

## STATIC LIGHT SCATTERING MEASUREMENT OF NATURAL RUBBER IN TOLUENE

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Natural rubber used in local tyre industry was characterized by light scattering technique in toluene solvent and at room temperature (25°). The molecular weight, size and shape of the rubber was determined by Zimm plot, turbidity and dissymmetry methods. The refractive index increment showed decrease with increase in concentration thus showing more solvation in dilute solutions. The molecular weight obtained by two methods is comparable. It was also observed that natural rubber has random coil conformation in toluene and further toluene is acting as good solvent for natural rubber.

**Key words:** Static, Light scattering, Natural rubber, Toluene.

### Introduction

Natural rubber can be obtained from nearly 500 different species of plants and have milky latex to solid form. It has extensive application in every day life in genreal and as tyre elastomer in particular. The production of synthetic rubber has put great challange on natural rubber producers as the market is shifting more towards the synthetic rubber. So it is very important to improve the uniformity and quality of the natural rubber product to match the synthetic one. In the present investigation an effort has been made to know the quality of the natural rubber used in local tyre industry because without knowing these basic informations further use is not wise. The quality of the product can be checked by knowing its shape, size and molecular weight. There are several methods [1,4] to determine the molecular weight, size and shape of rubber but light scattering is the absolute method for characterization of rubbers. Many scientists [2-9] characterized rubber by using this technique. We have attempted to characterize the various rubbers used in local markets for the manufacture of tyres etc. and this paper is on natureal rubber characterization.

### Experimental

Natural rubber was taken from Swat Tyre Ltd, Peshawar. The material was yellow in colour, elastic and semisolid form. Solutions of various concentrations (0.2 g/dL–1 g/dL) were prepared in toluene (Merck).

**Method.** The specific refractive index increment (dn/dc) was measured by using pre-calibrated differential refractometer of Brice-Phoenix Co., USA.

Light scattering studies were undertaken on universal light scattering photometer of Brice-Phoneix Co. USA. The molecular weight of the rubber was measured by using Zimm plot and turbidity methods. For Zimm plot method light scattering intensities of all the solutions were measured in the angular range 30-135° with an increment of 15°. The experimental data for the incident radiation of 436 and 546 nm wavelength were used to calculate the Rayleigh ratio ( $R_0$ ) using an equation given by Gruber *et al.* [10] as,

$$R_0 = \frac{I_\theta R_{90} (\text{Benzene} \sin\theta/1 + \cos^2\theta)}{I_{90} (\text{Benzene})} \quad (1)$$

where

$I_\theta$  = Intensity of light scattered by solution at angle  $\theta$ .  
 $I_{90} (\text{Benzene})$  = Intensity of light scattered by benzene at 90°.  
 $R_{90} (\text{Benzene})$  = Rayleigh ratios for benzene equal to  $48.4 \times 10^{-6} \text{ cm}^{-1}$  and  $16.3 \times 10^{-6} \text{ cm}^{-1}$  for 436 and 546 nm of incident light respectively. For Zimm equation:

$$KC/R_0 = 1/MP_0^{-1} + 2 A_2 C \quad (2)$$

where

$$K = \text{constant} = 2\pi^2 n_0^2 (dn/dc)^2 / N \lambda^4 \quad (3)$$

$n_0$  = refractive index of solvent  
 (dn/dc) = specific refractive index increment  
 $\lambda$  = wavelength of incident light  
 $A_2$  = second virial coefficient  
 $C$  = concentration in g/ml  
 $P_0$  = particle scattering factor

$$= \frac{1 + 16\pi^2}{3 \lambda^2} \langle S^2 \rangle^{1/2} \sin^2 \theta / 2 \quad (4)$$

Values of  $KC/R_0$  were plotted against  $\sin^2\theta/2 + KC$ , where  $K$  is an arbitrary constant, as suggested by Zimm. Intercept was obtained by double extrapolation of the  $KC/R_0$  lines of zero angle and zero concentration. The intercept is inversely proportional to the weight average molecular weight. The mean square radius of gyration  $\langle S^2 \rangle^{1/2}$  and second virial coefficient ( $A_2$ ) were obtained by the relation as given below.

$$\langle S^2 \rangle^{1/2} = \frac{3 \lambda^2}{16 \pi} \frac{(\text{Slope of the line } C = 0)}{\text{Intercept}} \quad (5)$$

$$A_2 = \frac{2 \lambda^2 n}{\lambda} \frac{(\text{Slope of the line } \theta = 0)}{2} \quad (6)$$

For turbidity method, the scattered light intensity measurements were made at 90° and 0° with respect to incident light

and turbidity ( $\tau$ ) was calculated, then the following equation was employed.

$$HC/\tau = \bar{M}_w + 2 BC \dots\dots\dots(7)$$

where

$$H = \text{constant} = 32 \pi^3 n^2 (dn/dc)^2 / 3 N \lambda^4 \dots\dots\dots(8)$$

- $\tau$  = turbidity
- $M_w$  = molecular weight
- $B$  = second virial coefficient
- $C$  = concentration

To obtain dissymetry ratio,  $Z$ , through the studies made on the same instrument, the following equation was used.

$$Z = \frac{(FD_{45}/D_w)_{\text{Solution}} - (FD_{45}/D_w)_{\text{Solvent}}}{(FD_{135}/D_w)_{\text{Solution}} - (FD_{135}/D_w)_{\text{Solvent}}} \dots\dots\dots(9)$$

where

- $Z$  = dissymetry ratio
- $D_{45}$  = scattered intensity at  $45^\circ$
- $D_{135}$  = scattered intensity at  $135^\circ$
- $D_w$  = scattered intensity at  $0^\circ$
- $F$  = neutral filter value

Intrinsic dissymetry ( $Z$ ) was obtained from the intercept of a plot of  $Z$  versus concentration.  $Z$  is related with particle scattering factor [11]. From the values of the scattering factor thus obtained, the shape of natural rubber molecule was estimated with the help of the theoretical prediction for various conformation [12,13].

**Results and Discussion**

The refractive index increment ( $\Delta n/c$ ) values for natural rubber are given in Table 1, which shows that the values of  $\Delta n/c$  decreases with increase in concentration. It can be concluded over here that the dependence of  $\Delta n/c$  upon concentra-

TABLE 1.  $\Delta n$  AND  $\Delta n/C$  VALUES FOR DIFFERENT CONCENTRATIONS OF NATURAL RUBBER IN TOLUENE MEASURED AT TWO WAVELENGTHS OF LIGHT AND ROOM TEMPERATURE ( $25^\circ\text{C}$ ).

Wavelength conc. (g/ml)x10 <sup>3</sup>	436 nm		546 nm	
	$\Delta n \times 10^5$	$\Delta n/C \times 10^3$ (ml/g)	$\Delta n \times 10^5$	$\Delta n/C \times 10^3$ (ml/g)
2.0	2.877	14.385	2.511	12.555
4.0	5.200	13.000	4.185	10.463
6.0	6.968	11.613	5.301	8.835
8.0	8.182	10.227	5.540	6.975
10.0	8.840	8.840	5.162	5.162
(dn/dc) <sub>c=0</sub>	15.772	14.280		

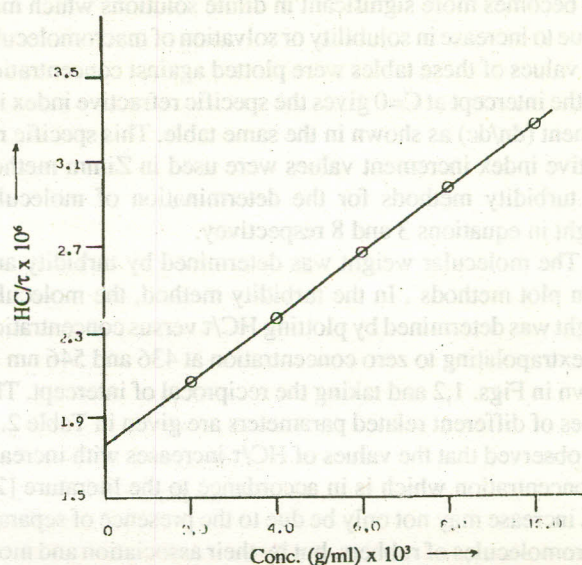


Fig. 1. Plot of  $HC/\tau$  vs concentration for natural rubber at 436nm.

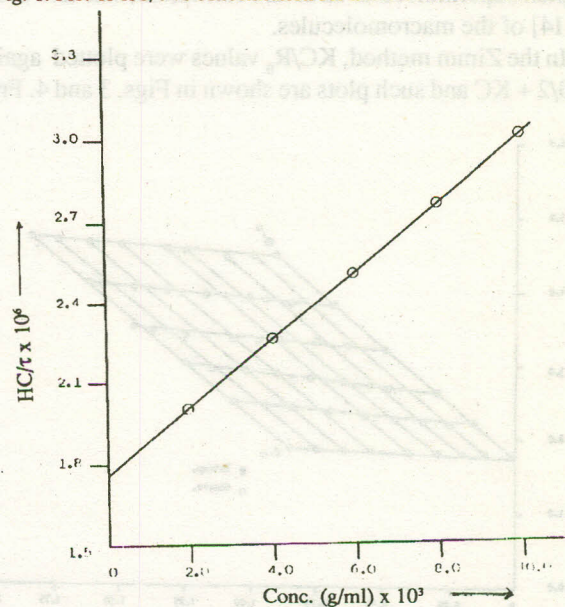


Fig. 2. Plot of  $HC/\tau$  vs concentration for natural rubber at 546nm.

TABLE 2.  $\tau$  AND  $HC/\tau$  VALUES FOR DIFFERENT CONCENTRATIONS OF NATURAL RUBBER IN TOLUENE MEASURED AT LIGHT OF 436 AND 546 nm WAVELENGTH AND ROOM TEMPERATURE ( $25^\circ\text{C}$ ).

Conc. (g/ml) x10 <sup>3</sup>	436 nm		546 nm	
	$\tau \times 10^4$ (cm <sup>-1</sup> )	$HC/\tau \times 10^6$ (moles/g)	$\tau \times 10^5$ (cm <sup>-1</sup> )	$HC/\tau \times 10^6$ (moles/g)
2.0	0.867	2.002	2.735	2.065
4.0	1.540	2.254	4.778	2.364
6.0	2.077	2.507	6.362	2.663
8.0	2.512	2.760	7.626	2.963
10.0	2.881	3.013	8.658	3.262

tion becomes more significant in dilute solutions which may be due to increase in solubility or solvation of macromolecule. The values of these tables were plotted against concentration and the intercept at  $C=0$  gives the specific refractive index increment ( $dn/dc$ ) as shown in the same table. This specific refractive index increment values were used in Zimm method and turbidity methods for the determination of molecular weight in equations 3 and 8 respectively.

The molecular weight was determined by turbidity and Zimm plot methods. In the turbidity method, the molecular weight was determined by plotting  $HC/\tau$  versus concentration and extrapolating to zero concentration at 436 and 546 nm as shown in Figs. 1,2 and taking the reciprocal of intercept. The values of different related parameters are given in Table 2. It was observed that the values of  $HC/\tau$  increases with increase in concentration which is in accordance to the literature [2]. This increase may not only be due to the presence of separate macromolecules of rubbers, but by their association and more complex supermolecular structure formation, size and ordering [14] of the macromolecules.

In the Zimm method,  $KC/R_\theta$  values were plotted against  $\text{Sin}^2\theta/2 + KC$  and such plots are shown in Figs. 3 and 4. From

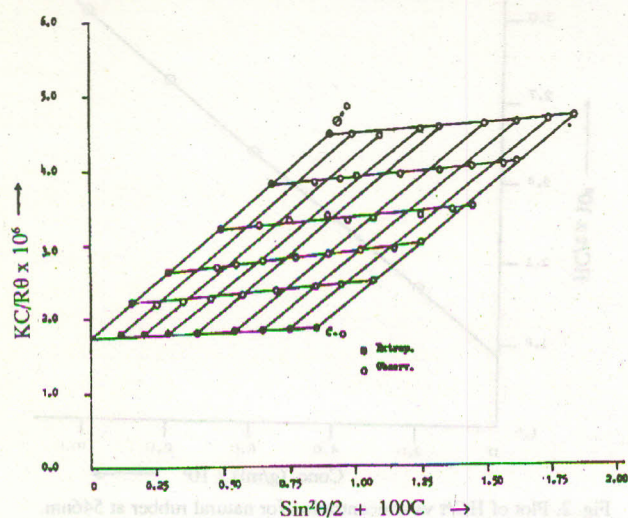


Fig. 3. Plot of  $KC/R_\theta$  vs  $K'C + \text{Sin}^2\theta/2$  for natural rubber at 436nm.

TABLE 3. VALUES OF SECOND VIRIAL COEFFICIENT AND MOLECULAR WEIGHT FOR NATURAL RUBBER BY ZIMM PLOT AND TURBIDITY METHOD AT 436 AND 546 nm WAVELENGTH.

	Wavelength (nm)	$\bar{M}_w \times 10^{-5}$ (g/mol)	$A_2 \times 10^5$ (mol.ml.g <sup>2</sup> )
Turbidity	436	5.718	6.32
Zimm plot			
Turbidity	546	5.664	7.49
Zimm plot			

the reciprocal of the intercept of double extrapolation, the molecular weight was obtained.

The molecular weight obtained by both the methods is given in Table 3. It can be seen that the values obtained by two different methods are comparable to each other. Further it is also clear from the tables that the results are different for different wavelengths, moreover, higher for shorter wavelength. This kind of trend is shown in the literature for styreneethylene oxide block copolymer in aqueous solutions [19]. Further it may be due to the polydispersity [15,16] of the system.

The second virial coefficient is also shown in Table 3. The second virial coefficient is the parameter which determines the thermodynamic interactions between the polymer segments and the solvent molecules. The literature [17,18] shows that for  $\theta$  solvent the second virial coefficient is equal to zero while it is less than zero and more than zero for poor and good solvents respectively. These values are greater than zero over here, and hence we can say that toluene is good solvent for natural rubber.

The values of radius of gyration given in Table 4 are found much coincident with the coil like molecules when the results

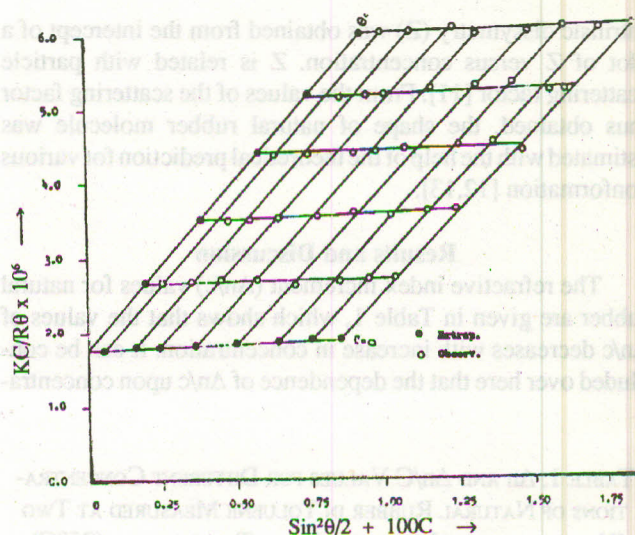


Fig. 4. Plot of  $KC/R_\theta$  vs  $K'C + \text{Sin}^2\theta/2$  for natural rubber at 546nm.

TABLE 4. VALUES OF RADIUS OF GYRATION FOR NATURAL RUBBER BY DISSYMETRY AND ZIMM PLOT METHODS AT 436 AND 546 nm WAVELENGTH.

Wavelength (nm)	Dissymetry (A°)	Zimm plot (A°)
436	317.21	324.00
546	327.42	330.00

are compared with radius of gyration calculated with the assumption that the molecules are coiled shape [3,6]. The relatively small difference between the dissymetry and Zimm plot values are presumably due to incorporation of the solvent within the scattering particle.

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TABLE I. Soil Characteristics

Soil type	Organic matter %	pH	Clay %	Silt %	Sand %	Moisture %
Clay	1.4	7.3	46.8	30.4	22.8	2.0
Sandy loam	1.4	7.3	46.8	30.4	22.8	2.0
loessial soil	1.4	7.3	46.8	30.4	22.8	2.0
Noncalcareous dark grey loessial soil	1.4	7.3	46.8	30.4	22.8	2.0
Red brown loessial soil	1.4	7.3	46.8	30.4	22.8	2.0

Soil treatment. Five or ten grams of each soil sample was taken in a 200 ml beaker and each sample 200-500 ml (for 2g soil) or 200-1000 ml (for 10 gm soil) of solutions of all the seven pesticides were added by using micro-litre pipettes and mixed well with a glassrod. Distilled water 1 or 2 ml was added to each sample to make the soils remaining field conditions and the stirring was continued until the mixture were uniform. Then 2-3 g of anhydrous sodium sulphate was added to each beaker, again mixed well, and allowed to stand at room temperature (32°).  
 Extraction. The samples were extracted separately with the following solvents:  
 (i) Ethyl chloroform: dichloromethane (1:1:1).  
 (ii) Light petroleum ether: benzene: dichloromethane: propanol (1:1:1:1)

Materials and Methods  
 Pesticides. Seven commonly used organophosphorus pesticides were used in the study. The general and the chemical names of the compounds are given as follows:  
 (1) Dithionon (2,2-dithionon dimethyl phosphorothioate),  
 (2) Prothion (methyl 3-dimethoxyphosphorothioate) but-2-enyl;  
 (3) Dimethoate (dimethyl 8-methylthioamoyl methyl phosphorothioate);  
 (4) Dazoxon (0-0-diethyl-0-2-phosphorothioate);  
 (5) Isoxypryl-6-methylpyrimidin-4-ylphosphorothioate);  
 (6) Malathion (dimethyl 2-1,3-dithioethoxy ethyl dithio-phosphate) and (7) Bromophos (4-bromo-2-dichlorophenyl dimethyl phosphorothioate). The samples (I)-(V) collected