Chapter II

EXPERIMENTAL

2.1 Materials.

1. Natural crumb rubber (ISNR - 5) with a weight average molecular weight 8,20,000, intrinsic viscosity in benzene at 30°C = 4.45 dl/g and Wallace plasticity Po = 39 was supplied by Rubber Research Institute of India, Kottayam, Kerala.

2. Toluene (Reagent grade) obtained from E. Merck (India) was used as the solvent without any further purification.

3. Methanol supplied by BDH India was used as such.

4. Hydrogen peroxide (30w%) supplied by E. Merck, India was used without further purification.

5. Toluene diisocyanate (TDI) 80/20 mixture of 2,4 and 2,6-isomers supplied by Fluka, Switzerland was used as received.

6. Ethylene glycol (EG) obtained from E. Merck India was dried with anhydrous calcium oxide and then distilled under reduced pressure.

7. Propylene glycol (PG) was also obtained from E. Merck India and dried using anhydrous calcium oxide and distilled under reduced pressure.

8. 1,3 -butane diol (1,3-BDO) was supplied by Merck Germany. It was dried using anhydrous calcium oxide and distilled under reduced pressure.

9. 1,4 -butane diol was also supplied by Merck Germany. It was dried using anhydrous calcium chloride and distilled under reduced pressure.

10. Bisphenol A, supplied by Merck, Germany was fused and dried in vacuum before use.
11. Dibutyl tin dilaurate (DBTDL) was obtained from Fluka, Switzerland. It was used as the catalyst without further purification.

12. Chloroform supplied by BDH, India was used as solvent after distillation.

2.2 Experimental.

2.2.1 Preparation of hydroxyl terminated liquid natural rubber (HTNR).

Hydroxyl terminated liquid natural rubber of different molecular weights were obtained by the photochemical depolymerisation of natural rubber by adjusting the exposure time\(^1\).

The natural crumb rubber was masticated for 15 minutes at room temperature. It is then cut into small pieces. About 100 g of it was introduced into a flat bottomed flask of 15L capacity. About 500 ml of toluene was added and allowed to swell. The swollen material was dissolved by adding 500 ml more of toluene. To this solution about 100 ml of 30\% (w/v) \(\text{H}_2\text{O}_2\) was added and mixed thoroughly. The mixture was then homogenised partially by adding about 150 ml methanol. The viscosity of the reaction mixture is slightly reduced by the addition of methanol since it is a nonsolvent for rubber\(^2\). The reaction mixture is then exposed to sunlight, and stirred occasionally to prevent the separation of layers. To obtain HTNR of different molecular weights the exposure time was varied. After the required exposure time, the reaction mixture was allowed to separate into two layers. The upper toluene layer was separated. Distilled off the solvent to get liquid HTNR. It was then stored in amber coloured bottles.

2.2.2 Determination of molecular weight of HTNR.

The molecular weight of HTNR was determined by measuring solution viscosity using Ubbelohde viscometer. The viscosity of a high polymer solution is related to the molecular weight of the polymer by the Mark–Houwink equation. \([\eta] = K M^n\) where \([\eta]\) is the intrinsic
viscosity, $\bar{M}_v$ is the viscosity average molecular weight, "K" and "a" are Mark–Houwink constants for a particular polymer solvent system at a given temperature. For isoprene-toluene system at $25^\circ C$ $K=5.02 \times 10^{-3}$ and $a = 0.667$.

Ubbelohde viscometer is a suspended level viscometer. The flow time measurements in it do not depend on the volume of liquid in the viscometer. Hence measurement of a series of solutions with different concentrations can be made by successive dilution within the viscometer.

The viscometer was suspended in a thermostat regulated within $\pm 0.01^\circ C$. A definite volume of solvent was taken in it and its flow time was noted. Rubber solution was added in definite quantities to prepare solutions of known concentrations and each time the flow time was measured. The time of flow of pure solvent $t_0$ from mark A to B for a given capillary is directly proportional to the driving force.

$$ t_0 = \frac{\eta_0}{h\rho_0 g} $$

If $t$ is the time of flow of the solution at a particular concentration

$$ t = \frac{\eta}{h\rho g} $$

then

$$ \frac{t}{t_0} = \frac{\eta\rho_0}{\rho_0 \eta_0} $$

i.e.,

$$ \frac{\eta}{\eta_0} = \frac{t\rho}{t_0 \rho_0} $$

But for very dilute solutions $\rho \approx \rho_0$

therefore

$$ \frac{\rho}{\rho_0} \approx 1 $$
\[ \frac{\eta}{\eta_0} = \frac{t}{t_0} = \eta_{\text{rel}} = \text{relative viscosity} \]

Specific viscosity \( \eta_0 = \eta_{\text{rel}} - 1 = \frac{\eta}{\eta_0} - 1 = \frac{t}{t_0} - 1 = \frac{t - t_0}{t_0} \)

\[ \frac{\eta_{sp}}{c} = \frac{t - t_0}{t_0 c} \]

Thus \( \frac{\eta_{sp}}{c} \) is calculated for different concentrations. A graph is plotted with \( \frac{\eta_{sp}}{c} \) versus \( C \).

The intrinsic viscosity \( [\eta] \) is obtained by extrapolation of the curve to zero concentration.

This value of \( [\eta] \) is substituted in the Mark-Houwink equation and the viscosity average molecular weight was calculated.

### 2.2.3 Estimation of the hydroxyl groups\(^8\).

The hydroxyl group in HTNR was estimated by acetylation method. The hydroxyl groups in the sample were acetylated using acetic anhydride in pyridine.

\[
R - (\text{OH})_n + n(CH_3CO)O \twoheadrightarrow R(OCOCH_3)_n + nCH_3COOH
\]

The excess acetic anhydride was converted into acetic acid and estimated by titration using a standard alkali.

Acetylation mixture was prepared by mixing one volume of acetic anhydride with three volumes of pyridine. About 3 g of HTNR was weighed out into a round bottomed flask. The flask was fitted with a water condenser and refluxed for 30 minutes after adding 20 ml of
acetylation mixture. A blank was also carried out. The mixture was cooled to room temperature and 50 ml of distilled water was added through the condenser. The free acid was determined by titration with standard alcoholic KOH using phenolphthalein.

The hydroxyl value is defined as the number of mg of KOH (equivalent to the amount of acetic acid) that reacts by acetylation with 1 g of the hydroxyl containing material.

\[
\text{Hydroxyl value} = \frac{56.1(B-S)N}{W}
\]

\(B\rightarrow\) volume of KOH required to titrate the blank.

\(S\rightarrow\) volume of KOH required to titrate the sample.

\(N\rightarrow\) normality of alcoholic KOH.

\(W\rightarrow\) weight of the sample in gm.

2.2.4 Determination of epoxy value.

About 2 g of HTNR was weighed out into a conical flask. About 220 ml of 0.2N HCl–dioxane solution was added. The sample was dissolved completely in the solution by heating to 40°C. To this solution 25ml neutralised cresol red-ethanol solution was added. The excess HCl was determined by back titration with 0.5N NaOH. The end point was the first appearance of a violet colour. A blank was also performed.

Notes:-Preparation of 0.2N HCl–Dioxane solution.

1. About 1.6 ml HCl (Sp.gr.1.9) was pipetted out in to 100 ml of dioxane in an amber coloured bottle and shaken well. The solution was used immediately after preparation.

2. Preparation of neutralised cresol red-ethanol solution.
About 1 g of cresol red sodium salt was dissolved in 100 ml of 50% ethanol. 1 ml of this solution was added to 100 ml 95% ethanol and neutralised with 0.1N methanolic NaOH.

2.2.5 Determination of iodine value

The iodine value is a measure of the degree of unsaturation of the material. It is determined by Wij's method.

About 1 g of HTNR was dissolved in 20 ml of chloroform in an Erlenmeyer flask. About 25 ml of Wij"s solution prepared by mixing iodine trichloride, iodine, and glacial acetic acid was added. Stoppered the flask and kept aside in the dark for 30 minutes. Then added 10 ml of 20% aqueous potassium iodide solution and 100 ml of distilled water. The excess iodine was back titrated with 0.1N sodium thiosulphate solution using starch as indicator. A blank was also conducted.

\[ \text{Iodine value} = \frac{12.69 (B - S)}{N/W} \]

Where

- \( S \rightarrow \) volume in ml of sodium thiosulphate
- \( B \rightarrow \) volume in ml of sodium thiosulphate required to titrate the blank
- \( N \rightarrow \) normality of sodium thiosulphate
- \( W \rightarrow \) Weight of sample in g

Note: Preparation of Wij"s solution.

Iodine 9 g and iodine trichloride (8 g) were dissolved in 1.1 glacial acetic acid. The resultant solution was filtered in to an amber coloured bottle and stored in the dark. The reagent must be used within 30 days.
After characterising HTNR by these methods of analysis it was used for the synthesis of block copolymers.

2.2.6 Synthesis of block copolyurethanes.

Segmented block copolyurethanes are prepared from HTNR and different diols along with toluene disocyanate. Dibutyl tin dilaurate was used as the catalyst. The two-shot processes was used for the synthesis.

Two-shot process.

HTNR was reprecipitated thrice from toluene using methanol and dried at 80-90°C in a vacuum oven. About 5 g of HTNR was weighed out in a flat bottomed flask equipped with a magnetic stirrer, reflex condensor and a dropping funnel. This was dissolved in chloroform to get a 25% solution. Required amount of catalyst was then added and the solution was brought to reflux with vigorous stirring. The stoichiometric amount of TDI dissolved in chloroform was then added in drops over a period of 30 minutes. Refluxing was continued for 1½ hour to endcap HTNR. Then the required amount of chain extender diol was added. Stirring was continued till the reaction mixture becomes highly viscous. The viscous polymer was then cast in trays treated with silicone release agent. After about 24 hrs. the sheets are removed, dried in a vacuum oven at 60°C and cured at 70°C for 24 hrs. This was followed by two weeks aging at room temperature in moisture free atmosphere.

2.2.7 Infra red spectral analysis.

The block copolymers were characterised by recording the IR spectrum on a Shimadzu IR Spectrometer using chloroform as the solvent.
2.2.8 **Differential scanning calorimetric analysis (DSC).**

The thermal behaviour of the polymers was studied by DSC analysis on a DSC Mettler Thermal Analyser equipped with a liquid nitrogen subambient cooling accessory at a heating rate of 10° C/min. The sample mass was approximately 10 mg. All DSC scans were first scans.

2.2.9 **Thermogravimetric analysis (TGA).**

The thermal stability of the samples was studied using a Delta Series TGA-7 Analyser at a scanning rate of 10° C/min in nitrogen atmosphere. The samples were scanned from 50° to 750° C.

2.2.10 **Scanning electron microscopic analysis (SEM).**

The fracture surfaces of samples from tensile test were sputter coated with gold and examined on a JEOL-JSM-T 330–A–Scanning Electron Microscope.

2.2.11 **Stress–strain behaviour (Tensile tests).**

Dumbbell shaped test specimen from the cast sheets were tested on a Zwick 1474 (UTM) Universal Testing Machine as per ASTM D-412-80 test method at room temperature at a constant cross head speed of 50 mm/min.

2.2.12 **Tear strength.**

Tear strength of the samples was tested on a Zwick 1474 (UTM) as per ASTM D. 624 – 81 test method using nicked 90° angle test specimen cut from the cast sheets.

2.2.13 **Hardness.**

The shore-A hardness of samples was measured at room temperature using 60 13805 type A Durometer as per ASTM D–2240–75 test method. The values were taken as the arithmetic
mean of five measurements at different positions on the test specimen. The readings were taken within 15 seconds after the presser foot was in firm contact with the specimen.

2.2.14 Polymer designation.

The polymer samples were designated as follows. For e.g., NR$_1$/PG(70/30) is a sample which contains 70% by weight of HTNR of molecular weight 8500 and 30% by weight of polyurethane prepared from the chain extender propylene glycol and TDI.

References: