Examination of a Master Curve Method
of Characterizing Steady-State Flow of Polymers

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Synopsis

Master curve methods or superposition techniques are rather widely used for characterizing the steady-state flow behavior of polymers.   One method, developed by Sabia,[1] is examined with respect to its applicability and limitations.   In the original development of the method, it was assumed that a universal curve (master curve) exists.   Based on this, a theoretical explanation was presented for the sample parameters.   Such explanation became dubious because experimental evidence was found later to nullify the master curve assumption.[2,3]   In this paper, Sabia's method is treated as a curve-fitting procedure to represent observed data.   In order to do so, the shear rates of observation must be limited to two or two and a half decades.   Also, the range of shear rates are defined from 1 to 1000 sec.[-1]   The results of curve fitting and molecular interpretation of the parameters are presented.

INTRODUCTION

Several years ago, Sabia[1] devised a master curve method to characterize the steady-state flow curves of polymers.   In this method, it was assumed that for a given type of polymer, for example, polyethylene, a fixed shape could be assigned to the flow curves irrespective of sample.   Later it was found that the shape of the curve was variable, depending upon the molecular weight distribution.[2,3]   Therefore, the basic question is the validity of the master curve concept with particular attention to Sabia's polydispersity parameter, K_d.   In this work, Sabia's method is examined with respect to the meaning of the parameters, to its applicability and limitations, and to the confidence limits of measurements.   Linear polyethylenes are used as examples.

CHARACTERIZATION METHODS FOR STEADY-STATE FLOW

The most widely used technique for steady-state flow measurement is the melt index.[4]   It provides a relative measure of molecular weight and flowability.   However, melt index being a single value, it ignores the non-Newtonian nature of flow.   Neither can it distinguish differences in molecular weight distribution.   The point is illustrated schematically in Figure 1, where the examples shown are steady-state flow curves of hypothetical resins
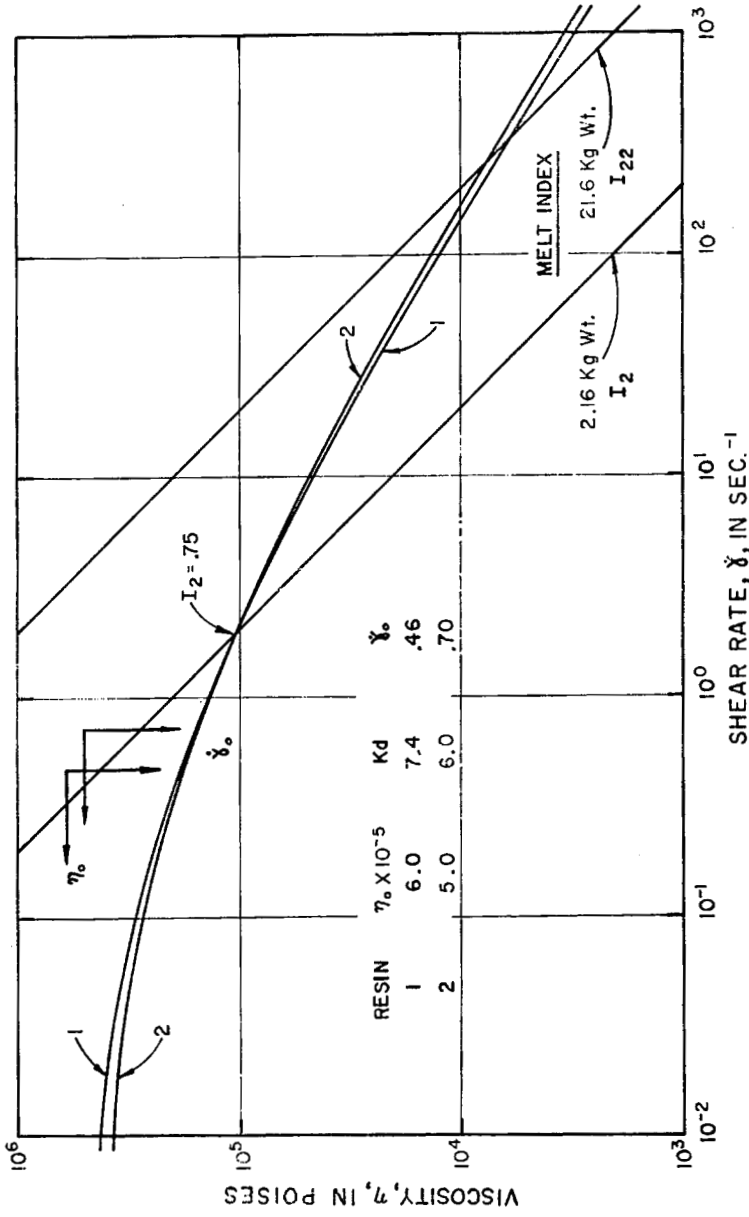
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Fig. 1. Schematic representation of steady-state flow curves, melt indices, and flow parameters.

1 and 2. These resins have the same melt indices, which are shown as the intercept of the constant stress line and the flow curves. The viscosities at other stress levels are different. In general, the dependency of viscosity on shear, the so-called "shear sensitivity," is another parameter needed for characterization. By measuring melt indices at two different stress levels, for example, with weights of 2.16 and 21.6 kg, the shear sensitivity value may be obtained (see Fig. 1). This approach has a drawback, however. The two points on the graph can provide only a linear relationship, "the power law flow," whereas the flow behavior is shown to be a curve.

If a capillary rheometer is used, the flow curves in the shear rate range between 1 and 1000 sec^{-1} can be observed for practically all commercial polyethylenes. The specific version of Sabia's method referred to here employs a capillary rheometer. It includes not only the treatment of the flow curves but also the procedure for the measurements. That is, Bagley's[5] and Rabinowitsch's[6] corrections are not made. Instead, an instrument and a particular die geometry are used. In this regard, the method may be interpreted as an expanded version of melt indices over the shear rate range mentioned above.

SABIA'S METHOD OF CHARACTERIZATION

Procedure

A gas pressure capillary rheometer, often referred to as the CIL viscometer,[5] is used with a die having a specific geometry, i.e., diameter 0.043 in., length 0.835 in., and an 80° included angle at the entrance. A cylinder of nitrogen gas is used. Proper care is taken in the packing and melting of the polymer in the rheometer barrel; several minutes are allowed to equilibrate the sample to the furnace temperature of 190°C. The molten polymer is extruded at constant pressure, starting with high pressure and proceeding to low. With high molecular weight polymers, the results are different if the measurements are started from low pressure. The difference is not only in the position of the observed flow curve, but also in its shape. For the purpose of curve fitting, therefore, it is extremely important to adhere to the same operating procedure.

The weight flow rates are measured by cutting and weighing the extrudate. Normally, 10 to 12 data points are taken. For example, with very high molecular weight polymer, the pressure range is 3000 psi down to 750 psi, obtained in 250-psi increments. With low molecular weight polymer, the range may be from 2000 psi down to 100 psi, in smaller increments, e.g., 200 psi.

Adequate care must be taken in stabilizing the sample. The entire measurements can be done with a single charge of about 20 g. Viscosity and shear rate are calculated in the usual manner from the observed data.

With experience and strict adherence to the operating procedure, the shape of the flow curve (log η vs. log $\dot{\gamma}$) is extremely reproducible, but the position of the curve is slightly shifted with each freshly charged sample.
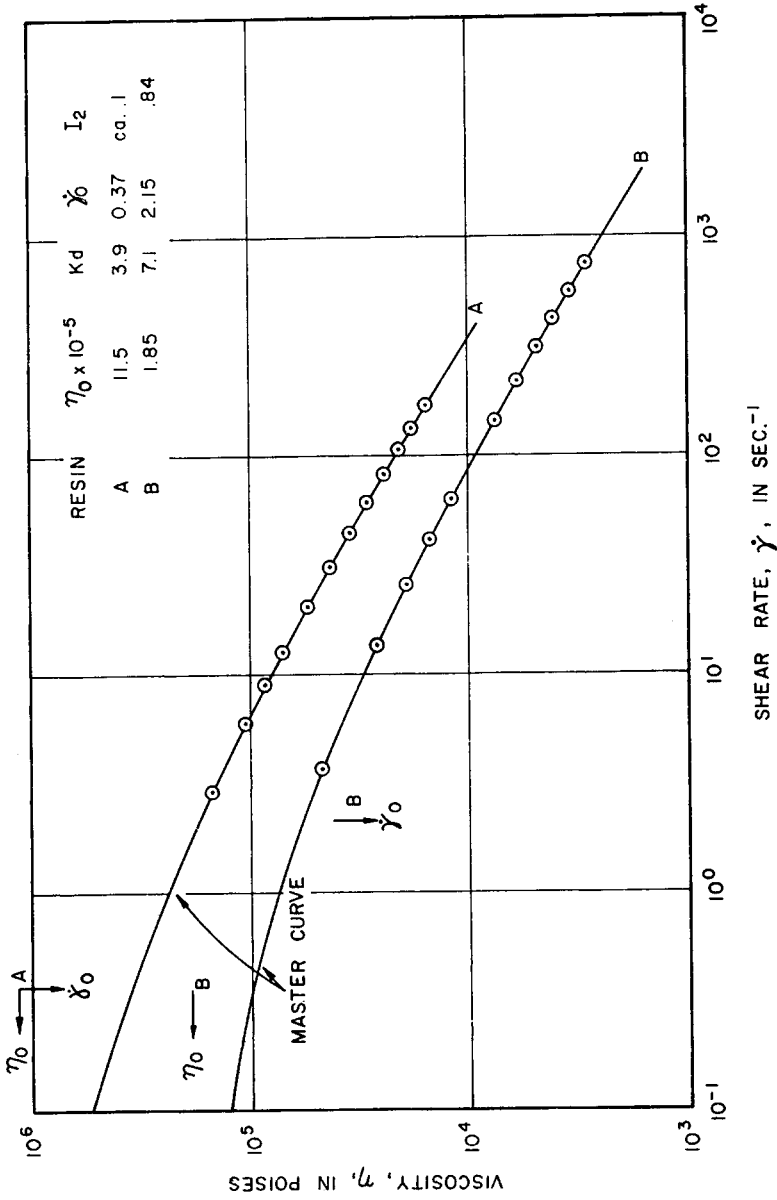
Fig. 2. Examples of capillary flow data and two-parameter curve fitting—perfect fit.

TABLE I
Comparison of Exact and Approximate Curve Fitting

Resin	Exact curve fitting (present method)			Approximate curve fitting		
	$\eta_0 \times 10^{-5}$	K_d	γ_0	$\eta_0 \times 10^{-5}$	K_d	γ_0
C	10.5	7.5	0.215	7.2	6.1	0.43
D	1.59	3.4	5.5	2.5	4.7	2.2

There seldom is a random scattering of data points, and all points can be connected with a smooth curve (Fig. 2). Therefore, discussion on the error of each point is irrelevant. Rather, the position of the curve and its reproducibility must be treated as a measure of error. This subject will be treated later as the error in determining the curve-fitting parameters. The solid curves shown are master curves:

$$\log (\eta/\eta_0) = (\eta/\eta_0 - a)\log [1 + (\dot\gamma/\dot\gamma_0)^b] \qquad (1)$$

Where $a = 2$, $b = 1/3$, and η_0 and $\dot\gamma_0$ are adjustable parameters of the curve fitting.

With some polyethylene samples, the observed curves do not fit the master curve exactly, unless one or two data points are ignored either at the highest shear rates or at the lowest shear rates. These deviations from the master curve are real, although very slight if an equal deviation is allowed for all data points (Fig. 3). In these cases, the curve fitting depends upon whether the highest shear rate points or the lowest shear points are ignored. The values of η_0 and $\dot\gamma_0$ thus obtained are different for these two cases. In the method described here, emphasis is placed on the interpretation of higher shear behavior, and a choice is made to ignore one or two of the low shear points if the entire curve (observed data points) cannot be fitted exactly. Since this is an arbitrary choice, it should be understood as a part of the instructions for the procedure. In Table I, values of η_0, $\dot\gamma_0$, and K_d from the exact curve-fitting method, which deemphasizes the low shear points, are compared to an approximate curve-fitting method which gives equal weight to all data points. There are significant differences between the two ways of curve fitting.

Summarizing at this point, Sabia's master curve method defined here is a curve-fitting procedure to represent observed data. It provides two independently adjustable parameters, η_0 and $\dot\gamma_0$. Instead of these parameters, Sabia used η_0 and K_d, the latter being derived by a combination of η_0 and $\dot\gamma_0$. Meanings of η_0 and K_d are discussed in the following section.

Calculation and Significance of K_d

Once values of η_0 and $\dot\gamma_0$ are obtained by curve fitting, K_d can be calculated according to

$$K_d = (\eta_0^{1.294}\dot\gamma_0)^{-1} \times 10^8. \qquad (2)$$

The K_d values for commercial polyethylenes vary from somewhat less than 2 to more than 12.
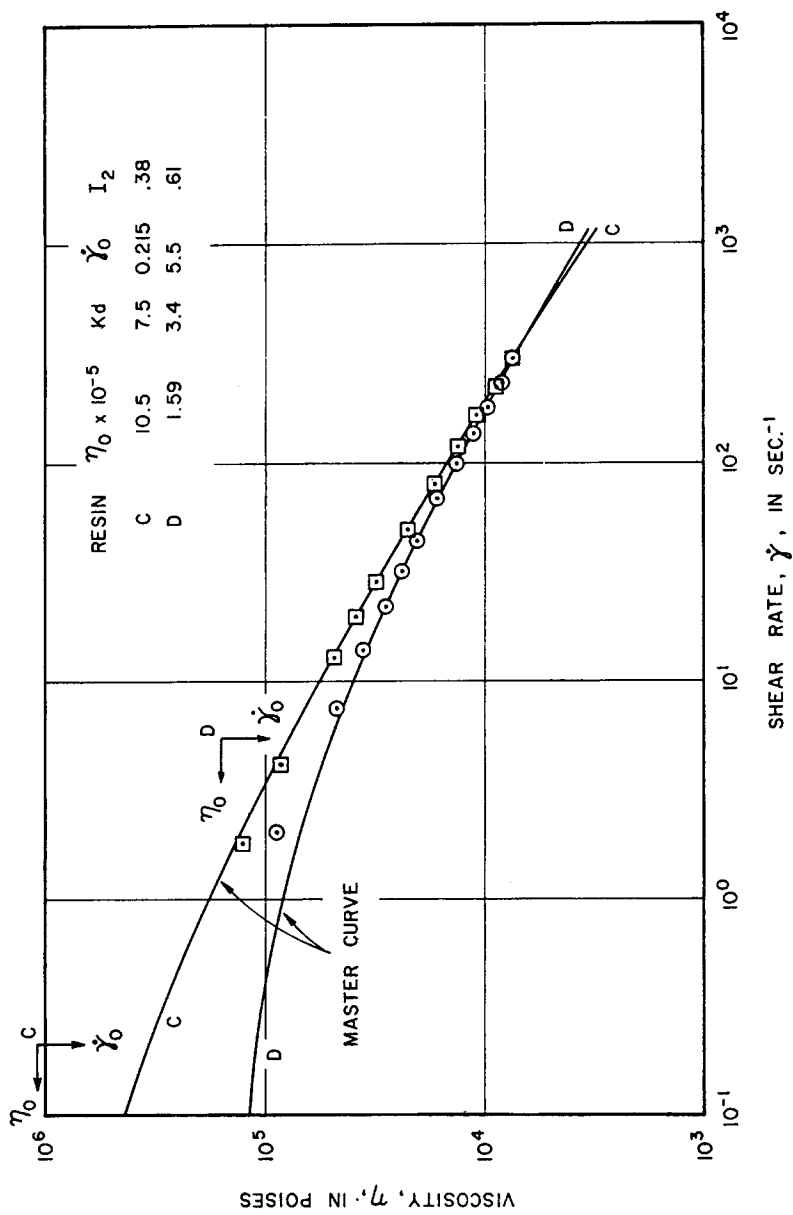
Fig. 3. Examples of capillary flow data and two-parameter curve fitting—imperfect fit.

Sabia explains the significance of K_d in the following manner[1,7]:

$$^1/\dot{\gamma}_0 = \tau = K' \eta_0 \bar{M}_r \qquad (3)$$

where τ is a characteristic relaxation time of a given polymer, K' is a universal constant, and $\bar{M}_r$ is the average molecular weight defined by the equation. Exactly what type of average molecular weight is assigned to $\bar{M}_r$ is not known. Assuming that $\bar{M}_r$ is different from the weight-average molecular weight, $\bar{M}_w$, Sabia defined a polydispersity parameter, $\bar{M}_r/\bar{M}_w$, in analogy with the more commonly used $\bar{M}_w/\bar{M}_n$.

If one assumes that

$$\eta_0 = K\bar{M}_w^{3.4}, \qquad (4)$$

Sabia's polydispersity parameter is derived from eqs. (3) and (4), i.e.,

$$\bar{M}_r/\bar{M}_w = \left(\frac{1}{K'\eta_0\dot{\gamma}_0}\right)\left(\frac{K}{\eta_0}\right)^{1/3.4} = K\left(\frac{1}{\eta_0^{1.294}\dot{\gamma}_0}\right). \qquad (5)$$

Hence,

$$K_d = 1/K(\bar{M}_r/\bar{M}_w) \times 10^8 \qquad (6)$$

where K is a universal parameter for a given polymer type, such as polyethylene. Thus, the parameter K_d, is precisely defined with respect to the operating procedure of the experiment and subsequent data treatment. However, the meaning of K_d in terms of the molecular makeup is not clear for the following reasons: first, what type of average molecular weight is to be assigned to $\bar{M}_r$ is not known; second, concerning eq. (1) and the curve fitting parameter η_0 is not a low-shear Newtonian viscosity, but an adjustable parameter in the particular curve-fitting procedure defined here; third, the relationship of eq. (4) is not established with commercial polyethylenes. Therefore, the molecular explanation for K_d must be found empirically.

Rewriting eq. (2) as

$$\dot{\gamma}_0 = (\eta_0^{1.294} K_d)^{-1} \times 10^8 \qquad (7)$$

tells us that an approximate universal relationship exists in fitting the master curve, that is, the reference shear rate, $\dot{\gamma}_0$, is proportional to the 1.294th power of the reference viscosity, η_0. More precisely, however, the approximate relationship must be modified by a factor K_d, which varies independently of η_0. As shown in Figure 1, the behavioral aspect of K_d is a measure of "shear sensitivity" for the range of shear rates defined previously. The larger the K_d value, the more "shear sensitive" is the flow behavior.

The molecular significance of K_d is shown in the following examples. First, in Figure 4, K_d is plotted against $\bar{M}_n$ for ten samples of the same class of resin produced experimentally. These samples have varying melt indices, but all measurable with the usual weight of 2.16 kg. The approximately 95% confidence limits of K_d and $\bar{M}_n$ determinations are indicated by the cross. With no other average molecular weight nor their combinations could K_d be related in a meaningful manner.
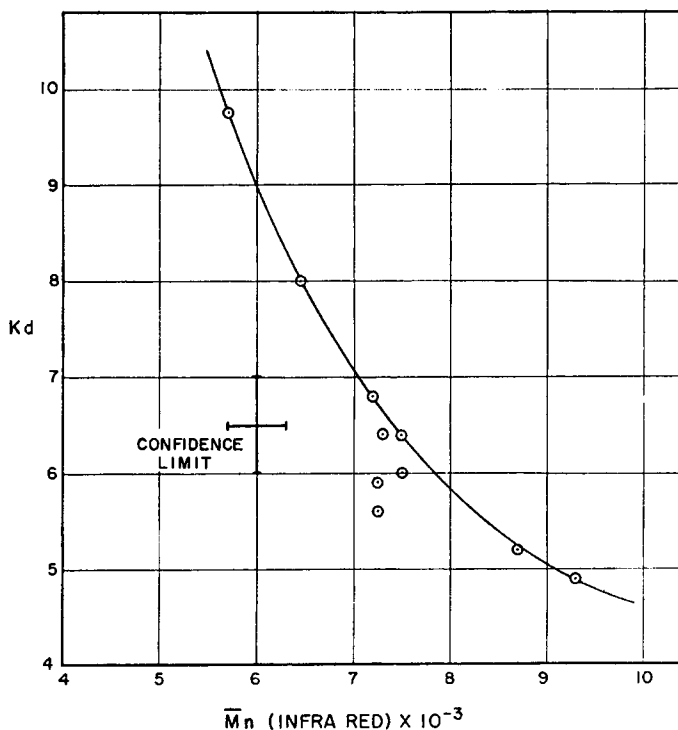
Fig. 4. Trend shown for polydispersity factor K_d with change of number-average molecular weight M_n.

A choice of $\overline{M}_n$ in the relationship may prejudice the issue, if it is interpreted that the flow has something to do with a colligative property. Rather, it probably means that the shear sensitivity, K_d, of the flow *in the shear rate range of the present interest* is related to the presence of low molecular weight fraction in analogy to $\overline{M}_n$, which is sensitive to the presence of such fraction. In Table II, K_d values are shown for blends having a varied amount of lower molecular weight resin and/or a linear polyethylene wax.

A trend is shown very clearly that increased amounts of low molecular weight component increase the value of K_d. These blends are prepared by mechanical mixing in melts. Such blends usually show different elastic

TABLE II

Flow Parameters η_0 and K_d of Blends Containing Low Molecular Weight Component

	Resin blend components			E/F	E/F/G		E/G
	E	F	G	65/35	50/30/20	45/25/30	50/50
η_0^a	1.5×10^8	2.4×10^3	3×10^{-2}	7.7×10^6	1.86×10^6	2.25×10^5	6.0×10^5
K_d	4.5	1.8	[b]	7.5	11.3	10.7	21.2

[a] At 190°C, in poises.
[b] A polyethylene wax, Newtonian flow.

TABLE III
Reproducibility of Flow Parameters η_0 and K_d

	Resin								
	H			I			J		
Melt index	ca. 5			ca. 0.4			HLMI[a] ca. 6		
Operator[b]	a	b	c	a	b	c	a	b	c
No. of runs	12	13	4	12	8	4	12	7	4
Period, months	13	13	4	13	13	4	13	12	4
$\eta_0 \times 10^{-4}$									
average	2.49	2.46	2.48	64	61.5	75.5	965	960	660
smallest	2.35	2.35	2.15	62	57	58	820	660	310
largest	2.59	2.55	2.75	67	65	108	1210	1280	860
K_d									
average	6.35	6.26	6.0	5.93	5.94	6.17	4.93	4.54	4.58
smallest	6.0	5.9	5.8	5.8	5.8	6.1	4.4	4.2	4.3
largest	6.0	6.6	6.2	6.3	6.1	6.3	5.5	5.0	5.2

[a] High load melt index with 21.6 kg weight.
[b] Different operator, different instrument, and different location.

responses from homogeneous material, e.g., die swell, melt fracture, etc. However, viscous responses of such blends are not detectably different from homogeneous materials. Sufficient care has been taken to achieve good mixing. The larger K_d values of blends are significantly well beyond the question of blend homogeneity. Although not shown here, homogeneous resins having a large amount of low molecular weight fraction are observed to have large K_d values.

Confidence Limits

One of the important considerations in characterization is the confidence limit of the data. Table III shows results of repeated measurements with three resins of different types. The confidence limits of the data are shown with the largest errors of the actual observation rather than with the usual expressions such as the standard deviation.

The errors in η_0 and K_d come from both experiment and curve fitting. The error in η_0 increases with the increase of molecular weight, i.e., J > I > H. The fact is inherent in the present master curve method; the observed flow curve of the higher molecular weight resin corresponds to the steep end, the right hand side of the master curve (Fig. 1), farther away from η_0, which is the left hand side of the extreme. For this reason, any small errors in data and curve fitting are magnified in η_0 values. On the other hand, K_d values have a much smaller error.

As has been stated earlier, the present method is a two-parameter and one-master-curve presentation of steady-state flow. The use of melt index and K_d is, therefore, equivalent to the use of η_0 and K_d. The use of melt index and K_d is preferable for two reasons: first, for the high molecular weight resins the melt index value is more reproducible than η_0; second, comparison of two resins having the same melt index and different K_d

TABLE IV
Estimated Newtonian Viscosities from Low-Shear Data and Extrapolation

Resin type	Example	Newtonian viscosity, poises		
		Cone plate[a]	CIL[b]	cone plate/CIL ratio
1	K	7.0×10^5	4.55×10^5	1.54
1	K'	2.8×10^5	1.9×10^5	1.47
2	L	7.52×10^5	1.62×10^5	4.64
2	L'	1.87×10^6	3.45×10^5	5.42
3	M	3.4×10^7	1.22×10^7	2.79
4	N	8.5×10^3	1.32×10^4	0.64
4	N'	8.9×10^3	1.45×10^4	0.61
4	N''	1.01×10^4	1.60×10^4	0.63
5	O	1.45×10^4	1.50×10^4	0.97
5	O'	1.75×10^5	9.20×10^4	1.90
6	P	7.6×10^3	5.3×10^3	1.43
6	P'	2×10^6	2.9×10^5	6.9
7	Q	4.8×10^4	4.4×10^3	10.9

[a] Estimated from low-shear data near 10^{-3}/sec.
[b] Extrapolated by the master curve from high-shear data.

is often more meaningful than the comparison of two resins having the same η_0 and different K_d. The reason is a practical one in that melt index is a universally accepted parameter, but η_0 of this method is not.

Limitation of Method

As has been emphasized already, the information obtained by this method is restricted to the shear rate range defined by the procedure. Extrapolating flow data with the master curve beyond the range of observation does not assure any degree of certainty. This is clearly illustrated in Figures 5, 6, and 7 with resins B, C, and D, where the range of observation is extended to as low a shear rate as 10^{-3}/sec with a cone-plate viscometer.[2,8] As is obvious, there is a substantial error if η_0 of this method is interpreted as the low-shear Newtonian viscosity, i.e., extrapolation with the master curve. This point is further illustrated in Table IV with 13 samples of seven different resin types; namely, the extrapolated η_0 values are compared with the Newtonian viscosities estimated from the low-shear flow curve by the cone-plate viscometer. There is as much as an order of magnitude difference when compared to the extrapolated η_0 value (sample Q).

DISCUSSION

The master curve method, which is one of the techniques of superposition, is rather widely used[1,7] for characterizing polymers. A tacit assumption is that for a given type of polymer, the steady-state flow curves have a prescribable shape. In general, this is not true. However, the master-curve method and superposition are used by allowing approximate curve fittings or by limiting the shear rate range of the observation. In the latter ap-
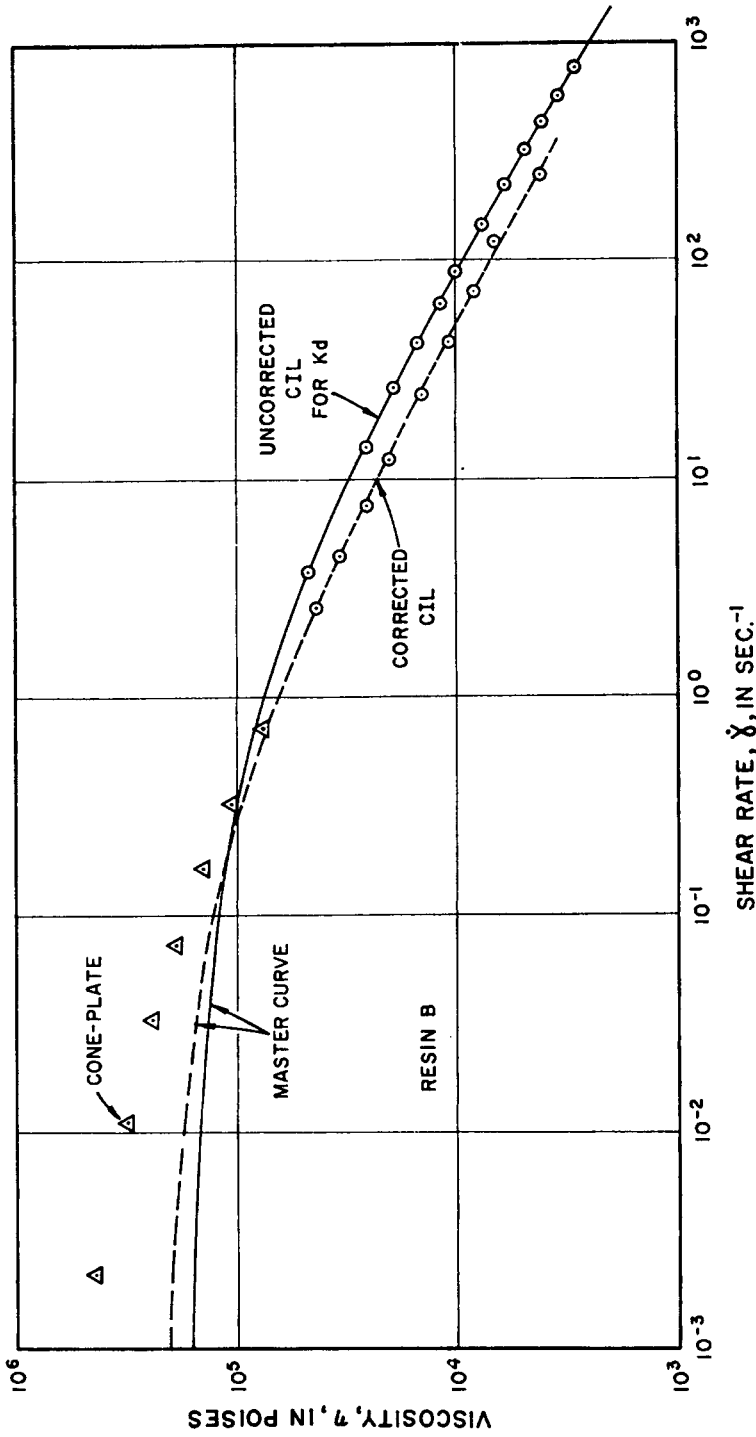
Fig. 5. Examples of capillary and cone-plate flow data showing inadequacy of two-parameter curve fitting—resin B.
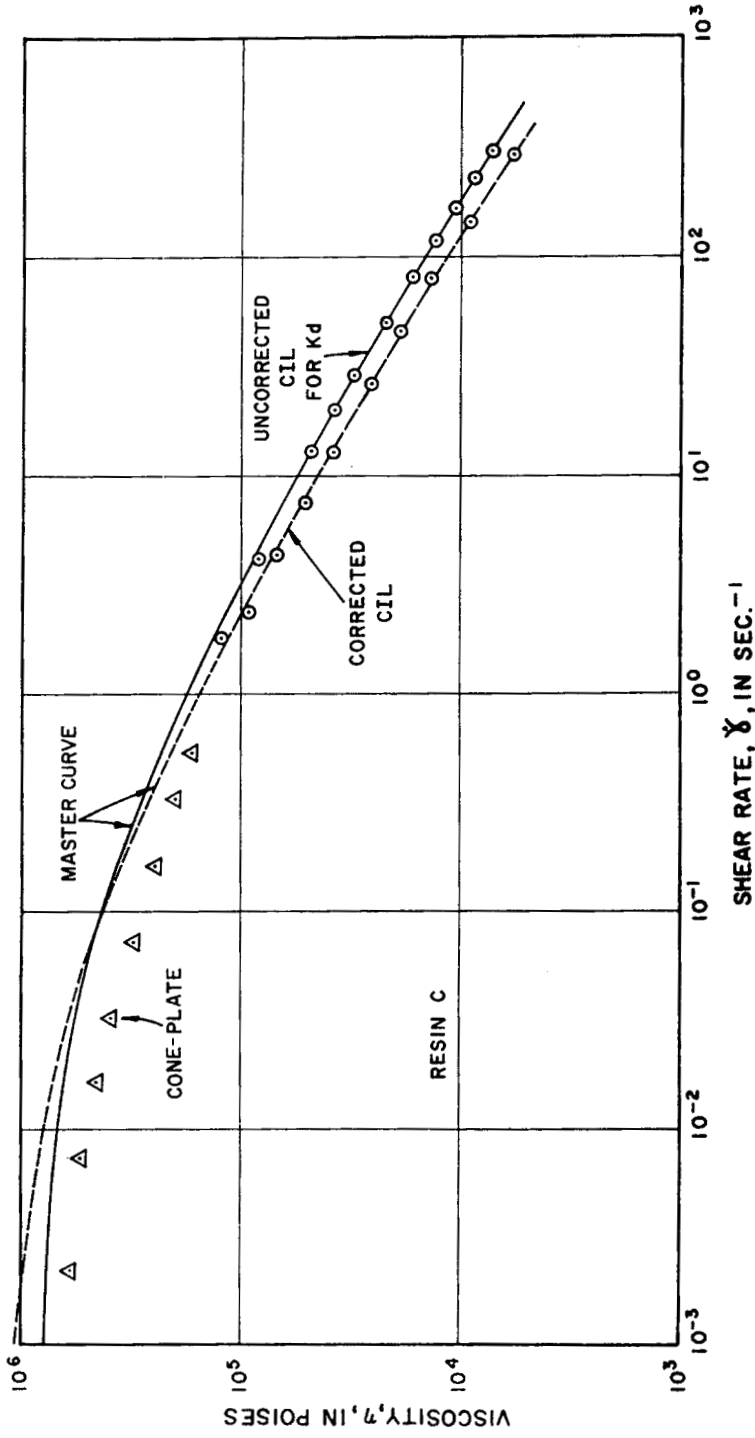
Fig. 6. Examples of capillary and cone-plate flow data showing inadequacy of two-parameter curve fitting—resin C.
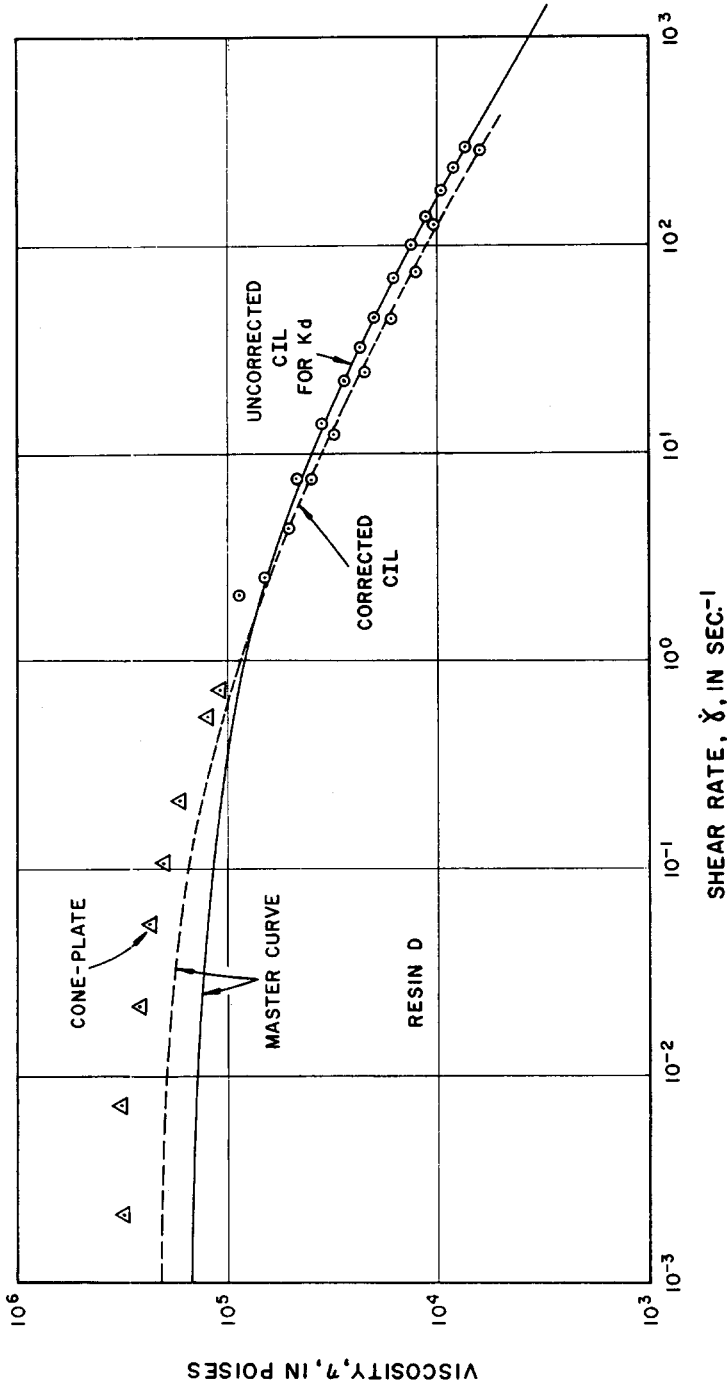
Fig. 7. Examples of capillary and cone-plate flow data showing inadequacy of two-parameter curve fitting—resin D.

proach, a precise curve fitting is possible. Sabia's method described here corresponds to such a procedure. From the curve fitting two independent sample parameters, η_0 and $\dot{\gamma}_0$, are obtained. Sabia transforms these parameters to η_0 and K_d. Since the curve fitting is strictly the method of representing the observed data, the meaning of these parameters must be associated with the observed ranges of shear rates. The parameters η_0 and $\dot{\gamma}_0$ define the position of the flow curves. If, instead, η_0 and K_d are used, η_0 is representing the viscosity level and K_d is a measure of "shear sensitivity," i.e., a manner of pseudoplastic flow. In this paper, use of melt index as the expression for the viscosity level is recommended, because it is universally accepted for polyethylenes. Either η_0 or melt index is, of course, an arbitrarily chosen expression for the molecular weight. The K_d parameter, on the other hand, is related to the relative amount of low molecular weight fraction. Evidence is presented with various blends and also with a relationship between K_d and $\bar{M}_n$. It means that in the shear rate range of 1 to 1000/sec, the manner of pseudoplastic flow of polyethylene is affected by the presence of low molecular weight fraction.

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