# Specific refractive index increments of Guayule rubber in several solvents

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The specific refractive index increments of Guayule rubber were determined in four solvents (hexane, chloroform, toluene and tetrahydrofuran) using two wavelengths (5461 and 4360 Å). The determinations took place at 25°C and the results were compared with those obtained in natural Hevea rubber and Natsyn. The values of $\upsilon$ obtained were Hevea > Guayule > Natsyn.

## INTRODUCTION

The specific refractive index increment, $\upsilon$, where

$$\upsilon = (\partial n/\partial c)_{\lambda,T} \quad (1)$$

is a fundamental parameter in the characterization of polymer solutions. The general equation for the determination of the weight-average molecular weight ($M_w$) by light scattering includes the optical constant $K^*$ given by the equation:

$$K^* = 2\pi^2\tilde{n}_0^2(\partial n/\partial c)^2_{\lambda T}\lambda^{-4}N^{-1} \quad (2)$$

where $\tilde{n}_0$ is the refractive index of the solvent, $\lambda$ is the wavelength of the light *in vacuo*, $N$ is Avogadro's number and $T$ is the temperature at which the experiment was run.

The experimental value of $\upsilon$ is obtained by measuring the increments of the refractive index ($\Delta\upsilon$) of solutions with various concentrations and extrapolating to infinite dilution according to:

$$(\partial n/\partial c)_{\lambda,T} = \lim_{c\to 0}(\Delta n/c)_{\lambda,T} \quad (3)$$

To obtain accurate values of $\upsilon$ the use of a precise differential refractometer is required which demands tedious time-consuming operations. Several studies were made in the past to simplify the determination of $\upsilon$ for a specific polymer in a single solvent and equations were proposed in order to obtain $\upsilon$ by previous knowledge of the solvent refractive index $\tilde{n}_0$ and the densities. The specific refractive index increment for a polymer–solvent pair depends mainly on the intrinsic refractive index for each individual component and on the density:

$$\upsilon = \tilde{n}_2/d_2 - (1/d_2)\tilde{n}_1 \quad (4)$$

It can be observed that by plotting $\upsilon$ against $\tilde{n}_0$ and extrapolating to $\upsilon = 0$ the refractive index $\tilde{n}_2$ of the polymer can be calculated.

Another mathematical treatment includes the Gladstone–Dale rule and the Lorenz–Lorentz equation. These methods have the inconvenience of giving frequent inaccuracies due to the extrapolation that has to be performed; however, errors are in the third decimal place. Another source of error is in the use of reciprocal densities sacrificing accuracy compared with the experimental determination of $\upsilon$. By plotting against the specific refractive index of the solvent a linear dependence is observed and from the extrapolation to $\upsilon = 0$ the refractive index $\tilde{n}_2$ of the polymer can be determined. In addition, this type of graph will permit the determination *a priori* of the specific refractive index increment for a specific polymer–solvent pair merely from knowledge of the refractive index of the solvent.

The specific refractive index increments, $\upsilon$, for Hevea natural rubber have been reported in several papers[4,5,14,17] with various solvents and temperatures. The values obtained experimentally were commonly used in the study of synthetic polyisoprene until, recently, a report appeared in the literature mentioning $\upsilon$ values for this synthetic polymer. At the same time several works[3,6,7] showed the dependence of $\upsilon$ on the molecular weight with asymptotic behaviour above 50 000.

*Hevea brasiliensis* (NR) is at present the only renewable source for rubber and this is one of the reasons for the interest in its properties. Commercial synthetic polyisoprene represents the elastomer most similar to NR. However, with the continued scarcity of petroleum derivatives and the necessity of supplying the demands of a growing population, several countries are initiating research to find alternatives to Hevea rubber. Guayule (*Parthenium argentatum*) is a shrub which grows wild in the Mexican desert. The main interest in it in the past was its high content (≃10%) of polyisoprenic rubber.

At present interest in the use of this plant is growing and an important project is being accomplished in Mexico. Guayule rubber (GR) presents identical features to Hevea rubber: it has a microstructure composed exclusively of *cis*-1,4 units according to 300 MHz[10] and $^{13}C$ n.m.r.[15] spectroscopy; also, the molecular weight by gel permeation chromotography is similar for both rubbers[11]. Differences are being found in gel content and in degree of long-chain branching; however, these studies are still in progress[12]. The purpose of this experiment was to obtain analytical data on the specific refractive index increments of its solutions and compare the results with those obtained from Hevea and synthetic polyisoprene under the same experimental conditions.

## EXPERIMENTAL

### *Materials*

*Hevea rubber.* Smoked sheet was used in the experiments. Thin pieces of rubber were cut and dissolved in the solvent and shaken continuously for a week. The solution was spun in a centrifuge at 2000 rev/min for 1h, in order to eliminate any gel. From the upper solution an aliquot was taken and the concentration was determined by evaporation. Subsequent concentrations were obtained by a simple dilution process with fresh solvent.

*Guayule rubber.* This was extracted from shrubs recently harvested, milled in a hammer mill and defibred in a blender for 10 min. Rubber 'worms' were obtained by skimming out after being floated in water. Owing to the presence of resinous impurities the worms were exhaustively deresinated in acetone, dissolved and filtered. Determination of concentrations and making up of solutions were prepared as described above.

*Synthetic polyisoprene.* Commercial Natsyn with high *cis*-1,4 content was employed. Molecular weight by gel permeation chromatography was approximately 0.7, similar to that found for the natural materials. Solutions were again prepared by the method already described.

*Solvents.* Hexane, tetrahydrofuran, chloroform and toluene were used in the experiments. All the solvents were distilled with glass chromatographic grade quality from Burdick and Jackson. Specific refractive indexes were:

| | $n^{25}_{5461}$ | $n^{25}_{4360}$ |
|---|---|---|
| Hexane | 1.3737 | 1.3802 |
| Chloroform | 1.4446 | 1.4536 |
| Toluene | 1.4980 | 1.5151 |
| Tetrahydrofuran | 1.4066 | 1.4134 |

### *Differential refractometry*

A Brice–Phoenix differential refractometer was utilized in all the experimental runs. The model was a BP-2000-V, where the difference between the refractive index of a solution and its solvent is measured as a lateral displacement of a slit image in the focal plane of a microscope adapted with a filar micrometer eyepiece. In order to obtain the absolute values it was necessary to perform a series of experiments with solutions of known refractive index.

The instrument constant $\phi$ was determined by using NaCl solutions from which the displacement was measured, and $\phi$ was calculated according to equation (7):

$$\Delta n = \phi \Delta d \tag{7}$$

where $\Delta d$ is the displacement observed[12]. The $\upsilon$ values used in the calibration were taken from previous reports in the literature[13].

Concentrations used were below $0.9 \times 10^3$ g/ml. Eight experimental determinations of $\Delta n$ were performed for each concentration with two different wavelengths (5461 and 4360 Å), and taking the average, by the least-square method, $\upsilon$ was calculated from the extrapolation to concentration ($c$) = 0. Temperature was maintained in a circular constant-temperature bath with a stability of ±0.01°C, at a constant 25°C.

## RESULTS AND DISCUSSION

Experimental values of the specific refractive index increments, $\upsilon$, for the rubber–solvent systems studied in this work are shown in *Table 1;* it should be noted that there are slight differences between the values of $\upsilon$ for the three types of rubber being studied. Relations between $\upsilon$ and the solvent refractive index for the two wavelengths of 5461 and 4360 Å are illustrated in *Figures 1* and *2* respectively. Besides

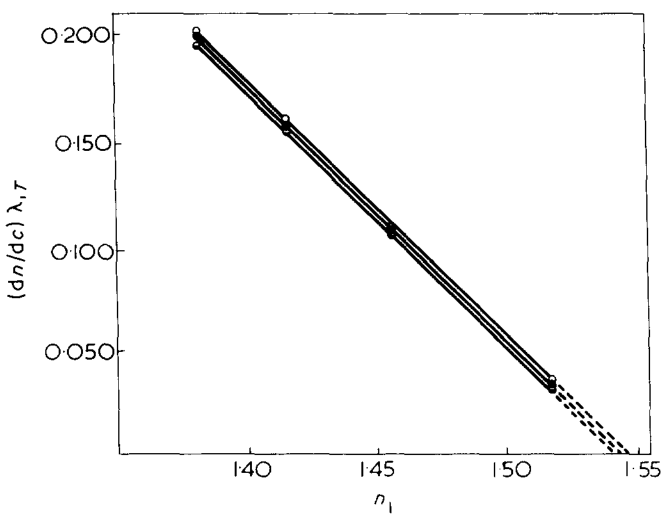


*Figure 1* Specific refractive index increments $\upsilon$ for natural Hevea rubber (○), Guayule rubber (●) and Natsyn (◒), determined at λ = 4360 Å and 250°C

*Table 1* Specific refractive index increments for natural and synthetic polyisoprenes

| Rubber | Hexane λ 4360 Å | Hexane λ 5461 Å | THF λ 4360 Å | THF λ 5461 Å | Chloroform λ 4360 Å | Chloroform λ 5461 Å | Toluene λ 4360 Å | Toluene λ 5461 Å |
|---|---|---|---|---|---|---|---|---|
| Hevea (smoked sheet) | 0.2000*<br>0.1886** | 0.1980*<br>0.1802** | 0.1600* | 0.1563*<br>0.160 ‡ | 0.1065*<br>0.1000** | 0.1039*<br>0.095 ** | 0.0336*<br>0.0335** | 0.0316*<br>0.0308** |
| Guayule | 0.1981* | 0.1932* | 0.1566* | 0.1534* | 0.1081* | 0.1015* | 0.0331* | 0.0304* |
| Synthetic polyisoprene | 0.1920* | 0.1910*<br>0.168 † | 0.1530* | 0.1485* | 0.1938* | 0.1005* | 0.0303* | 0.0284*<br>0.0280† |

* Values obtained from this work; ** values reported in ref 14; † values reported in ref 3 determined at 20°C; ‡ values reported in ref 15

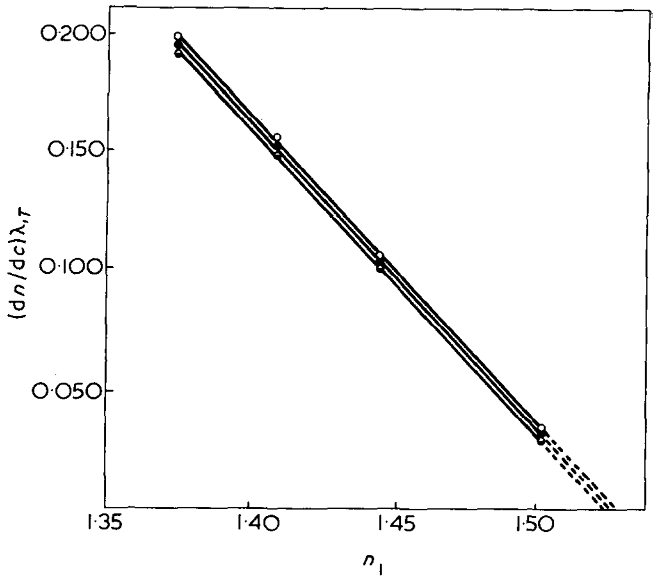


*Figure 2* Specific refractive index increments υ for natural Hevea rubber (○), Guayule rubber (●) and Natsyn (◒), determined at λ = 5461 Å and 25°C

*Table 2* Specific refractive index for natural and synthetic polyisoprenes

| Rubber | $n^{25}_{5461}$ | $n^{25}_{4360}$ |
|---|---|---|
| Hevea rubber (smoked sheet) | 1.5205 | 1 5415 |
| Guayule rubber | 1.5196 | 1.5421 |
| Synthetic polyisoprene | 1.5184 | 1.5403 |

the classical linear behaviour the difference between the several rubbers in the order: υ Hevea > υ Guayule > υ synthetic, can be observed, in agreement with Reed and Urwin[3]. The value obtained for hexane in this work is 5% higher than that reported by Schulz[4]; the only difference is that in these experiments smoked sheet was used instead of pale crepe. Using chloroform there are two reported values for natural Hevea rubber, 0.095 and 0.100, for 5461 and 4360 Å respectively, and again the values were 5% higher. In toluene the values are identical to those reported before and the same agreement is found with tetrahydrofuran.

From the υ values and using equation (1), the mathematical expressions for each individual rubber were calculated by the least-square method and are shown below.

Hevea rubber smoked sheet:

$$n^{25}_{5461} = 2.0717 - 1.3625\,\tilde{n}_0$$

$$n^{25}_{4360} = 1.9121 - 1.2402\,\tilde{n}_0$$

Guayule rubber:

$$n^{25}_{5461} = 2.0322 - 1.3373\,\tilde{n}_0$$

$$n^{25}_{4360} = 1.8809 - 1.2197\,\tilde{n}_0$$

Synthetic polyisoprene:

$$n^{25}_{5461} = 2.0150 - 1.3270\,\tilde{n}_0$$

$$n^{25}_{4360} = 1.8494 - 1.2006\,\tilde{n}_0$$

The refractive index for each individual rubber was obtained where $n = 0$. The values are presented in *Table 2.* As can be seen, the values for all the rubbers are in agreement with the reported value for Hevea rubber of 1.52 at 5461 Å, and 1.54 at 4360 Å. The υ values for all the rubbers were in close agreement to within 0.12%.

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## REFERENCES

1 Evans, J. M. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, New York, 1972, pp 89–164
2 Huglin, M. B. in 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, New York, 1972, pp 165–331
3 Reed, P. J. and Urwin, J. R. *Aust. J. Chem.* 1970, **23**, 1743
4 Altgelt, K. and Schulz, G. V. *Makromol. Chem.* 1960, **36**, 209
5 Bywater, S. and Johnson, P. *Trans. Faraday Soc.* 1951, **47**, 105
6 Margerison, D., Bain, D. R. and Kiely, B. *Polymer* 1973, **14**, 133
7 Barrall, E. M., Cantow, M. J. R. and Johnson, J. E. *J. Appl. Polym. Sci.* 1968, **12**, 1373
8 Papers presented at the Symposium 'Shaping the Future of the Rubber Industry', 110th Congress of the Rubber Chemistry Div., Am. Chem. Soc., October 1976, San Francisco, California, USA
9 CONACYT-CONAZA programme on the 'utilization of Guayule', 1975–1976
10 Campos-López, E. and Palacios, J. *J. Polym. Sci.* 1976, **14**, 1561
11 Campos-López, E. and Angulo-Sánchez, J. L. *J. Polym. Sci. (Polym. Lett. Edn)* 1976, **14**, 649
12 Technical Manual, Brice Phoenix
13 Kruis, A. *Z. Phys. Chem. Abt. B* 1936, **34**, 13
14 Schulz, G. V., Alegelt, K. and Cantow, H. J. *Makromol. Chem.* 1956, **20**, 13
15 Bristow, G. M. and Westall, B. *Polymer* 1967, 8, 610
16 Bovey, F. *Panel on Guayule, National Academy of Science, Tucson, Arizona,* November 1975
17 Wood, L. A. and Tilton, L. W. *J. Res. Nat. Bur. Stand.* 1949, **43**, 57