Viscosity–Molecular Weight Relationship for Masticated Natural Rubber

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Synopsis

Intrinsic viscosity and osmotic molecular weight data are presented for toluene solutions of several types of natural rubber after mastication in air. For $[\eta] < $ ca. 4 *all* these data fit the relationship, $[\eta] = 7.11 \times 10^{-7} \bar{M}_n^{1.25}$. At higher molecular weights deviations from this relation are found, the extent of which depend on the type of natural rubber used. These deviations are attributed to differences in initial molecular weight distribution.

The relationship between the number-average molecular weight and the intrinsic viscosity of benzene or toluene* solutions of masticated natural rubber has been determined several times in these laboratories,[1,2] and recently analogous data for a synthetic cis-1,4-polyisoprene have been reported.[3] The relationship found for this latter material differs appreciably from that published for natural rubber,[2] a deviation which has been attributed to differences in molecular weight distribution of the unmasticated materials.

Though the viscosity and molecular weight results reported previously, and those presented here, fit an equation of the Mark-Houwink type, $[\eta] = KM^\alpha$; this is essentially fortuitous, since α is much greater than the values normally observed for polymers in good solvents. Watson et al.[1] have indicated how this pseudo Mark-Houwink equation can be interpreted in terms of the preferential rupture of large molecules during mastication.

Data for natural rubber solutions reported recently[4] have shown that in the determination of number-average molecular weight by osmometry, plots of $(\pi/c)^{1/2}$ versus c are to be preferred to those of (π/c) versus c previously adopted here. This change in extrapolation procedure generally results in somewhat reduced values of $\bar{M}_n$, especially for $\bar{M}_n > 3 \times 10^5$ and necessitates some alteration in the constants of the $[\eta]$–$\bar{M}_n$ equation. The opportunity has been taken therefore to present rather more extensive data than those previously quoted, these data covering three types of natural rubber.

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* The intrinsic viscosities of natural rubber in these two solvents are related by $[\eta]_{tol} = 1.076\,[\eta]_{bz} - 0.15$, (for $[\eta]$ in dl./g) and are therefore closely comparable for the usual range of $[\eta]$ values.

TABLE I
Viscosities and Molecular Weights of Masticated Natural Rubber

	$[\eta]$, dl./g.	$\bar{M}_n \times 10^{-5}$	Γ_2, ml./g. $\times 10^{-2}$
RSS1	7.35[a]	5.16	2.15
	6.70[a]	4.10	1.99
	4.24	2.48	1.45
	3.64	2.53	1.38
	3.40	2.15	1.39
	2.39	1.62	1.09
	2.33	1.62	0.99
	2.11	1.54	1.13
	1.61	1.10	0.77
	1.19	1.04	0.78
Pale crepe	5.96[a]	4.66	2.47
	5.45[a]	3.81	2.33
	4.61[a]	2.66	1.42
	3.57[a]	2.48	1.39
	2.76	1.93	1.12
	2.76	1.88	1.10
	2.71	1.69	0.95
	2.52	1.70	1.10
	2.47	1.62	1.10
	2.47	1.65	1.12
	2.08	1.44	0.91
	1.83	1.39	1.02
	1.83	1.32	
	1.55	1.18	0.88
	1.02	0.80	0.53
Sol rubber	5.08[a]	4.41	2.38
	4.90[a]	3.24	1.99
	4.49	2.79	1.78
	4.16	2.63	1.75
	3.61	2.16	1.31
	3.03	1.96	1.21
	2.84	1.83	1.29
	1.87[b]	1.28	1.08

[a] Values not used in deriving $[\eta]-\bar{M}_n$ relation.

Yellow circle RSS1 and pale crepe rubber were extracted with hot acetone for 24 hr. and dried *in vacuo*. A much purer rubber hydrocarbon, conveniently called sol rubber, was prepared by soaking unmilled extracted crepe in cold cyclohexane for 2–3 days and recovering the dissolved rubber by freeze drying the filtered cyclohexane solution. This sol rubber had a nitrogen content of ca. 0.01%.

Mastication was effected either in the laboratory masticator previously described[5] or on a micromill. Samples were removed successively at suitable time intervals as mastication proceeded. Probably as a result of better sample homogeneity, this procedure was found to give more consistent results than masticating each sample individually.
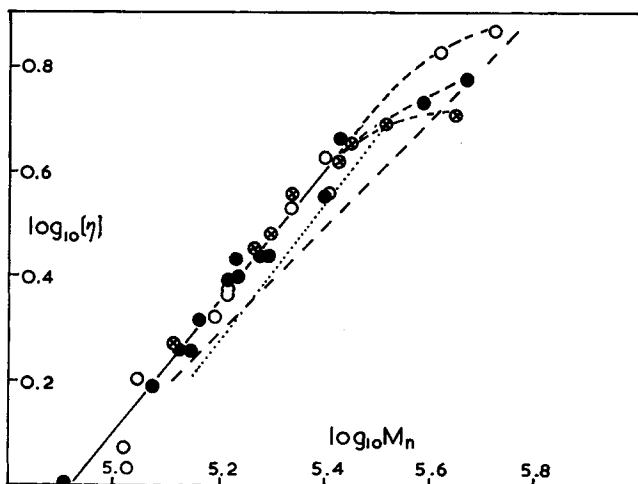
Fig. 1. Plots of log [η] vs. log $\bar{M}_n$: (O) yellow circle RSS1; (●) pale crepe; (⊗) sol rubber; (———) least-squares plot, $7.11 \times 10^{-7}\bar{M}_n^{1.25}$; (- -) cis-1,4-polyisoprene, data of Bristow;[3] (. . .) data of Mullins and Watson[2] ($2.29 \times 10^{-7}\bar{M}_n^{1.33}$).

Intrinsic viscosities of the rubbers in toluene solution were determined in Ubbelohde suspended-level viscometers at $25 \pm 0.1°C$. Values of η_{sp}/c were determined for at least three concentrations and the plot of η_{sp}/c versus c extrapolated linearly to give the intrinsic viscosity.

The osmometers were of the Zimm-Meyerson type fitted with Ultracella filter "feinst" membranes. These were conditioned from water to absolute ethanol, assembled in the osmometer under ethanol, and then conditioned successively in 1:1 toluene–ethanol and toluene. Only osmometers having membrane permeabilities between 4 and 12×10^{-4} hr.$^{-1}$ and solvent–solvent asymmetries <0.01 cm. of solvent were used. As a final test before use, the osmometer was required to indicate an osmotic head of 1.16 ± 0.02 cm., constant for 72 hr., when filled with a standard polystyrene solution. Osmotic pressures of the rubber solutions were measured at four or five concentrations over the range 0.2–1.0% (w/w) using the same osmometer for all solutions of a given sample. Values of $(\pi/c)_{c=0}$ were derived by graphical extrapolation of $(\pi/c)^{1/2}$ versus c, since in general the precision of the data did not necessitate the use of the method of least squares. Values of the second virial coefficient, Γ_2, were derived from the slopes of the plots, Γ_2 being defined by

$$(\pi/c)^{1/2} = (\pi/c)_0^{1/2}(1 + \tfrac{1}{2}\Gamma_2 c)$$

as required by the Flory dilute solution theory.[6]

Values of [η], $\bar{M}_n$, and Γ_2 are given in Table I, and log [η] is plotted versus log $\bar{M}_n$ in Figure 1. The relation derived for cis-1,4-polyisoprene[3] is included in the figure for comparison.

Figure 1 shows the three rubbers have a common [η]–$\bar{M}_n$ relation for all but the highest molecular weights. The differences between the

several rubbers in the high molecular weight region are doubtless due to variations in molecular weight distribution of the unmasticated rubbers; as mastication proceeds, these differences disappear, and a common molecular weight distribution is established. Further, the data for cis-1,4-polyisoprene, while initially divergent, converge with that for natural rubber as mastication proceeds. Application of the method of least squares to the data of Table I (other than those of the highest molecular weight), gives for the $[\eta]$–$\bar{M}_n$ relation,

$$[\eta] = 7.11 \times 10^{-7}\bar{M}_n{}^{1.25}$$

with a standard deviation of $\pm 4.6\%$ for 25 points. The line corresponding to the relation previously derived by Mullins and Watson[2] is included in
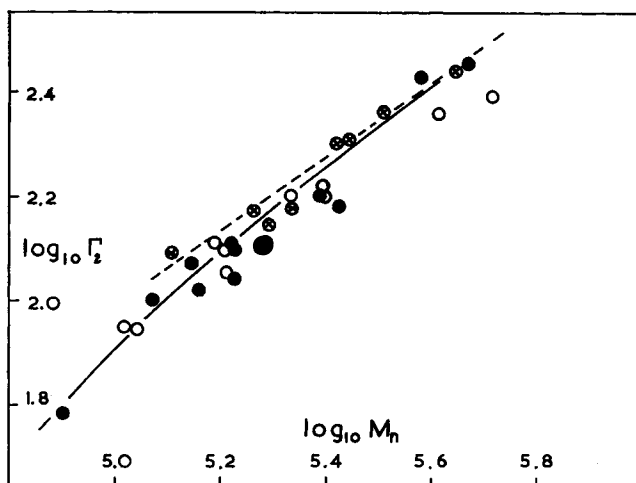

Fig. 2. Plots of log Γ_2 vs. log $\bar{M}_n$: (O) yellow circle RSS1; (●) pale crepe; (⊗) sol rubber; (- -) cis-1,4-polyisoprene, data of Bristow.[3]

Figure 1 for comparison. The discrepancy between the present data and their line is due at least in part to the use of the $(\pi/c)^{1/2}$ rather than the (π/c) extrapolation for the estimation of $\bar{M}_n$.

In Figure 2, log Γ_2 is plotted as a function of $\bar{M}_n$. As is usually found, Γ_2 increases with molecular weight, though little quantitative significance can be attached to this change since Γ_2 in the Flory dilute solution theory[6] is a complex function of molecular weight distribution, and polymer-solvent interaction. The relation for cis-polyisoprene is also plotted in Figure 2, and there would appear to be no significant difference in Γ_2 for the two polymers.

Finally although the $[\eta]$–$\bar{M}_n$ relation derived above probably gives better absolute values of $\bar{M}_n$ for a given $[\eta]$ than those derived previously,[1,2] its use for the conversion of $[\eta]$ to $\bar{M}_n$ in estimates of crosslink density of vulcanizates by the Mullins, Moore, Watson[7,8] calibration would be inap-

propriate. This calibration was established by using values of $[\eta]$ as the primary observed data and values of M_n were derived by use of the relation,

$$[\eta] = 2.29 \times 10^{-7} \bar{M}_n^{1.33}$$

Hence, the continued use of this expression in subsequent applications of this calibration is demanded.

References

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Résumé

On donne les poids moléculaires obtenus par viscosité intrinsèque et par osmose pour des solutions dans le toluène de plusieurs types de caoutchouc naturel, après mastication à l'air. Pour des $[\eta] <$ ca. 4, *tous* ces résultats suivent la relation $[\eta] = 7.11 \times 10^{-7} \bar{M}_n^{1.25}$. Pour des poids moléculaires plus élevés on a observé des déviations à cette relation, dont l'importance dépend du type de caoutchouc naturel employé. Ces déviations sont attribuées à des différences de distribution initiale du poids moléculaire.

Zusammenfassung

Daten für die Viscositätszahlen und das osmotische Molekulargewicht für Toluollösungen einiger Naturkautschuktypen nach Mastizierung unter Luft werden vorgelegt. Für $[\eta] <$ ca. 4 gehorchen *alle* Daten der Beziehung $[\eta] = 7,11 \times 10^{-7} \bar{M}_n^{1.25}$. Bei höheren Molekulargewichten traten Abweichungen von dieser Beziehung auf; ihr Ausmass hängt vom Typ des verwendeten Naturkautschuks ab. Diese Abweichungen werden auf Unterschiede in der Ausgangsmolekulargewichtsverteilung zurückgeführt.