were reported by Mohammed. S. Al-Mehadawe et al.\textsuperscript{7} Scott et al 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{8-10} Antioxidants like styrenated phenol, diphenylamine etc bound to hydroxy terminated liquid natural rubber by modified Friedel-Crafts reaction were also found to be effective in improving ageing resistance.\textsuperscript{11} Natural rubber-bound diphenylamine antioxidants were reported by S. Avirah and R. Joseph.\textsuperscript{12}

Polymer-bound antioxidants have many advantages but the main disadvantage is that the mobility of the network-bound antioxidants is restricted. Hence it does not bloom to the surface and ozone attack cannot be effectively controlled.\textsuperscript{13} Most of the polymer-bound antioxidants reported have an unsaturated back bone. So during the process of vulcanisation their backbone gets attached to the main chain through sulphur crosslinking and it loses its mobility further.\textsuperscript{14} Polymer-bound antioxidant with a saturated backbone may help to overcome this problem. This chapter describes the preparation of amine type polymer-bound antioxidants with saturated backbone.

\textbf{PART I}

3.1 Preparation and Characterisation of Polyisobutylene-Bound Paraphenylene Diamine

3.1.1 Experimental

\textit{a) Materials}

Polyisobutylene (PIB) was supplied by Cochin Refineries Balmer Lawrie Ltd. Ambalamughal, Kerala, Paraphenylene diamine, methanol, carbon tetrachloride, ether, toluene, dioxan, triethylamine were of reagent grade supplied by E. Merck India was used.

\textit{b) Chlorination of polyisobutylene}

Polyisobutylene (PIB) was dissolved in $\text{CCl}_4$ (50% solution) in a one litre flask fitted with a two hold cork carrying an inlet and outlet tube. Through the inlet
tube, pure dry chlorine gas was passed and the outlet tube was connected to a jar containing sodium hydroxide in order to absorb the HCl gas evolved. The chlorine gas was passed for 5hrs. The resulting solution was poured into water at 80°C and excess chlorine and CCl₄ were removed. The chlorinated sample was dissolved in toluene and reprecipitated using methanol. The chlorinated polyisobutylene (PIB-Cl) was dried in a vacuum oven.

**c) Binding of PIB-Cl with paraphenylene diamine**

The chlorinated sample was dissolved in dioxan and mixed with paraphenylene diamine (PD) dissolved in dioxan in the ratio 2:1. The reaction mixture was made alkaline in order to neutralise the HCl evolved during the condensation reaction by adding triethylamine. 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 48hrs. Dioxan and triethylamine were distilled off and the mixture was washed with methanol a number of times in order to remove the unreacted PD. The resulting mixture was reprecipitated using a toluene-methanol (1:1 v/v) mixture and polyisobutylene-bound paraphenylene diamine (PIB-PD) was dried in vacuum oven.

**3.1.2 Analysis of PIB-Cl and PIB-PD**

Analysis of chlorinated polyisobutylene and polyisobutylene-bound paraphenylene diamine was carried out using infrared spectroscopy (IR), proton magnetic resonance spectroscopy ('HNMR), Vapour phase osmometry (VPO) and Thermogravimetric analysis (TGA). The chlorine content and iodine value were also determined.

The 'HNMR spectra of the samples were recorded from a solution in CCl₄ using a JEOL-JNM spectrometer. IR spectra of the samples were taken on a Perkin-Elmer Model 377 IR spectrometer. Molecular weight was determined by using Knauer Vapour Phase Osmometer.

**3.1.3 Results and Discussion**

The Figs. 3.1, 3.2 and 3.3 show the IR spectra of PIB, PIB-Cl and PIB-PD. The IR Spectrum of PIB shows peaks at 2950cm⁻¹ corresponding to aliphatic −CH
strecthing, at 1480 cm\(^{-1}\) due to \(-\text{CH}\) bending, 1650 cm\(^{-1}\) corresponds to C=C. The IR spectrum of PIB-Cl (chlorinated PIB) shows a new peak at 780 cm\(^{-1}\) due to the presence of C-Cl stretching. The IR spectra of PIB-PD shows additional peaks at 3390 cm\(^{-1}\) due to NH stretching, 1620 cm\(^{-1}\) due to NH bending and 1500 cm\(^{-1}\) due to aromatic ring present in PD. This confirms the chemical binding of PD to PIB.\(^{15}\)
Fig.3.3 IR spectrum of PIB-PD

Figs. 3.4 and 3.5 show the $^1$H NMR spectra of PIB and PIB-PD. There are peaks $\delta=1.22$ (-CH$_2$) and $\delta=1.6$ ppm (-CH$_3$). Fig. 5 shows additional peaks at $\delta=7.2$ ppm and $\delta=3.5$ ppm corresponding to aromatic ring and Ar-NH-R present in PIB-PD. This again confirms the chemical binding of PD to PIB.$^{14}$

Fig.3.4 $^1$H NMR spectra of PIB
The molecular weight of the samples were determined by VPO. The molecular weights of PIB, PIB-Cl, PIB-PD and PD are 934, 1005, 2330 and 106 respectively. This shows that polyisobutylene is bound to para phenylene diamine at both the ends.

The iodine value of PIB and PIB-Cl indicates that addition reaction has taken place at the double bonds. The chlorine content of the PIB-Cl is found to be 7.6%. This also confirms the addition of chlorine at the double bond.

Fig. 3.6 shows the thermograms of PD, PIB, and PIB-PD. The low molecular weight PD volatilises easily while polymer-bound PD is less volatile. This again confirms the chemical bonding of PD to PIB.
From the above data the chlorination and binding reaction between PIB and PD may be as shown below. The polyisobutylene is chlorinated with pure dry chlorine and the chlorinated product is condensed with paraphenylenediamine.

![Diagram of chlorination and binding reaction]

Scheme 3.1
PART II

3.2 Preparation and Characterisation of Chlorinated Paraffin Wax-Bound Paraphenylene Diamine

3.2.1 Experimental

a) Materials

Chlorinated paraffin wax (CPW), dioxan, triethylamine, para-phenylene diamine (PD) were used.

b) Preparation of chlorinated paraffin wax bound PD

The chlorinated paraffin wax (CPW) and PD, were dissolved in dioxan, were mixed in the ratio 1:1. The reaction mixture was made basic by adding triethylamine, to neutralise 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. Unreacted 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.

3.2.2 Characterisation of CPW-PD

Characterisation of chlorinated paraffin wax-bound para phenylene diamine were carried out using infrared spectroscopy (IR), proton magnetic resonance spectroscopy (1H NMR), Vapour phase osmometry (VPO) and Thermogravimetric analysis (TGA).

3.2.3 Results and discussion

Figs. 3.7 & 3.8 show the IR spectra of CPW and CPW-PD. The IR spectrum of CPW-PD shows additional peaks at 3400 cm⁻¹ due to NH-stretching primary, at 3387 cm⁻¹ due to NH-stretching secondary, at 1614.6 cm⁻¹ due NH- bending, and 1500 cm⁻¹ corresponding to aromatic ring in paraphenylene diamine.²⁵
Figs 3.9 & 3.10 show the $^1$H NMR spectra of CPW and CPW-PD. $^1$H NMR spectrum of CPW-PD shows additional peaks at 7.27 $\delta$ and 5.978 $\delta$ correspond to aromatic ring present in paraphenylenediamine. Note that the peak due to NH is masked by other peaks of the sample.
Fig. 3.11 shows the thermograms of PO, CPW and CPW-PD. The low molecular weight PD volatilises easily while rubber bound PD is less volatile. This again confirms the chemical binding of PD onto CPW.
The molecular weight 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 chlorinated paraffin wax is bound to paraphenylene diamine. From the above data the condensation reaction of chlorinated paraffin wax and paraphenylene diamine may be represented as scheme 3.2.

\[
\begin{align*}
\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2\frac{\text{Cl}}{\text{Cl}}_n & \quad + \quad \text{H}_2\text{N}-\text{CH}_2\text{-CH}_2\text{-NH}_2 \\
\downarrow & \\
\text{CH}_2\text{-CH}-\text{CH}_2\text{-CH}_2\frac{\text{Cl}}{\text{NH}}_n & \quad + \quad \text{H}_2\text{N}-\text{CH}_2\text{-CH}_2\text{-NH}_2
\end{align*}
\]

Scheme 3.2
PART-III
3.3 Preparation and Characterisation of Polyethylene Glycol-Bound Paraphenylene Diamine

3.3.1 Experimental

a) Materials

Polyethylene glycol (PEG) with molecular weight 600, methanol, thionyl chloride, ether, dioxan, triethylamine, para-phenylene diamine were used.

b) Chlorination of Polyethylene Glycol

0.1 mol of polyethylene glycol was weighed and dissolved in dioxan and to it 0.1 mol SOCl₂ was added drop wise with constant stirring by keeping the reaction mixture in an ice bath. It was then heated under reflux for 3 hrs. The chlorinated polyethylene glycol (PEG-Cl) was separated.

c) Preparation of Polyethylene glycol bound paraphenylene diamine

The chlorinated polyethylene glycol was dissolved in dioxan and mixed with paraphenylene diamine (PD) dissolved in dioxan in the ratio 2:1. The reaction mixture was made alkaline in order to neutralise the HCl evolved during condensation reaction by adding triethylamine. 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 48h. Dioxan and triethylamine were distilled off and the mixture was washed with heptane number of times in order to remove the unreacted PD. The chlorinated polyethylene glycol (PEG-Cl) was separated and dried in a vacuum oven.

3.3.2 Analysis of PEG-Cl and PEG-PD

Analysis of polyethylene glycol-bound para phenylene diamine (PEG-Cl) was carried out using thin layer chromatography (TLC), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and vapour phase osmometry (VPO).
3.3.3 Results and discussion

The Figs. 3.12 shows the Thin layer chromatography (TLC) of PEG, PEG-PD and PD. The $R_i$ value of PEG-PD was found to be slightly lower than that of PEG. This indicates that paraphenylenediamine gets chemically attached to PEG to form PEG-PD.

Fig 3.13 shows the IR spectra of PEG-PD. The IR Spectra of PEG-PD shows peaks at 3400 cm$^{-1}$ and 2950 cm$^{-1}$ corresponding to -NH stretching, at 1480 cm$^{-1}$ due to -NH bending, 1650 cm$^{-1}$ corresponds to aromatic ring. This confirms the chemical binding of PD on to PEG.$^{15}$

Fig. 3.14 shows the thermograms of PD, PEG and PEG-PD. The low molecular weight PD volatilises easily while polyethylene glycol bound PD is less volatile. This again confirms the chemical bonding of PD to PEG.

3.12 TLC of PEG, PEG-PD and PD
Chapter 3

3.13 TGA of C-PD, B- PEG and A- PEG-PD

3.14 IR Spectrum of PEG-PD
The molecular weight of the samples were determined by VPO. The molecular weights of PEG, PEG-PD and PD were 590, 1250 and 110 respectively. This again confirms the binding of polyethylene glycol to paraphenylene diamine. From the above data the binding reaction of chlorinated polyethylene glycol and paraphenylene diamine may be represented as shown below. The PEG is chlorinated using thionyl chloride. The chlorinated polyethylene glycol is bound to paraphenylene diamine by the condensation reaction.

\[
\text{H(OCH}_2\text{-CH}_2\text{)}_{n}\text{OH} + \text{SOCl}_2 \rightarrow \text{H(OCH}_2\text{-CH}_2\text{)}_n\text{Cl}
\]

\[
\text{H(OCH}_2\text{-CH}_2\text{)}_n\text{Cl} + \text{H}_2\text{N} \begin{array}{c}
\text{NH}_2
\end{array}
\]

\[
\text{H(OCH}_2\text{-CH}_2\text{)}_n\text{NH} \begin{array}{c}
\text{NH} - (\text{CH}_2\text{-CH}_2\text{O})_n\text{H}
\end{array}
\]

Scheme 3.3

PART IV

3.4 Preparation and Characterisation of Polyisobutylene-Bound Diphenylamine Antioxidant.

3.4.1 Experimental

a) Materials

Polyisobutylene, diphenylamine, methanol, carbon tetrachloride, ether, toluene, dioxan, triethylamine, anhydrous zinc chloride and sodium carbonate were used.

b) Preparation of Polyisobutylene-bound diphenylamine

The chlorinated polyisobutylene(PIB-Cl) was dissolved in dioxan and mixed with diphenylamine (DA) dissolved in dioxan in the ratio 1:2 and taken in a two
necked flask fitted with a thermometer and a soxhlet extraction unit packed with fused CaCl₂. 0.5 mol of anhydrous zinc chloride was introduced into the flask. The reaction mixture was heated at 100°C on a hot plate with magnetic stirring for 24hrs. There was no appreciable degradation of the polymer during this prolonged exposure to high temperature as seen by molecular weight measurements, probably due to anaerobic atmosphere inside the set-up. When the reaction was complete, the reaction mixture was neutralised with sodium carbonate and washed several times with water to remove the catalyst. The contents of the vessel were then poured into excess methanol with stirring to precipitate the liquid polymer bound antioxidant. The unreacted DA was removed by repeated reprecipitation using a toluene-methanol (1:1 v/v) mixture and the product dried in a vacuum oven. The rubber bound antioxidant was obtained in the form of a brown viscous liquid.

3.4.2 Characterisation of PIB-DA

Characterisation polyisobutylene-bound diphenylamine were carried out using infrared spectroscopy (IR), thermogravimetric analysis (TGA) and vapour phase osmometry (VPO).

3.4.3 Results and discussion

Fig 3.15 shows the IR spectra of PIB-DA. The IR Spectra of PIB-DA shows peaks at 3497 cm⁻¹ corresponding to -NH stretching, at 1480 cm⁻¹ due to -NH bending, 1600 cm⁻¹ corresponds to aromatic ring. This confirms the chemical binding of DA to PIB-DA.¹⁵

Fig. 3.16 shows the thermograms DA, PIB and PIB-DA. The low molecular weight DA volatilises easily while PIB-DA is less volatile. This again confirms the chemical bonding of DA to PIB.
Preparation And Characterisation Of Amine

3.15 IR Spectrum of PIB-DA

3.16 TGA of A-DA, B- PIB, C- PIB-DA
Chapter 3

The molecular weights of the samples were determined by VPO method. The molecular weights of DA, PIB-Cl and PIB-DA are 169, 1005 and 1200 respectively. This confirms the binding of PIB-Cl to diphenylamine.

From the above data scheme of reaction can be summarised as follows:

\[
\begin{align*}
\text{scheme 3.4} & \quad \text{Scheme 3.4}
\end{align*}
\]

Conclusions
1. PIB can be chlorinated by passing dry chlorine through a solution of PIB in CCl₄.
2. p-phenylene diamine (PD) can be chemically attached to chlorinated PIB by condensation reaction.
3. PD can also be attached to chlorinated paraffin wax in a similar manner by condensation reaction.
4. Polyethylene glycol can be chlorinated using thionyl chloride and the chlorinated product was attached to PD.
5. Chlorinated polyisobutylene was bound to diphenylamine by modified Friedel Crafts reaction.
References


