

Correlating Mooney Viscosity to Average Molecular Weight

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Synopsis

Copolymers of styrene and butadiene of the same chemical composition, but widely different molecular weight distributions, were characterized by gel permeation chromatography. A very good correlation was obtained between the logarithm of the Mooney viscosity and the logarithm of the geometric mean of the number- and weight-average molecular weights. Instead of this molecular weight average, one can equally well use the very convenient " $\bar{M}_v \log M$," which is a weight-average molecular weight, using a logarithmic molecular weight scale. This correlation makes it possible to predict the Mooney viscosity from GPC data with a precision of about 15% (\pm one standard deviation), independent of the molecular weight distribution of the polymer. The obtained correlation was much better than with either weight-average molecular weight or viscosity-average molecular weight with $\alpha = 0.67$.

INTRODUCTION

The Mooney viscosity cannot predict the processing behavior of rubbers in general, although its usefulness in control testing is well documented. However, it is worth noting that most commercial non-oil extended synthetic rubbers have Mooney viscosities in the range of 30-90 (ML 10 min at 100°C), i.e., less than one decade in Mooney viscosity. When one considers the power dependence of viscosity on molecular weight, this is a surprisingly narrow range compared to the range of molecular weights present in some rubbers.

It is therefore of interest to be able to predict an approximate Mooney viscosity from the molecular weight distribution curve. This has become increasingly important with the development of new polymerization systems such as anionic polymerization, since with some of these systems it is possible to make widely different molecular weight distributions.

Bueche¹ derived the following expression for the bulk viscosity η as a function of molecular weight M for monodisperse polymers:

$$\eta = KM^{\alpha}$$

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where K is a constant and a is unity for low molecular weights and 3.5 for high molecular weights. A relationship of this form had already been established experimentally by Fox and Flory.^{2,3} They found the value of a to be about 3.4 for the viscosity of relatively high molecular weight fractions measured at low shear rates. The value of a decreases with increasing shear rate.⁴

For polydisperse polymers of relatively high molecular weight, Bueche⁵ derived the expression

$$\eta = KM_t^{3.5}$$

where $M_w \leq M_t \leq M_z$ for very wide distributions. Experiments by Fox and Flory³ and Fox and Loshaek⁶ indicated that M_t should be the weight-average molecular weight M_w . However, Rudd⁴ observed that high shear-rate viscosity relates to some molecular weight average between the number-average, M_n , and weight-average, M_w , molecular weights. More recently, Busse and Longworth⁷ reported that for molten polyethylene the best correlation was obtained with the viscosity-average molecular weight, M_v . The same was found by Drexler⁸ for very wide-distribution butyl polymers of low molecular weight.

It should be remembered that the shear rate in the Mooney machine is not a constant throughout the cavity. The average shear rate is of the order of 1 sec^{-1} , which for many polymers already is in the non-Newtonian range. This means that the Mooney machine measures a quantity proportional to an average non-Newtonian flow.⁹

EXPERIMENTAL

Widely different molecular weight distributions were obtained by blending anionically prepared copolymers of styrene and butadiene with the same chemical composition. Using a logarithmic molecular weight scale, some were skewed toward low molecular weights, some were skewed toward high molecular weights, and some were approximately symmetrical. The final series of polymers had weight-average molecular weights ranging from about 100,000 to about 300,000, covering the practical range of Mooney viscosities at 100°C .

All the polymers were characterized as follows: The Mooney viscosity was measured at 100°C with the large rotor, using the value reached after 10 min of shearing (ML 10 min at 100°C). The dilute solution viscosity was measured in toluene at 25°C (0.2 g of polymer per 100 cm^3). The polymers were characterized by gel permeation chromatography (GPC) at 65°C , using toluene as a solvent. Five columns with the following Waters Associates designations were used: 10^2 , 10^3 , 10^4 , 10^5 , and 10^6 \AA . The plate count of the column set was 1114 plates per foot, using 1,2,4-trichlorobenzene as the plate count sample. Eleven polystyrene samples were used to calibrate the columns. The molecular weights ranged from

2.1×10^3 to 1.8×10^6 , the three lowest being 2100, 4800, and 10,000. A Q -factor of 14.8 was used to convert from \bar{A} size to molecular weight of the styrene-butadiene copolymers.

The following molecular weight averages were calculated from the GPC curves, which were uncorrected for peak-broadening effects: number-average, M_n ; weight-average, M_w ; z -average, M_z ; and viscosity-average, $M_v = (\sum_i W_i M_i^\alpha)^{1/\alpha}$, with $\alpha = 0.67$. Three additional parameters were calculated: "Av log M ," "breadth," and "skewing₅₀" (see Appendix A). Av log M turns out to be the logarithm of the geometric mean of the weight distribution; breadth and skewing₅₀ characterize in a rough way the shape of the GPC curve.

RESULTS AND DISCUSSION

The characterization data for all the polymers is shown in Table I. The very wide range in molecular weight distributions can be seen from the ratio M_w/M_n and from the two parameters "breadth" and "skewing₅₀." Values for the z -average molecular weight are not included in the table since the correlation between Mooney viscosity and M_z was very poor. The last five columns in Table I show the logarithms of the various molecular weight averages so that comparisons can be easily made.

Plots of the logarithm of the Mooney viscosity versus the logarithms of number- and weight-average molecular weights gave poor correlations, as shown in Figure 1. As observed by Rudd,⁴ the points for broad molecular weight distributions are shifted toward lower molecular weights for the number-average and toward higher molecular weights for the weight-average molecular weights.

Figure 1 also indicates that it should be possible to remove most of the scatter by taking the arithmetic mean of $\log M_n$ and $\log M_w$. However,

$$^{1/2}(\log M_n + \log M_w) = \log (M_n M_w)^{1/2}$$

i.e., the logarithm of the geometric mean of the number- and weight-average molecular weights.

Figure 2 shows that a very good correlation between Mooney viscosity and $\log (M_n M_w)^{1/2}$ is indeed obtained. The remaining scatter is only slightly larger than the precision of the GPC characterization data. The solid line in Figure 2 is a straight line with a slope of 2.08. The data are not sufficient to distinguish between a straight line and a line which has a decreasing slope with increasing molecular weight, as found by Buchdahl et al.¹⁰ who covered several decades in the viscosity of polystyrenes.

In order to obtain a numerical value for the scatter in the data in the various plots, a least-squares fit to a straight line was performed for each of the molecular weight averages given in the last five columns in Table I,

$$\log ML_{10} = a_0 + a_1 \log M_{ave}$$

TABLE I
Characterization Data for the Polymers

Polymer no.	ML 10' at 100°C	DSV, dl/g	GPC Data						$\log (M_w/M_n)^{1/2}$	Av log M
			M_w/M_n	Breadth	Skewing ₅₀	$\log M_n$	$\log M_w$	$\log M_o$		
5495	13	1.5	1.6	0.73	0.82	4.75	4.97	4.94	4.86	4.87
5786	26	1.6	1.5	0.72	2.04	4.93	5.09	5.06	5.01	5.00
5494	27	1.6	1.2	0.41	0.90	4.93	5.00	4.99	4.97	4.97
5490	28	1.7	1.1	0.37	0.94	4.97	5.03	3.02	5.00	5.00
5788	29	1.6	1.6	0.74	0.68	4.87	5.07	5.04	4.98	4.98
5787	31	2.0	2.9	1.22	1.46	4.75	5.21	5.14	4.98	4.98
5408	41	1.9	1.8	0.76	1.39	4.93	5.18	5.13	5.05	5.04
5784	44	2.0	2.3	1.03	0.78	4.85	5.20	5.15	5.03	5.04
5406	48	3.0	3.9	1.37	1.31	4.80	5.39	5.30	5.10	5.09
5789	59	2.9	2.8	1.14	1.72	4.94	5.39	5.30	5.17	5.14
5790	64	2.6	2.7	1.14	0.83	4.89	5.32	5.26	5.11	5.13
5491	68	2.3	1.2	0.44	0.83	5.11	5.20	5.19	5.16	5.16
5489	71	2.4	1.9	0.92	0.92	4.99	5.27	5.23	5.13	5.14
5783	74	2.4	1.5	0.74	1.94	5.13	5.31	5.28	5.22	5.21
5791	82	3.8	4.1	1.42	0.90	4.93	5.54	5.46	5.24	5.25
5493	92	2.3	1.6	0.77	0.65	5.08	5.29	5.26	5.19	5.20
5793	96	3.0	2.5	1.09	0.69	5.02	5.41	5.37	5.22	5.25
5785	96	2.4	1.5	0.67	0.75	5.13	5.30	5.28	5.22	5.22
5792	107	2.8	1.7	0.82	1.33	5.17	5.40	5.36	5.29	5.28
5488	107	2.4	1.1	0.39	0.99	5.20	5.25	5.25	5.23	5.23
5492	117	2.9	2.1	1.00	1.02	5.13	5.46	5.41	5.30	5.30

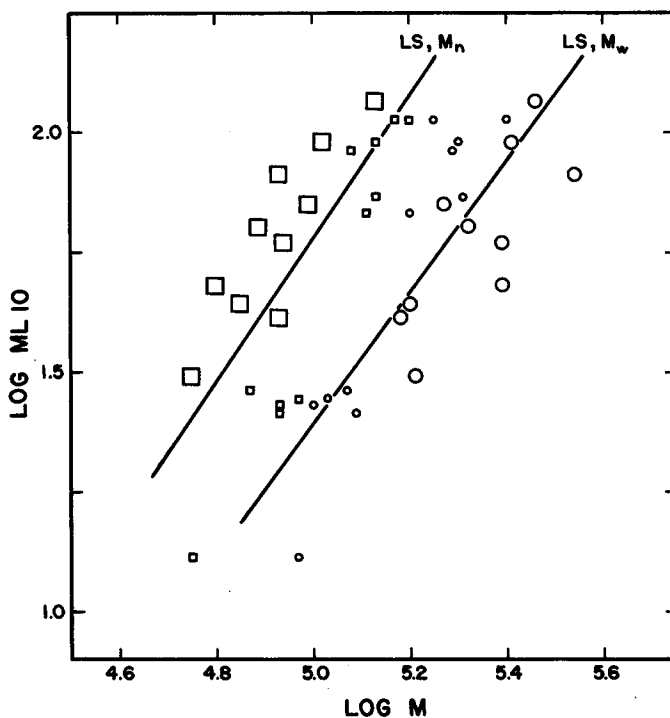


Fig. 1. Logarithm of the Mooney viscosity vs. logarithm of average molecular weight: (\square) M_n ; (\circ) M_w ; small squares and circles for $M_w/M_n < 1.8$; Large squares and circles for $M_w/M_n \geq 1.8$. The least-squares fit to a straight line is also shown.

where the intercept a_0 and the slope a_1 are the fitting parameters. The standard error of the estimate, σ , was calculated from the following expression:

$$\sigma = \left[\frac{\sum [y_i - (a_0 + a_1 x_i)]^2}{n - 2} \right]^{1/2}$$

where y_i are the observed values of log ML 10, x_i are the observed values of log M_{ave} , and n is the number of data points. The results are given in Table II. The value of σ is a measure of the scatter in the data. It

TABLE II
Least-Squares Fit of Data to a Straight Line

log M_{ave}	a_0	a_1	σ
log M_n	-5.69	1.493	0.169
log M_w	-5.50	1.378	0.152
log M_v	-6.74	1.627	0.124
log $(M_n M_w)^{1/2}$	-8.91	2.080	0.065
Av log M	-8.97	2.092	0.056

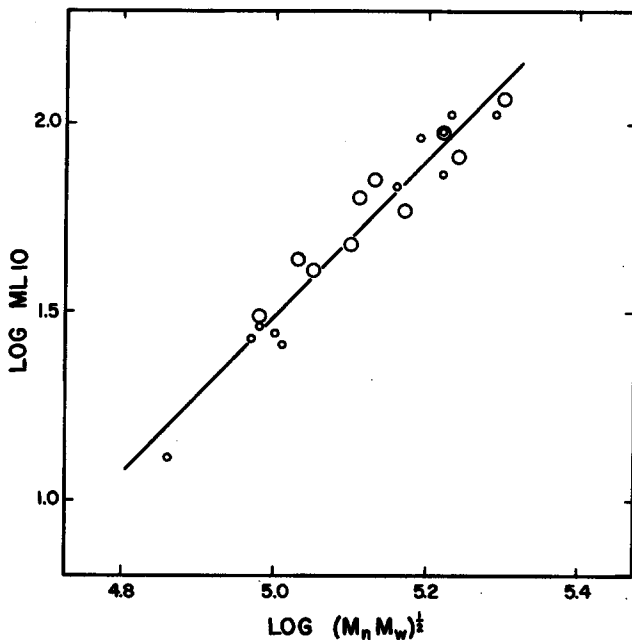


Fig. 2. Logarithm of the Mooney viscosity vs. logarithm of the geometric mean of number- and weight-average molecular weights: small circles for $M_w/M_n < 1.8$; large circles for $M_w/M_n \geq 1.8$. The solid line is a least-squares fit to a straight line.

may clearly be seen that the scatter is much lower in the case of $\log (M_n M_w)^{1/2}$ or $\text{Av log } M$ than in the case of $\log M_v$, $\log M_w$, or $\log M_n$. The standard error for $\log \text{ML } 10$ is about 6% in the case of $\log (M_n M_w)^{1/2}$ and $\text{Av log } M$. This corresponds to 15% for the Mooney viscosity itself.

CONCLUSIONS

Unlike the results reported for the viscosity measured at very low shear rates, the so-called Mooney viscosity does not give a good correlation with weight-average molecular weight. A much improved correlation is obtained by plotting the logarithm of the Mooney viscosity against $\log (M_n M_w)^{1/2}$ or "Av log M ." The slope of the straight line formed by the method of least squares is about 2.1, i.e., well below the value of 3.4 which is found at very small shear rates. A slope of less than 3.4 is not surprising, considering the high molecular weights combined with the quite high shear rates in the Mooney machine, causing the flow to become non-Newtonian.

Most elastomers consisting of linear molecules should be expected to exhibit a similar correlation as for this series of copolymers of styrene and butadiene. The precision of predicting Mooney viscosity from GPC data appears to be about 15% (\pm one standard deviation).

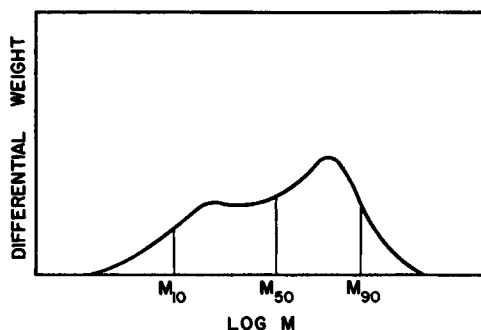


Fig. 3. Differential weight fraction of polymer with respect to the logarithm of molecular weight vs. logarithm of molecular weight. The molecular weights given by M_{10} , M_{50} , and M_{90} are used to characterize the breadth and skewing of the molecular weight distribution.

Appendix A

Characterization of the GPC Curve

E. J. Carlson from our laboratories has introduced three parameters, "Av log M ," "breadth," and "skewing₅₀," to characterize the molecular weight average and the shape of the molecular weight distribution curve. Figure 3 is a plot of differential weight fraction (differential with respect to log M) against the logarithm of molecular weight. The molecular weights M_{10} , M_{50} , and M_{90} are used to characterize the breadth and skewing of the distribution (see below). M_{10} is the molecular weight for which 10 weight-% of the polymer has lower molecular weights and 90 weight-% of the polymer has higher molecular weights than M_{10} ; M_{50} and M_{90} are similarly defined.

Molecular weight average is defined as follows:

$$\text{Av log } M = \sum_i W_i \log M_i$$

where W_i is the weight fraction with logarithmic molecular weight, log M_i . Using this definition it may easily be shown for a blend of n polymers that

$$[\text{Av log } M]_{\text{blend}} = \sum_{j=1}^n W_j [\text{Av log } M]_j$$

where W_j is the weight fraction of polymer j . This simple relation makes Av log M a very convenient parameter.

Breadth of the distribution is defined as follows:

$$\text{Breadth} = \log M_{90} - \log M_{10}$$

Skewing of the distribution is defined as follows:

$$\text{Skewing}_{50} = \frac{\log M_{90} - \log M_{50}}{\log M_{50} - \log M_{10}}$$

It is not practical to use skewing with respect to the peak since the GPC curve might be polymodal in nature:

$$\text{Skewing}_{50} \begin{cases} < 1, \text{ "skewed toward low molecular weights"} \\ \simeq 1, \text{ "symmetrical"} \\ > 1, \text{ "skewed towards high molecular weights."} \end{cases}$$

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References

1. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962.
2. T. G. Fox and P. J. Flory, *J. Amer. Chem. Soc.*, **70**, 2384 (1948).
3. T. G. Fox and P. J. Flory, *J. Phys. Chem.*, **55**, 221 (1951).
4. J. F. Rudd, *J. Polym. Sci.*, **44**, 459 (1960).
5. F. Bueche, *J. Polym. Sci.*, **43**, 527 (1960).
6. T. G. Fox and S. Loshaek, *J. Appl. Phys.*, **26**, 1080 (1955).
7. W. F. Busse and R. Longworth, *J. Polym. Sci.*, **58**, 49 (1962).
8. L. H. Drexler, *J. Appl. Polym. Sci.*, **14**, 1857 (1970).
9. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970, p. 614.
10. R. Buchdahl, L. E. Nielsen, and E. H. Merz, *J. Polym. Sci.*, **6**, 403 (1951).

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