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On Estimating The Zero-Shear-Rate Viscosity: Tests With PIB And PDMS

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Abstract. The zero-shear-rate viscosity η_0 is a limiting value that cannot be measured directly; rather, it must be estimated by extrapolation. The value determined by extrapolation will depend on the model used, and the range and quality of the data used for the extrapolation. The error can be surprisingly large. The ongoing study described in this paper has several objectives including development of methods for bracketing the true value, and for improving the estimation process with less-than-ideal sets of data. These methods have been evaluated using data for two room-temperature polymer melts: poly(dimethyl siloxane) (PDMS) and poly(isobutylene) (PIB).

INTRODUCTION

The zero-shear-rate viscosity (often called zero-shear viscosity) is a widely used and fundamental descriptor of the flow resistance of polymer melts and solutions [1, 2]. It is important for characterizing rheological response at low stress, for finding flow activation energy, and for examining the influence of molecular architecture on resistance to flow. The common variable symbol for the zero-shear-rate viscosity is η_0. It can be defined as a limiting value of viscosity, i.e.,

$$\eta_0 = \left.\frac{\sigma}{\dot{\gamma}}\right|_{\dot{\gamma}\to 0} \tag{1}$$

where σ is the shear stress and $\dot{\gamma}$ is the shear rate. Its relationship to the relaxation modulus $G(t)$ is

$$\eta_0 = \int_0^\infty G(t)dt = \int_{-\infty}^{\infty} G(t)t\,d\ln t \tag{2}$$

Examination of Eq. 1 illustrates the problem with the usual experimental determination of η_0 via direct measurement of stress σ at a particular value of $\dot{\gamma}$ (or a direct measurement of $\dot{\gamma}$ at a particular value of σ). Clearly if both shear stress and rate are subject to error, as they will be, the relative error in their quotient could be considerable. Most worrisome, and difficult to detect at low stress, is systematic error. This same issue is seen with many important limiting material quantities; examples that come to mind are intrinsic viscosity and the Mooney equation parameters C_1 and C_2 [3].

Use of Eq. 2 was attempted decades ago [4], but obtaining values of the relaxation modulus $G(t)$ over a wide range of time at a given, fixed temperature was, and still is, a significant problem. As with Eq. 1, the usual "fix" is extrapolation, with all the associated concerns.

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Extrapolation

With Eq. 1, we are quite confident that the relationship between stress and shear rate at low shear rates is linear, i.e.,

$$\sigma = \eta\dot{\gamma} \tag{3}$$

For simple fluids, this obtains exactly. For polymer melts, problems arise because the value of η depends on a huge array of experimental conditions: the usual thermodynamic variables, the shear rate itself, time and often, sadly, the geometry used for the measurement. Considering time alone, attempts to reach true steady state may take hours. Meanwhile, gravity acts on the specimen to distort its shape, microphase separation appears, chemical changes occur, components leave or enter the specimen, etc. The net result is an extrapolation of data obtained under much more favorable and reproducible conditions.

Everyone learns that extrapolation is dangerous. A valid question, however, is how dangerous is it? Practical results may demand precision of only a few percent. However, the literature suggests that extrapolation may miss by considerably more than a few percent. For example, Schott [5] examined low-density PE resins using capillary viscometry, and found by extrapolation that log (η_0, Pa s) = 3.382 vs. an "experimental" value of 3.220, an error of 45%. ("Log" in this paper denotes log base 10.) Schott used a linearized form of the Cross model with a fixed exponent of 2/3 (see Table 1 for model forms). Reanalysis of the Schott data using modern non-linear methods and the Cross model gives an estimated value of $\log\eta_0$ of 2.73 ± 0.2 , where the ± is the 95% confidence interval. This exercise is shown in Fig. 1.

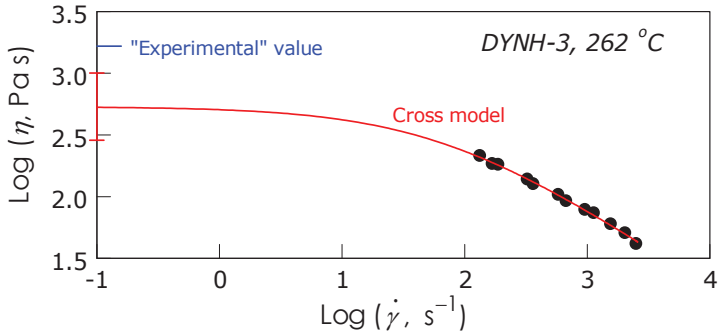


FIGURE 1. Illustration of extreme extrapolation where the estimated error in η_0 (bracket at left) fails to include the "experimental" value. Data are from Schott [5]; used by permission of Springer-Verlag.

The lesson here is quite extreme, and arguably picked for that reason. However, it illustrates a practical problem: given some data, people want η_0, and will go to extremes to obtain a value.

Empirical Models

Empirical, generalized-Newtonian-fluid models abound. A partial list if these is provided in Table 1. Of course, some "fit" the data better than others; the best ones are logically preferred on the seemingly reasonable assumption that the better fit will persist at unreachably low shear rates. However, the better fit conveys a penalty; the prediction band for the estimate of η_0 may be so small that it will not include the real value. Because the data are often gathered using a rate or frequency "sweep," the points are not independent, giving a curve that is too smooth. The resulting low random error will contribute to the unrealistically narrow confidence interval with a "good-fit" model. Simply gathering more closely space points will have a similar effect.

Fitting of Data

Data can be gathered either using oscillatory or steady shear. One does not need to invoke the Cox Merz rule; the value of η_0 should be the same for either. Generally gathering $|\eta^*|$ data is easier. Because the viscosity values can vary over a wide range, it can be important to fit models to the logarithm of the data. This is also in accord with

the general observation that the variance is more independent of frequency if the log transform is done. Models with a large number of parameters (e.g., 4) can be difficult to fit. The result can be strong parameter interaction and high error in the parameters. Thus the advantage of a slightly better fit, i.e., lower standard error of estimate (SEE), can result in an inferior estimate of η_0.

TABLE 1. List of Models for Describing Generalized Newtonian Behavior

Parameters	Model Name	Equation [b]	Code
2	Bueche-Harding	$y=1/(1+x^{3/4})$	BU
	DeHaven [c]	$y=1/[1+(xy)^2]$	DH
	Eyring	$y=(\sinh^{-1}x)/x$	EY
	Ferry	$y=\left(-1+\sqrt{1+4x}\right)/2x$	FY
	Spencer Dillon [d]	$y=\exp(-xy)$	SP
3	Adams-Crane	$y=1/(1+x^{1/a})^a$	AC
	Carreau	$y=1/(1+x^2)^{(1-n)/2}$	CA
	Carreau type	$y=1/(1+x)^{1-n}$	CA2
	Cross	$y=1/[1+x^{(1-n)}]$	CR
	Ellis [d]	$y=1/[1+(xy)^{(\alpha-1)}]$	EL
	Sutterby	$y=[(\sinh^{-1}x)/x]^{1-n}$	SU
4	Sabia [e]	$y=1/(1+x^2)^{(1-n)/a}]^{a-y}$	SA
	Vinogradov	$y=1/[1+ax^{(1-n)/2}+x^{1-n}]$	VN
	Generalized rate	$y=1/(1+x^a)^b$	GR
	Generalized stress	$y=1/(1+(xy)^a)^b$	GS

[a] Parameters include the scaling parameters η_0 and $\dot{\gamma}_0$, and dimensionless parameters n, a and b, as needed.

[b] $y=\eta/\eta_0$ or $|\eta^*|/\eta_0$; $x=\dot{\gamma}/\dot{\gamma}_0$ or ω/ω_0. The product xy is the reduced shear stress.

[c] Can be written in explicit form.

[d] No explicit form, except for special cases. Converted shear rate (frequency) to shear stress to use. (Some statistical issues with this step.)

[e] Convergence difficulties with this model even with Simplex method.

One interest is the distribution of results on fitting real data. Given diverse sets of data, it can then be asked if there is a pair of models from this list that will always bracket the actual value of η_0. Of course, to answer this question, the measurement of the actual value of η_0 must be addressed. The handling of sets gathered over a limited frequency or shear-rate range is also an important consideration.

EXPERIMENTAL

Materials

To make any headway on the problems addressed in the Introduction, polymers of very high stability must be chosen. Because stability is enhanced by low temperatures, amorphous polymers with low glass-transition temperatures were preferred. Reasonable choices given these restrictions include PDMS and PIB. For the former, an SE-30 resin was chosen; it was originally supplied by GE. For the PIB, a Vistanex LM-MS from Exxon Chemical was used. Both of these were in the form of clear, unfilled resins; both are chemically very stable. The molecular weights of each were measured by GPC calibrated with PS standards. For PIB, the results were M_n = 23 kDa and M_w = 53 kDa, while for the PDMS the results were 422 and 646 kDa for M_n and M_w, respectively. The absence of crystallinity was confirmed using DSC. IR spectroscopy failed to detect any additives.

Measurements

Two rheometers—an ARES and an AR-G2—were used to gather data. The temperature was held at 25 °C, which is very close to the average room temperature in the lab. Generally, data were gathered using frequency sweeps, both with increasing and decreasing frequency scans. For one run using PDMS, determinations were made at random frequencies using a fresh loading at each frequency. "True" values of η_0 were found using constant-rate experiments at very low stresses on the AR-G2, or oscillatory measurements at very low frequencies. These runs often lasted for days. Before every run on the AR-G2, the bearing was "mapped" to correct for slight bearing friction irregularities.

RESULTS AND DISCUSSION

Distribution of Predicted η_0 Values

Figure 2 shows the η_0 predictions using a truncated set of PDMS data, also shown. The "real" value is shown as a dotted line in Figure 2b..

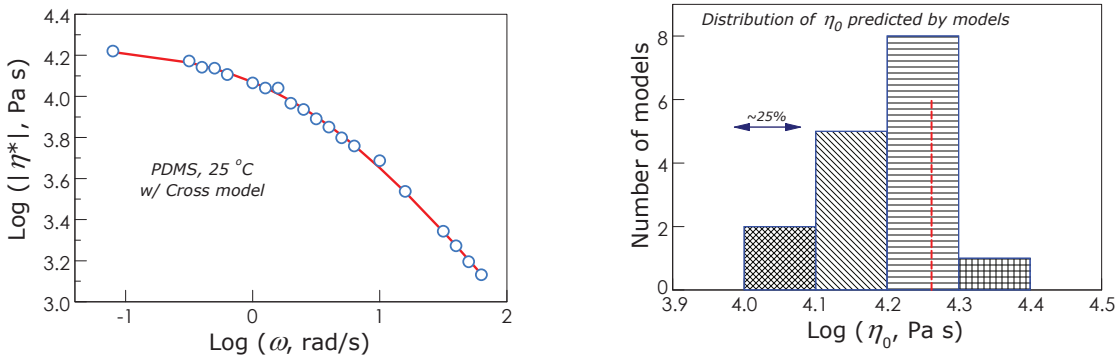


FIGURE 2. (a) Truncated PDMS data set used for determining η_0. Frequencies shown were run at random with a fresh loading for each frequency; thus, they are truly independent observations. (b) Histogram of log η_0 values found using the models listed in Table 1. The vertical dotted line is the "true" value measured at very low frequencies.

As can be seen, the predicted value η_0 of can be considerably off, given a particular model. Rather than pick the "best" model, which may give the best estimate for this material, but not others, it seems preferable to search for a pair of models that will surely bracket the real value, and possibly a model that can be used in an iterative fashion to provide a series of estimates that can in themselves be used to produce a better estimate of the true value.

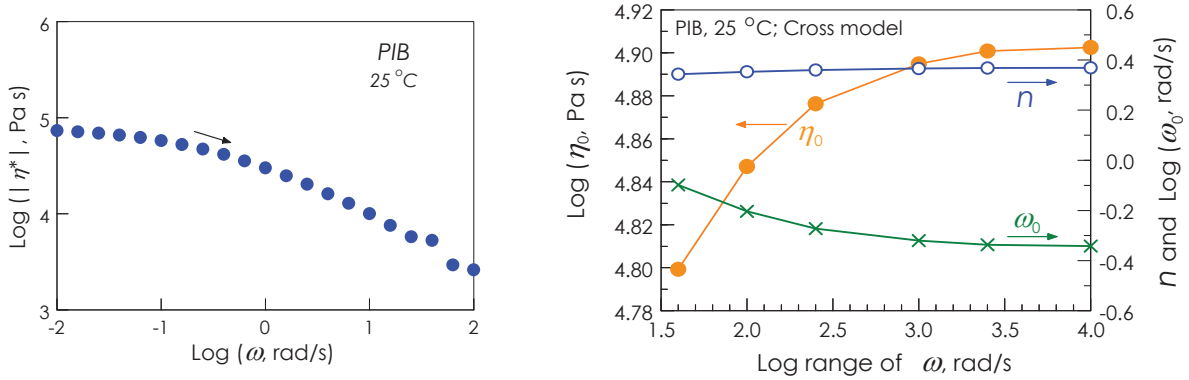
Bracketing Using Pairs of Models: PIB

Bracketing of PDMS was reported at the 2012 International Congress on Rheology. It was found that a reliable pair consisted of the Carreau model for the low end (4.213), and the Adams-Crane model (4.294) for the high end, regardless of the degree of truncation. By including more low-frequency data, the bracket was narrowed. Here, tests using polyisobutylene (PIB) data are described.

PIB resins are much more difficult to work with than PDMS; thus, some short cuts were needed. Typically, a frequency sweep down was followed by a frequency sweep up, followed by constant-rate runs in the range 0.01 to 0.001 s^{-1}. These data are shown in Fig. 3a, which importantly shows that the "Newtonian" region has not been reached. Analysis with the Cross model is depicted in Figure 3b, which demonstrates the huge variation of its three parameters with truncation of the data set, although the values of η_0 seem to approach a limiting value as more and more of the low-frequency data are included. Extrapolation of these results to an infinite number of decades yields a log η_0 value of 4.903 ± 0.003. (All residuals were in the 4th decimal place.)

While this process appears to be a convenient method of finding η_0, there were some disturbing observations. Steady-state shear measurements using the same loading exhibited an upward trend as the shear rate was decreased to 0.001 rad/s. In another test with PIB, low-frequency (0.01 to 0.003 rad/s) measurements were taken while decreasing the stress amplitude from 4 to 0.4 Pa. Without exception, the results showed an increase in $|\eta^*|$ with decreasing stress. These observations suggest that PIB develops some structure if the stress is exceedingly low. (For comparison, gravitational stress on a 1-mm-thick film of PIB will be around 9 Pa s.) If this is the case, then η_0 becomes ill-defined in terms of the models shown in Table 1.

Does the CA-AC pair of models bracket the value of 4.903? With the full data set, the lower end of the bracket (CA model) was 4.898, while the upper end (AC model) was 5.026. So, as with the PDMS data, the "real" value of η_0 was safely bracketed.



(a) (b)

FIGURE 3. (a) Example PIB data found using an increasing-frequency sweep. (b) Trends of Cross-model parameters from analysis of truncated sets of the PIB data shown in Fig. 3b. See Table 1 for definitions of the parameter symbols

CONCLUSIONS

While the empirical generalized Newtonian models commonly used by rheologists are convenient for characterizing the steady flow properties of polymer melts and solutions, it must be kept in mind that the polymer behavior is not prescribed by the model and may even be poorly described by the model. The limiting viscosity at zero stress may not exist; even if it does, finding its value may be imprecise or impossible with present methods. While it can be argued that 10% or even 20% is good enough, that sort of precision may well be inadequate when comparing similar materials with, say, different processing characteristics [1].

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