

Is There Any Universal Expression for Representing the Steady-State Flow Curves of Polymers?

A master curve representation of the steady-state flow curve has been rather in common use since Bueche and Harding devised the method.¹ Sabia² provided a particular mathematical expression for the master curve:

$$\log (\eta/\eta_0) = (\eta/\eta_0 - a) \log [1 + (\dot{\gamma}/\dot{\gamma}_0)^b] \quad (1)$$

where η and $\dot{\gamma}$ are the observed viscosity and shear rate, respectively. He assigned $a = 2$ and $b = 1/3$ for linear polyethylene. This equation reduces to

$$\eta = \eta_0 \text{ at } \dot{\gamma} \rightarrow 0$$

and to

$$\eta/\eta_0 = (\dot{\gamma}/\dot{\gamma}_0)^{-ab} \text{ at } \dot{\gamma} \gg \dot{\gamma}_0$$

with $\eta/\eta_0 \ll a$ and $\dot{\gamma}/\dot{\gamma}_0 \gg 1$. The former limit corresponds to the low-shear Newtonian flow and the latter limit, to the high-shear "power law flow." The parameter $\dot{\gamma}_0$ is the intersection of two lines, $\log (\eta/\eta_0) = 0$ and $\log (\eta/\eta_0) = -ab \log (\dot{\gamma}/\dot{\gamma}_0)$.

The master curve method assumes the presence of a universal curve; it is a two-parameter representation, with η_0 and $\dot{\gamma}_0$ as the parameters. Sabia's equation further defines a smoothly shaped curve traversing between the two limits. The slope of the high-shear limit is defined as a constant, $-ab = -2/3$.

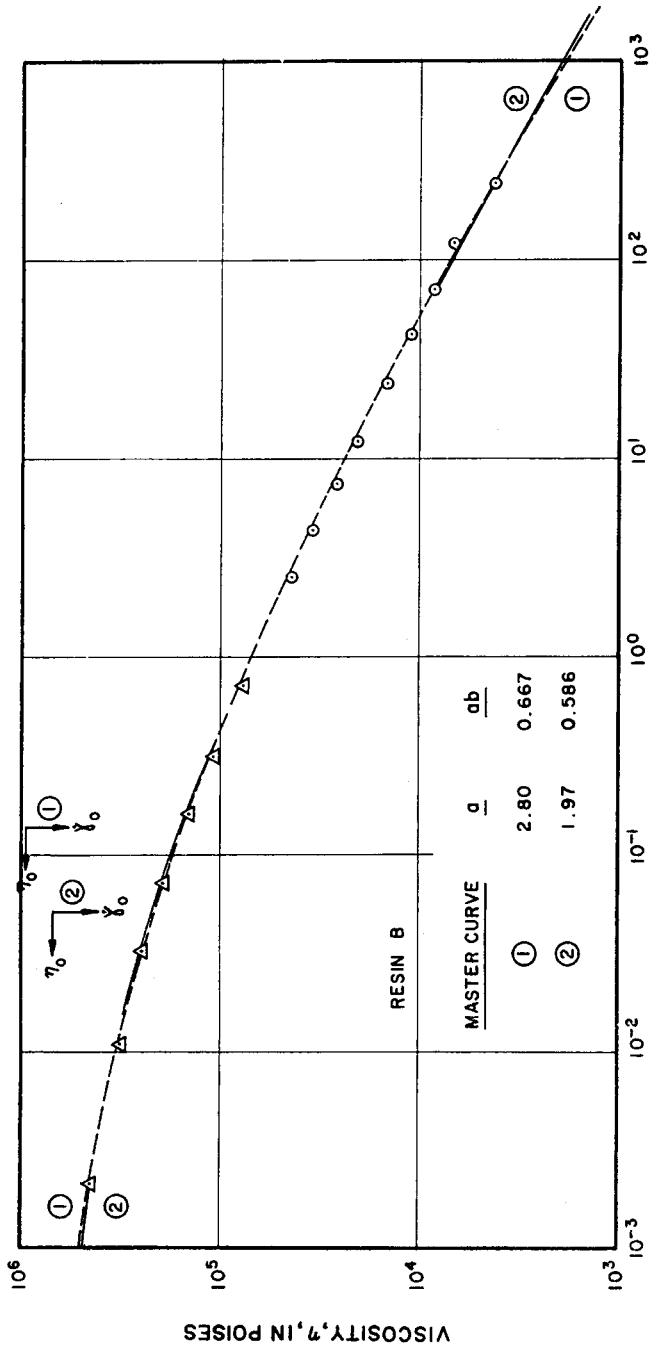
Later, evidence was found to nullify the master curve concept.^{3,4} In order to represent each differently shaped curve for each sample, therefore, the following modification was made of Sabia's treatment. In addition to the two adjustable parameters η_0 and $\dot{\gamma}_0$, a was also made to be adjustable. However, the high-shear limiting slope, ab , was kept constant, i.e., $2/3$ for linear polyethylene and $3/4$ for polypropylene.^{3,4} The variable a provided a family of an infinite number of curves, thus enabling representation of most of the observed curves. This method may be called a three-parameter representation. However, there were exceptions, which required the variable ab .

At this point, a question may be asked whether there is a universal expression for representing the steady-state flow curves. If there is, how many adjustable parameters are required, three or four?

In Figures 1, 2, and 3, the flow curves of linear polyethylenes are shown, where it is very difficult to judge whether the three-parameter or four-parameter representation gives a better fit. A set of parameters given for curve 1 corresponds to the three-parameter representation, i.e., $ab = 2/3$; and another set for curve 2 corresponds to the four-parameter representation. Noteworthy is the fact that two differently shaped curves can represent the observed data almost equally well. When a molecular theory of flow based on a model is tested against observed data, the first requirement is that the theoretical curve fit the data within the error of measurements. Although this is the necessary requirement, it does not seem to be a satisfactory condition to demonstrate the validity of the assumed molecular model. There is a possibility that another theory based on a different model may result in the same curve or even a different curve and that it represents the data equally well.

In the three flow curves of linear polyethylenes shown in Figure 4, the high-shear limiting slope ab is not $2/3$. Combining the examples of Figures 1-4, it is obvious that at least four independently adjustable parameters are needed for the "universal representation" of the flow curves.

The cases presented in Figure 5, again with linear polyethylenes, show the importance of extending the measurements to sufficiently high shear rates. This was done by using the Instron capillary rheometer. Quite different results may be obtained in curve fitting when the Instron data are included.



SHEAR RATE, $\dot{\gamma}$, IN SEC.⁻¹

Fig. 1. Three-parameter and four-parameter curve fittings.

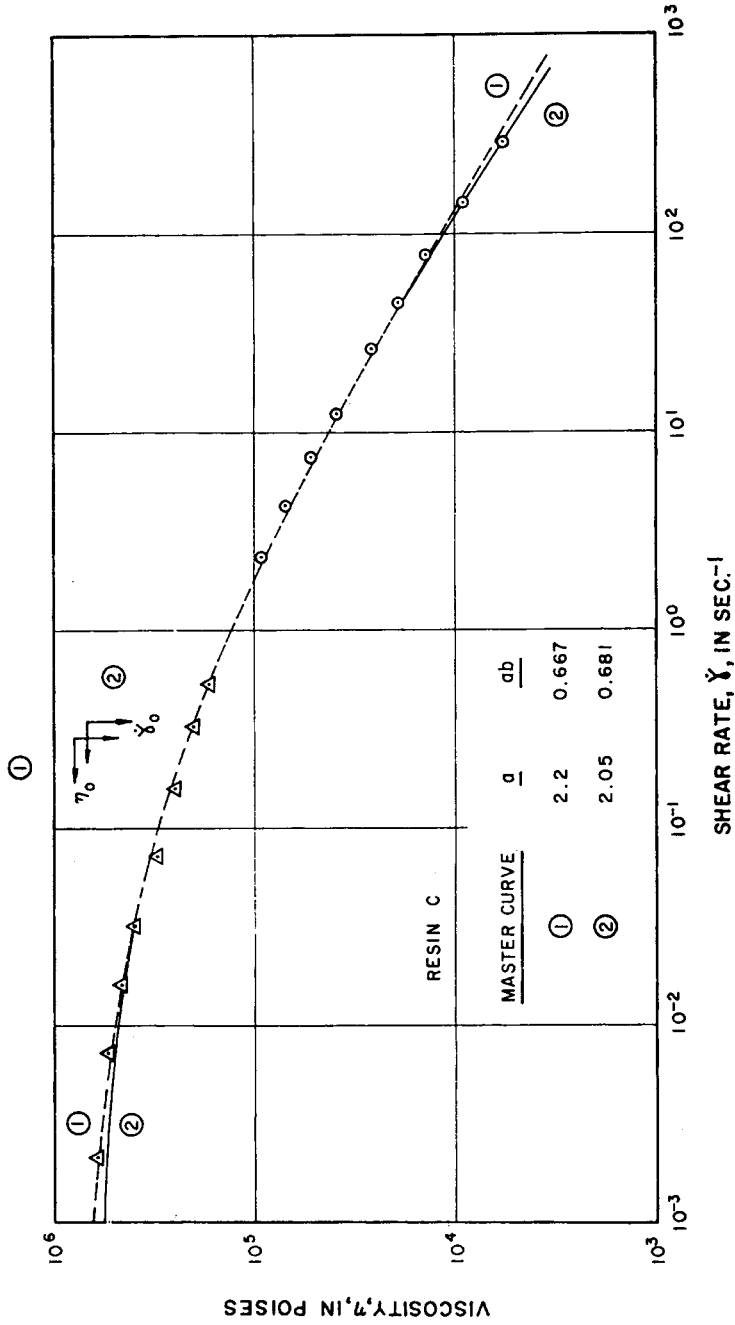


Fig. 2. Three-parameter and four-parameter curve fittings.

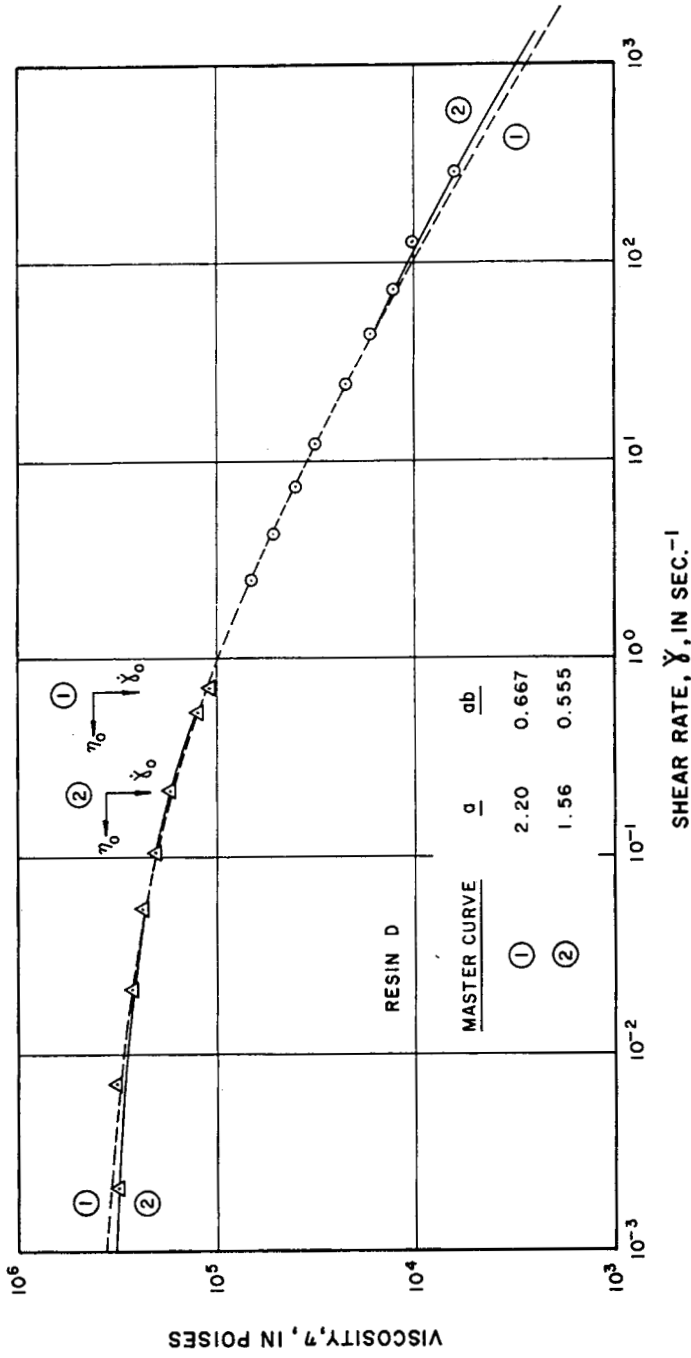


Fig. 3. Three-parameter and four-parameter curve fittings.

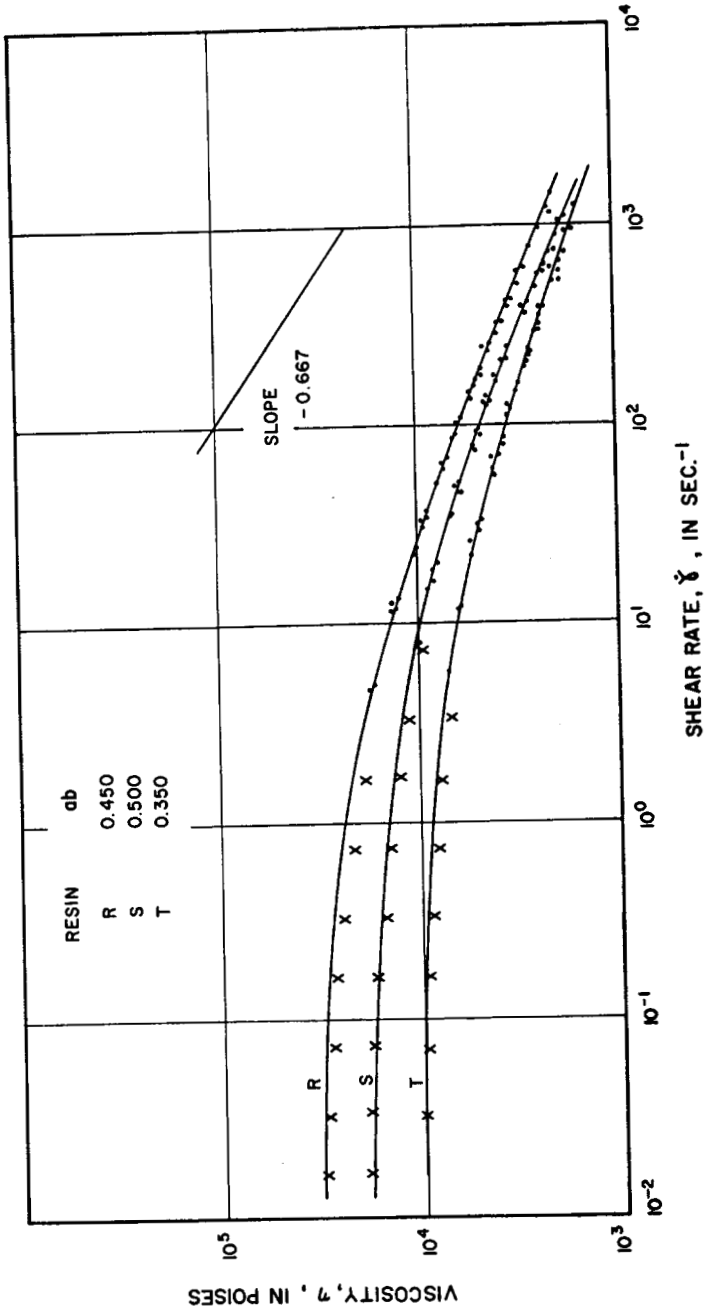


Fig. 4. Examples of flow data showing the high-shear limiting slope not equal to $2/3$.

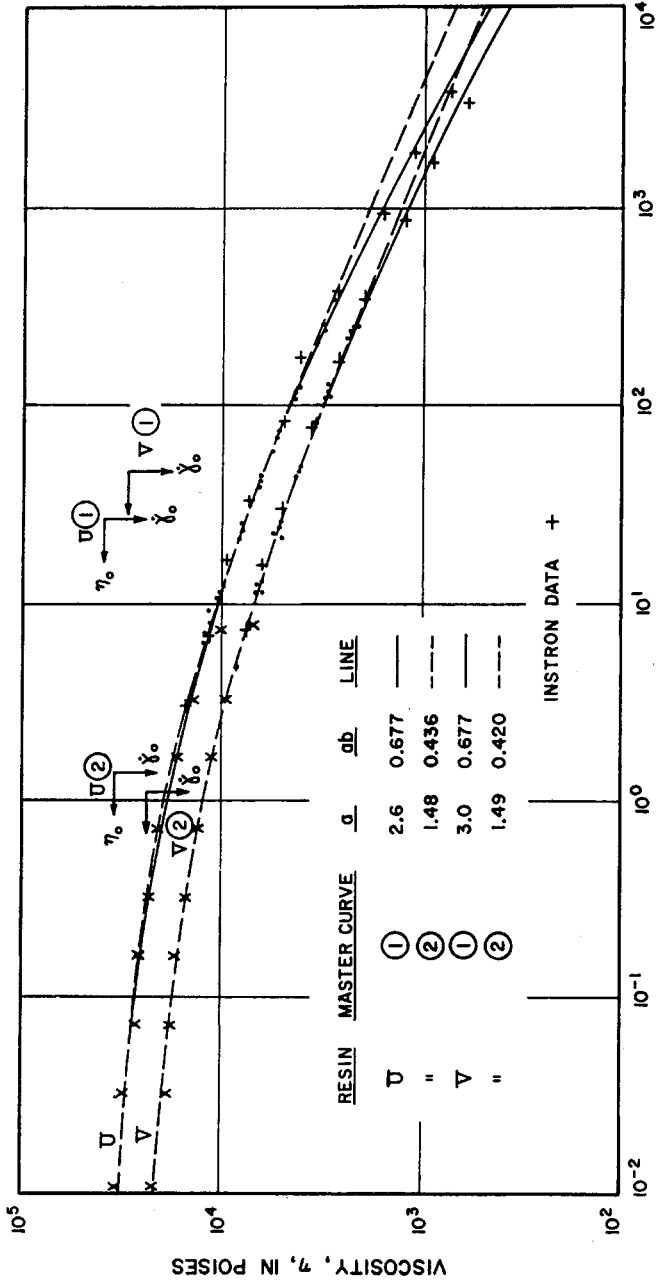


Fig. 5. Examples of flow data showing determination of the high-shear limiting slope.

Thus far, all examples discussed are flow curves having a smoothly changing slope. On the other hand, there are examples which do not follow the pattern. They are polymers containing small crosslinked particles^{3,5} and a blend of narrow fractions whose molecular weights are sufficiently different.⁶ In the flow curves of the above examples, inflection points are found. It appears that no universal expression can be found for curve-fitting of all these examples. It is this writer's opinion that there is no universal expression for representing the steady-state flow curves of all polymeric systems. Just as there are infinite variations of composition, there will be infinite variations in the shapes of the flow curves.

References

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