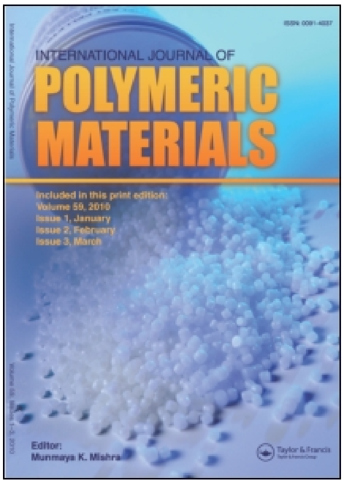

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Intrinsic Viscosity Characterization of Poly(*cis*-isoprene) in *Hevea* Natural Rubber

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Intrinsic viscosity [η] characterizes flow, polymerization, or degradation of dilute polymer solutions. Unlike other high polymers, natural rubber hardly completely dissolves in most organic solvents, and eliminating the insoluble phase undermines the quality of the measurement and its interpretation. On using some natural and synthetic polyisoprene samples, the Huggins and Schulz-Blaschke best-fits were most suitable for estimating [η] for very dilute polyisoprene solutions (<0.06 g/dL in cyclohexane at 30°C). Logarithmic linearization of the Mark-Houwink-Sakurada equation ($[\eta] = K.M^a$; M is molar mass) and a curvilinear model on untransformed data gave different Mark-Houwink constants (K and a) for polyisoprene standards, differences that seemed to have no bearing on their viscosity-average molar masses ($\overline{M}_V$). Plots of $\overline{M}_V$ against weight-average molar mass enabled differentiation of the polyisoprenes into larger groupings, differences that could be attributed to different extents of branching or of aggregation between macromolecules.

Keywords: intrinsic viscosity, molecular mass, natural rubber, poly(*cis*-1,4-isoprene)

INTRODUCTION

The flow characteristics of raw natural rubber (NR), during extrusion and other profiling operations, and even in bulk viscosity measurements, depends largely on its average molar mass [1–3]. Hence, differences in the processing behavior of NR would partly be attributed to its rather wide molar mass distribution.

Dilute solution viscosity measurements are very useful in characterizing polymerization and degradation in polymers [4,5]. The determination of a polymer's intrinsic viscosity or limiting viscosity

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number, like other techniques employing very dilute solutions, makes use of their soluble fractions only. Contrary to other high polymers like polybutadiene that completely dissolve in classical solvents like cyclohexane, are less branched and contain little or no gel [6], NR in its native state hardly completely dissolves in even the most classic solvents for polyisoprene, leaving a substantial gel fraction of highly crosslinked chains [7]. The extent of dissolution is a function of the polymer/solvent interaction and would therefore influence solution viscosity measurements [8]. The intrinsic viscosity $[\eta]$ of a polymer solution and the average molar mass of the polymer are related (Eq. 1).

$$[\eta] = K.\mathrm{M}_\mathrm{v}^\mathrm{a} \tag{1}$$

M_v is the average viscometric molar mass, a and K are Mark-Houwink coefficients, constants for a given polymer—solvent—temperature system. Equation 1 is only valid for macromolecules in a solution endowed with good flexibility. Generally, the value of $\overline{\mathrm{M}}_\mathrm{V}$ lies between the weight-average molar mass ($\overline{\mathrm{M}}_\mathrm{W}$) and the number-average molar mass ($\overline{\mathrm{M}}_\mathrm{n}$), though closer to $\overline{\mathrm{M}}_\mathrm{W}$. Earlier on, good relations have been obtained between $[\eta]$ and K values for masticated, but not for non-masticated NR [9], probably due to the presence of branching in the non-masticated samples. Indeed, a close and inverse association has been demonstrated between the values of K and the extent of branching in the rubber [10].

Although polymer coils in very dilute solutions are widely separated and do not overlap, their hydrodynamic volumes start to touch at a critical concentration (transition from extremely dilute to dilute regions) leading to entanglements that nonlinearly increase viscosity [11]. On the other extreme, a decrease in the concentration of the solution leads to a concomitant decrease in the solution's viscosity. Below a critical concentration, the viscosity of the solution approaches that of the solvent such that the viscosity number (η_{sp}/C) does not vary linearly with concentration. This experiment was undertaken therefore to determine a suitable concentration range for the measurement of the intrinsic viscosity of sol fractions of *cis*-polyisoprene in *Hevea* rubber, and to ascertain the suitability of some model relationships for $[\eta]$ determination.

EXPERIMENTAL

Natural Rubber and Synthetic Poly(*cis*-isoprene) Samples

A synthetic poly(*cis*-1,4-isoprene), Cariflex IR305® from Shell Co. (France) and some NR of conventional ribbed-smoked and technically

TABLE 1 Bulk Rheological and Intrinsic Properties of Samples Studied

Grades	Mooney viscosity, ML(1 + 4)@100°C	Plasticity retention index, PRI (%)	Acetone extract (%w/w)
TSR 10	91	71	1.94
TSR 3CV	64	81	3.58
RSS 1	90	82	3.63

Values are means of quintuplicate measurements.

specified latex (TSR 3CV) and coagula grades (TSR 10) were used for this study. These samples were quite different in terms of their bulk viscosity (Mooney viscosity), susceptibility to thermo-oxidation as measured by their PRI values, and their acetone-soluble extracts (Table 1).

Latex collected from about 300 *Hevea brasiliensis* trees (clone GT 1) was used for the preparation of the technically specified NR samples (grades TSR 3CV and TSR 10). Fresh latex from half of the trees was collected in cups and bulked. Some ammonia (NH_4OH at 50 g/L) was added (1 L for 100 L latex) to prevent premature coagulation and some hydroxylamine sulphate too (0.8 g/kg dry rubber) to stabilize the rubber and prevent aggregation [12]. Later on, formic acid was added (0.15% v/v latex) and the latex was coagulated at pH 5. After maturing for about 16 h, the coagula were crumbed, washed, dried for 4 h at 115°C on an industrial production line and compacted. To process the TSR 10 rubber, latex from the remainder of the trees was left to coagulate naturally in the collection cups for 3 days. The coagula were retrieved, left to mature in barns for 2 weeks and then crumbed, washed, dried for 5.5 h at 115°C, and compacted.

Preparation of Dilute Solutions and Viscosity Measurement

Pure cyclohexane was used to prepare the polymer stock solutions, because of the closeness of the solvent's solubility parameter to that of polyisoprene, and its inability to form peroxides that could provoke molecular chain degradation or possible crosslinking [13]. The stock mixture (40 g/dL) was stored at 30°C in the dark for 1 week, then stirred daily for 1 h in the second week. The mixture was centrifuged at room temperature at 35000 g for 1 h and the insoluble precipitated fraction (macrogel) quantified after drying at 50°C *in vacuo* to constant weight.

The sol fraction was decanted and diluted to different concentrations (0.625 to 20 g/dL). Efflux measurements were conducted on a thoroughly cleaned and dried Type 1 Ubbelohde viscometer (0.63 mm diameter) at 30°C. All measurements, to 0.01 s, were repeated until three consecutive runs differed by less than 0.1 s. From the mean efflux times, the specific viscosity $\{\eta_{\mathrm{sp}} = (t - t_0)/t_0\}$, the relative viscosity $\{\eta_{\mathrm{r}} = t/t_0\}$, the viscosity number $\{\eta_{\mathrm{sp}}/C\}$, the logarithmic viscosity number $\{\ln \eta_{\mathrm{r}}/C\}$, and the ratios $\eta_{\mathrm{sp}}/\eta_{\mathrm{r}}$ and $\eta_{\mathrm{sp}}/\eta_{\mathrm{r}} \cdot C$ were calculated. The parameters t_0 and t were the respective efflux times of the pure solvent and the rubber solutions, and C their concentrations (in g/dL). Intrinsic viscosity values $[\eta]$ were obtained by extrapolation to infinitely diluted concentrations using separately the Huggins, Kraemer, Peterlin, and Schulz-Blaschke equations, respectively Eqs. 2 to 5 [14]. $\mathrm{k}'_{\mathrm{H}}, \mathrm{k}'_{\mathrm{K}}, \mathrm{k}'_{\mathrm{P}}$ and $\mathrm{k}'_{\mathrm{SB}}$ are the respective Huggins, Kraemer, Peterlin and Schulz-Blaschke constants.

$$\eta_{\mathrm{sp}}/C = [\eta] + \mathrm{k}'_{H}[\eta]^2 \cdot C \tag{2}$$

$$\ln(\eta_{\mathrm{r}})/C = [\eta] - \mathrm{k}'_{K}[\eta]^2 \cdot C \tag{3}$$

$$\eta_{\mathrm{sp}}/C = [\eta] - \mathrm{k}'_{P}[\eta] \cdot \eta_{\mathrm{sp}} \tag{4}$$

$$\eta_{\mathrm{sp}}/C = [\eta] + \mathrm{k}'_{SB}[\eta] \cdot \eta_{\mathrm{sp}} \tag{5}$$

Determination of Weight-Average Molar Masses and Molar Mass Distributions

Average molar masses were measured by steric exclusion chromatography using cyclohexane as eluent. The sol fractions obtained after centrifugation were diluted to 2 g/dL, filtered through a 1 μm sieve and injected into a chromatograph as described elsewhere [15].

RESULTS AND DISCUSSION

Concentration Range for Measurement of Viscosity Number, $[\eta]_{\mathrm{sp}}/C$

Determination of a suitable concentration range for the determination was done using the Huggin's equation (Eq. 2) on two technically specified NR samples: TSR 10 and TSR 3CV. Indeed, the plot of η_{sp}/C versus C was linear for concentrations of up to 0.06 g/dL for the viscosity-stabilized rubber (TSR 3CV) and about 0.04 g/dL for the non-viscosity stabilized TSR 10 rubber (Figure 1). At concentrations above these indicated values, the plots became rather curvilinear

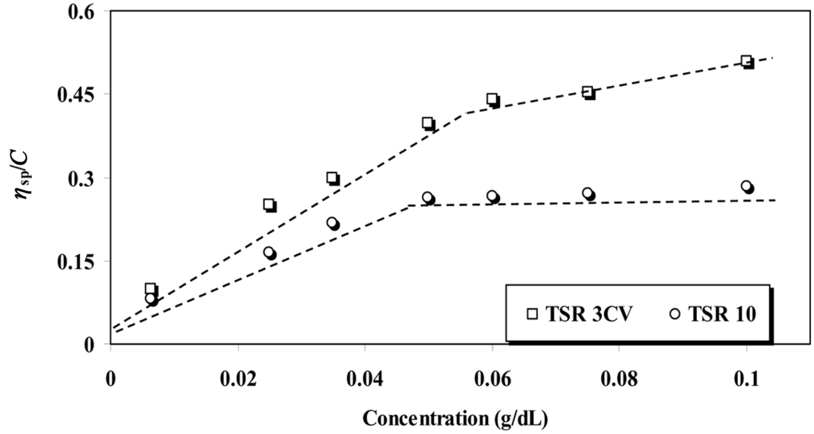

FIGURE 1 Evolution of viscosity number $[\eta]_{sp}/C$ with concentration $[C]$ for poly(*cis*-1,4-isoprene) in cyclohexane (at 30°C) for grades TSR 10 and TSR 3CV natural rubber.

and increases in the solution concentration did not seem to be associated with any linear increases in the values of η_{sp}/C. This indicates that the solutions were already transitioning from extremely dilute to dilute, with overlapping hydrodynamic volumes of the polymer [11].

The evolution of $[\eta]_{sp}/C$ with C (in g/dL) was much different for the less branched synthetic poly(*cis*-1,4-isoprene), IR 305®, for which the concentration range was significantly higher (Figure 2). These results

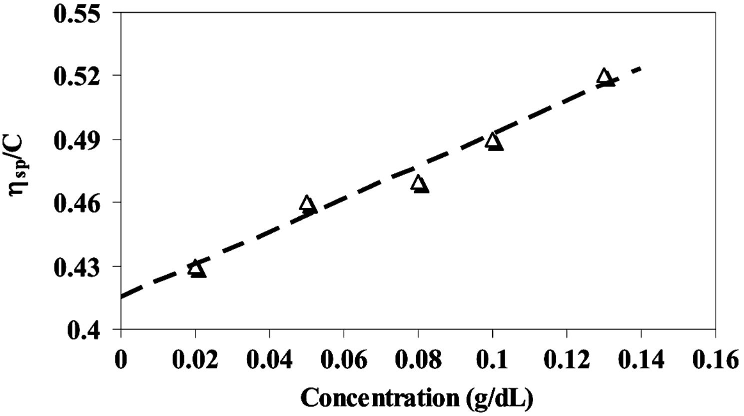

FIGURE 2 Evolution of viscosity number $[\eta]_{sp}/C$ with concentration $[C]$ for a synthetic poly(*cis*-1,4-isoprene) IR 305® in cyclohexane at 30°C.

on the natural and synthetic rubber samples confirm the possible influence of chain branching (crosslinks between polymer chains) and/or the average molar mass or length of the constitutive polyisoprene, as previously suggested [10]. The use of solution concentrations above the critical level increases the scatter of the $[\eta]_{sp}/C$ vs. C distribution and as a consequence, reduces the simple linear correlation coefficient characterizing the distribution.

Suitability of Model Equations for [η] Determination

Several mathematical models, proposed in the literature for the estimation of [η] from solution viscosity measurements [14], were tested to ascertain their suitability and the existence of any biases associated with their average molar masses.

Although on the whole, the limiting viscosity numbers obtained using the Huggins equation (for NR samples TSR 10, TSR 3CV and RSS 1) were slightly lower than those obtained using the other equations, these values did not seem to vary significantly ($P = 0.05$) with the model relationships used (Table 2). However, this was not the case for gradients of the slopes as there was a great discrepancy for the different samples tested. In a systematic manner, the highest values were obtained with the k' parameter (Huggins equation), followed by the Kraemer β constant and the Schulz-Blaschke (k'_{SB}). The Peterlin constant (k'_C) was the least. The coefficient of determination (R) of best-fit equations was used as the last criterion to evaluate the suitability of the model equations. The best and most reproducible R values were obtained using the Schulz-Blaschke and Huggins equations (Table 2), while the Peterlin equation was least appropriate.

At equivalent concentrations, polymer solutions are highly viscous due to the strong solvation of the polymer chains that yield strongly

TABLE 2 Precision in [η] Measurement of Sol Fractions Using Different Model Equations

	Huggins			Kraemer			Peterlin			Schulz-Blaschke		
Sample	[η]	k'	R	[η]	β	R	[η]	k'_C	R	[η]	k'_{SB}	R
TSR 10	0.241	3.517	0.94	0.245	2.189	0.87	0.246	−1.013	0.73	0.251	1.853	0.93
TSR 3CV	0.311	1.930	0.97	0.319	0.893	0.89	0.321	−0.187	0.42	0.325	1.113	0.96
RSS 1	0.258	2.415	0.93	0.269	1.117	0.86	0.274	−0.289	0.55	0.274	1.295	0.96

R is the simple linear correlation coefficient. The constants k', β, k'_C and k'_{SB} are described after Equations 2 to 5.

TABLE 3 Mark-Houwink Coefficients for Poly(*cis*-1,4-isoprene) Standards in Cyclohexane at 30°C

Method of determination	a	K (in dL/g)
Obtained as log – log	0.8225	0.551×10^{-4}
Without data transformation	0.7614	1.282×10^{-4}

expanded coils which are more exposed to the velocity gradient during flow of the solution. The hydrodynamic interactions between polymer coils in solution could be expressed as [5]:

$$\eta_{\mathrm{sp}} = k_0[\eta]C + k_1[\eta]^2C^2 + k^2[\eta]^3C^3 + \ldots \tag{6}$$

where k_0, $k_1, \ldots$ are dimensionless constants and $k_0 = 1$.

At infinite dilution, Eq. 6 is truncated and rearranged to give Eq. 1, as below:

$$\eta_{\mathrm{sp}}/C = [\eta] + k'[\eta]^2 \cdot C$$

The results in Table 2 could indicate that the terms of C^2 and higher that are normally ignored in Eq. 6 could be more significant with a greater influence on $[\eta]$ estimation.

Mark-Houwink Coefficients for Natural and Synthetic Poly (*cis*-1,4-isoprene)

The Mark-Houwink coefficients could be obtained by linearizing Eq. 1 using a logarithmic transformation. A plot of Ln$[\eta]$ against Ln(M) (M: molar mass of standard samples) should give a straight line with slope "a" intersecting the ordinate at ln[K]. Otherwise, "a" and "K"

TABLE 4 Viscosity-Average Molar Mass ($\overline{\mathrm{M}}_{\mathrm{V}}$), Number-Average ($\overline{\mathrm{M}}_{\mathrm{n}}$) and Weight-Average ($\overline{\mathrm{M}}_{\mathrm{W}}$) Molar Masses for a Synthetic Poly(*cis*-1,4-isoprene), Cariflex IR305® (Cyclohexane as Solvent at 30°C) ($k' = 0.458$)

Average molar mass	All/log – log a = 0.8225; K = 0.5501×10^{-4}	All/curvilinear a = 0.7614; K = 1.2816×10^{-4}
$\overline{\mathrm{M}}_{\mathrm{n}}$	334 000	334 000
$\overline{\mathrm{M}}_{\mathrm{V}}$	857 000	844 600
$\overline{\mathrm{M}}_{\mathrm{W}}$	1 235 000	1 235 000

Values of Mark-Houwink coefficients "a" and "k" were derived from triplicate measurements obtained over 8 months on five poly(*cis*-1,4-isoprene) standards.

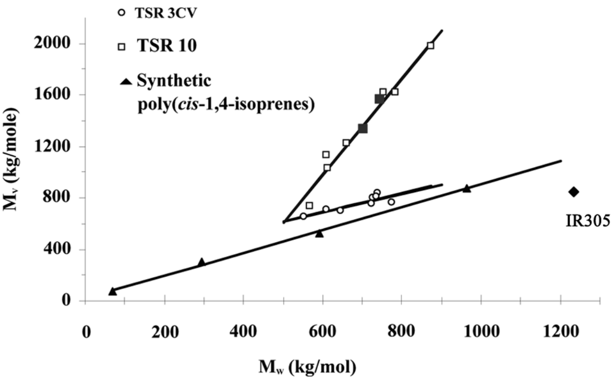

FIGURE 3 Relations between $\overline{M}_V$ and $\overline{M}_W$ for some natural rubber and synthetic polyisoprene samples.

could be obtained directly with untransformed experimental data, using a curvilinear model. These two methods, on transformed and on untransformed data, were compared using data from five standard monodispersed poly(*cis*-1,4-isoprene) samples with weight-average molar masses ranging from 1.97×10^3 g/mol to 1.2×10^6 g/mol, and intrinsic viscosity values $[\eta]$ varying from 0.0280 dL/g to 5.5401 dL/g. The results obtained gave rather different Mark-Houwink constants values for the poly(*cis*-1,4-isoprene) samples studied (Table 3).

The mean intrinsic viscosity, $[\eta]$, of some NR samples was estimated after double extrapolation of experimental results using the Huggins and Kramer equations. The Huggins constant (k') and the viscosity-average molar mass ($\overline{M}_V$) were calculated using the mean $[\eta]$ and the two sets of Mark-Houwink coefficients obtained using the transformed and untransformed data. Despite the rather large differences between these coefficients (Table 3), the $\overline{M}_V$ were very similar for the poly(*cis*-1,4-isoprene), IR 305®, with values between the number-average ($\overline{M}_n$) and weight-average molar masses, $\overline{M}_W$ (Table 4). Figure 3 shows the excellent relations between $\overline{M}_V$ and $\overline{M}_W$, relations that were typical for the different types of rubber (synthetic polyisoprene, TSR 3CV and TSR 10 natural rubber).

CONCLUSIONS

The intrinsic viscosity $[\eta]$ of poly(*cis*-1,4-isoprene) in *Hevea* natural rubber was investigated with a view to account for the variability in processing behavior of some commercial grades of bulk natural rubber

(TSR 3CV and TSR 10), estimate a suitable concentration range for its measurement, and ascertain the suitability of some model relationships for this determination. Determination of $[\eta]$ in cyclohexane (at 30°C) of poly(*cis*-1,4-isoprene) from *Hevea* rubber requires solutions more dilute than 0.06 g/dL. The Huggins and Schulz-Blaschke equations were most suitable for obtaining reproducible and acceptable $[\eta]$ values. Plots of viscosity-average molar mass ($\overline{M}_V$) as a function of weight-average molar mass ($\overline{M}_W$) enabled differentiation of the poly(*cis*-1,4-isoprene) samples into three large groups: the isomolecular synthetic standards, grade TSR 3CV of latex origin, and grade TSR 10 of cup-lump origin. These differences could be attributed to the different extents of branching or of macromolecular aggregation.

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