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Empirical Correlation of Flow Properties of Poly(vinyl Chloride)*

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Synopsis

Empirical correlations of flow properties of poly(vinyl chloride) were made using data reported by a number of investigators. Correlation was made by plotting the reduced variable viscosity η/η_0 versus $(\eta_0\dot{\gamma}\bar{M}_w)/(\rho RT)$ or $(\eta_0\dot{\gamma}\bar{M}_w^{0.5})/(\rho RT)$ for unplasticized PVC and versus $(\eta_0\dot{\gamma}\bar{M}_w^{0.5})/(\rho RTW_2^a)$ with polymer concentration, W_2, for PVC containing plasticizer.

INTRODUCTION

A recent article has reviewed the work of numerous authors on determining flow properties of poly(vinyl chloride), PVC.[1] There appears to have been no attempt to correlate, on an empirical or other basis, the variety of experimental results reported. This paper considers such correlations both for PVC and PVC plus plasticizers.

CORRELATION OF FLOW PROPERTIES OF UNPLASTICIZED PVC

From Bueche's theory,[2] a master curve should be obtained from a logarithmical plot of the reduced viscosity, η/η_0 versus $(\eta_0\dot{\gamma}\bar{M}_w)/(\rho RT)$, where η is the melt viscosity at a given shear rate; η_0 is the melt viscosity at zero shear rate; ρ is the density of the polymer, in this case calculated by McGowan's[3] equation; $\dot{\gamma}$ is the shear rate; $\bar{M}_w$ is the weight-average molecular weight; R is the gas constant; and T is the absolute temperature. Such a plot is shown in Figure 1 for data on a series of poly(vinyl chlorides) at a number of temperatures and shear rates. Table I identifies the source of the sample, the density as calculated or observed, the weight-average molecular weight, the temperatures at which measurements were made, and the shear rates covered. There is some general correlation in Figure 1, and, in fact, although there is considerable scatter, it could still be used to make useful predictions. A somewhat better fit is obtained by substituting the square root of the weight-average molecular weight for the molecular

* Part XXIII of a series on Flow Properties of Polymeric Systems.

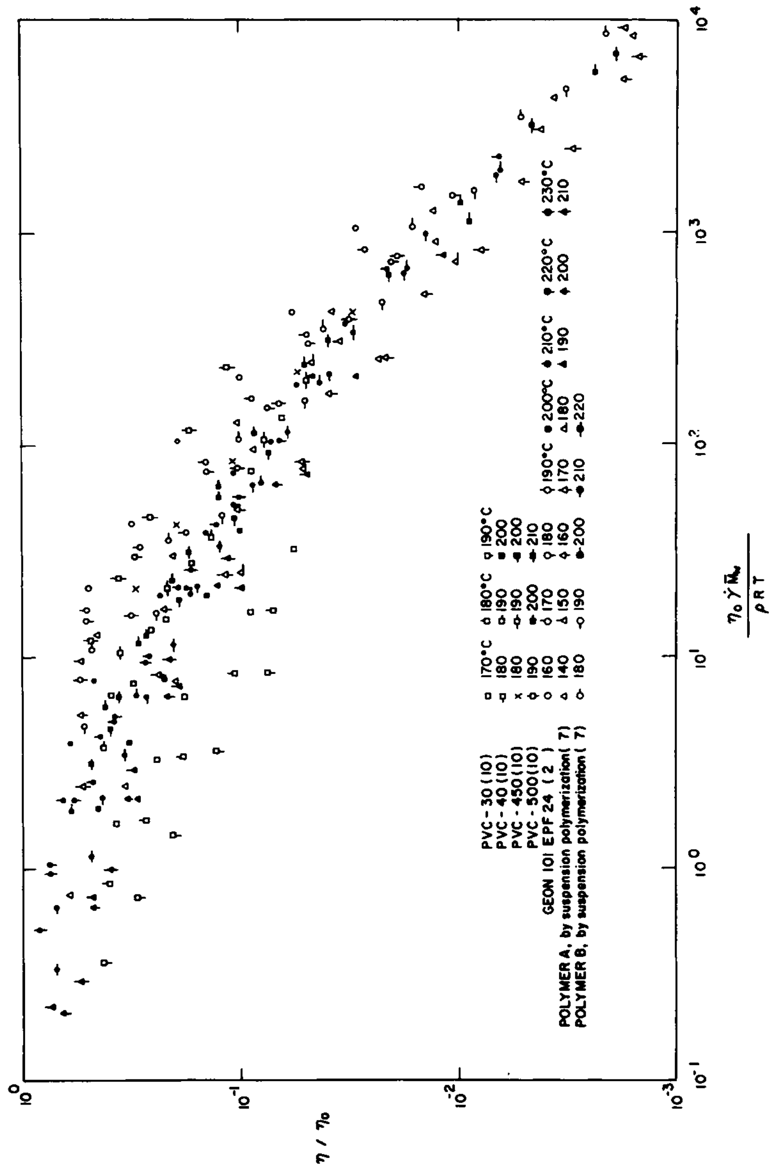

Fig. 1. Log–log plot of reduced viscosity η/η_0 vs. $\eta_0\dot{\gamma}\bar{M}_w/\rho RT$ for PVC resins.

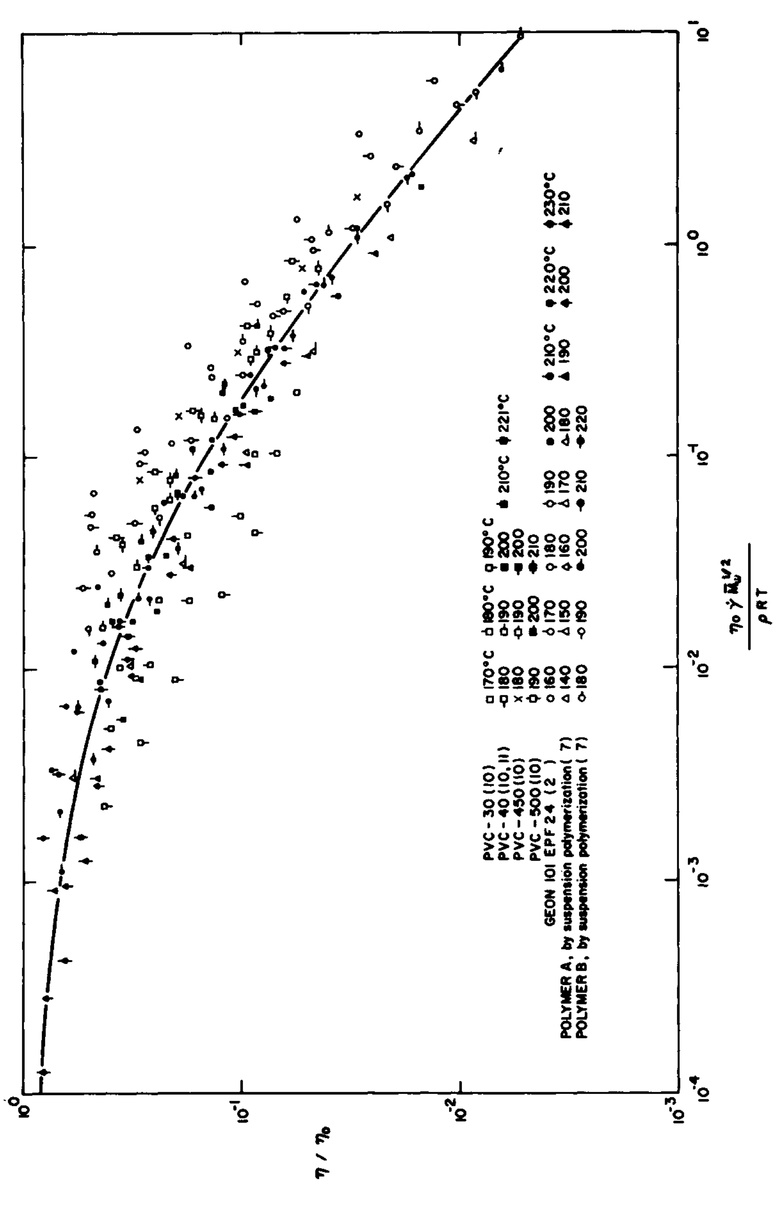

Fig. 2. Log–log plot of reduced viscosity η/η_0 vs. $\eta_0\dot{\gamma}\bar{M}_w^{0.5}/\rho RT$ for PVC resins.

TABLE I
Characterization and Properties of PVC Resins

Sample	Source	Density at 200°C, g/cm³	$\bar{M}_w \times 10^{-3}$	Temp. range, °C	Shear rate range, sec⁻¹
PVC-30	Mayrick and Sieglaff[4]	1.275	58 (GPC)	170–199[1]	1–400
PVC-40	Mayrick and Sieglaff[4]	1.275	96 (GPC)	180–200	1–400
PVC-450	Mayrick and Sieglaff[4]	1.275	108 (GPC)	180–200	1–400
PVC-500	Mayrick and Sieglaff[4]	1.275	136 (GPC)	190–210	1–400
Geon 101 EPF 24	Collins and Krier[5]	1.275	132.3 (GPC)	160–230	1–200
Polymer A	Collins and Metzger[6]	1.275	60 (?)	140–210	1–1000
Polymer B	Collins and Metzger[6]	1.275	105 (?)	180–220	1–1000
Sicron 548	Pezzin, Ajroldi, and Garbuglio[7]; Pezzin, Samartin, and Zilio-Gradi[8]	1.36 (at 170°C)	48–155 (L.S.)	170	1–1000
Breon 121	Cawthra, Pearson, and Moore[9]; Moore and Hartley[10]	1.39 (at 25°C)	83 (intrinsic viscosity)	25	1–1000

weight, as shown in Figure 2. The deviation from the master curve at lower temperatures (the unfilled data points in Figs. 1 and 2) may be due to the difference in the flow activation energy of the low-temperature region and high temperature-region. The deviation of the data from the master curve for the low molecular weight polymer, PVC-30 (see Figs. 1 and 2) may be due in part to the change in the value of the exponent of the η–$\bar{M}_w$ equation from a value of approximately 1 below the critical molecular weight to about 3.4 above the critical molecular weight. In any case, although the scatter of the data is considerable, this type of plot does provide a method for estimating the melt viscosity of poly(vinyl chloride) as a function of molecular weight, temperature, and shear rate. Such approximations may find value in preliminary engineering calculations.

CORRELATION OF FLOW PROPERTIES OF PLASTICIZED PVC

For the case where the polymer is mixed with plasticizers, which is the commonly encoutered case, the log–log plot of η/η_0 versus $(\eta_0\dot{\gamma}\bar{M}_w^{0.5})/(\rho RT)$ is no longer a master curve but is markedly dependent on the concentration of polymer W_2, as shown in Figure 3. The addition of significant amounts of low molecular weight material will markedly affect the weight-average molecular weight of the mixture, and therefore it becomes a question of what molecular weight to be used. It is found empirically that if the molecular weight of the polymer is retained for $\bar{M}_w$, a term for the density is added, the zero-shear rate viscosity is that of the polymer plus plasticizer, and the weight concentration of polymer (W_2) to the fifth power is used, then a reasonably good agreement is found for PVC-450 plasticized with di-2-ethylhexyl phthalate (DOP)[4] up to 50% over a temperature and shear rate range. This is given in Figure 4. A similar set of data taken by Sieglaff[11] gives results very like those of Figure 4. However, in this case a better correlation is obtained with the fourth power of the weight concentration of polymer rather than the fifth (Fig. 5). From

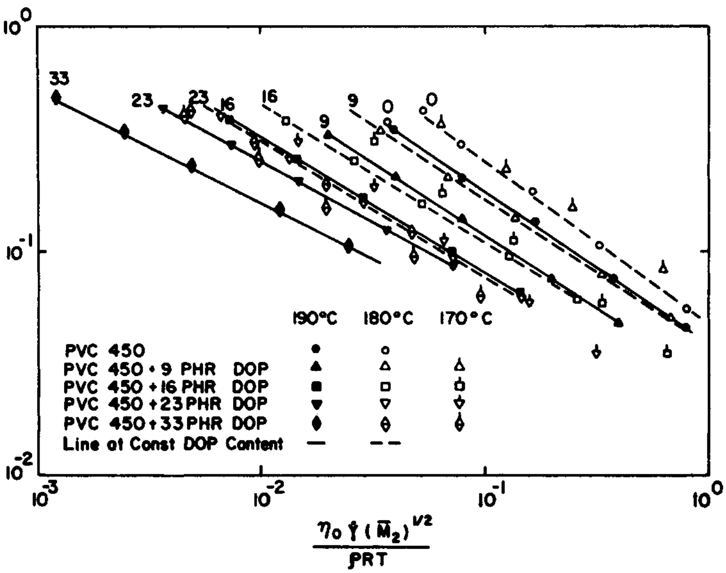

Fig. 3. Log–log of reduced viscosity η/η_0 vs. $\eta_0\dot{\gamma}\bar{M}_w^{0.5}/\rho RT$ for PVC-450 plastiziced with DOP at various concentrations.

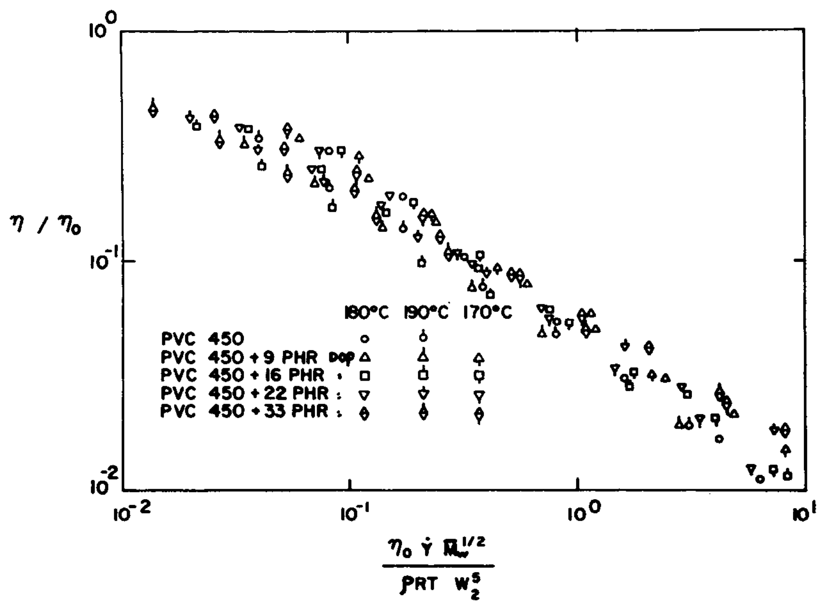

Fig. 4. Log–log plot of reduced viscosity η/η_0 vs. $\eta_0\dot{\gamma}\bar{M}_w^{0.5}/\rho RTW_2^5$ for PVC-450 plasticized with DOP at various concentrations.[8]

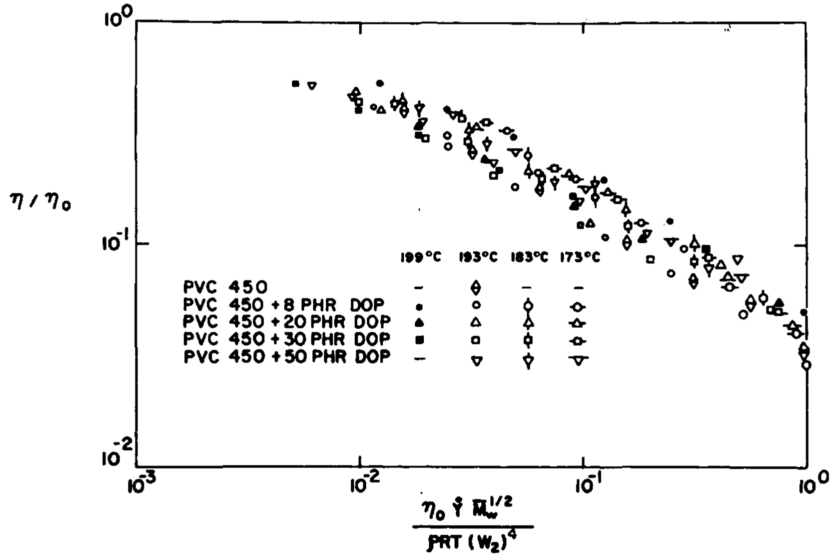

Fig. 5. Log–log plot of the reduced viscosity η/η_0 vs. $\eta_0\dot{\gamma}\bar{M}_w^{0.5}/\rho RTW_2^4$ for PVC-450 plasticized with DOP at various concentrations.[11]

inspection of the η–W_2 equation,[1] it appears that a general form, $(\eta_0\dot{\gamma}\bar{M}_w^{0.5})/(\rho RTW_2^a)$ can be used because the η-W_2 functional relations are very similar to those of η-$\bar{M}_w$ and η–T.[1] It has been found that the value of the exponent a is dependent on the nature of the plasticizers used, for example, $a \simeq 6$ for Sicron 548 + 60 phr DBP (dibutyl phthalate)[7] and $a \simeq 9$ for Breon 121 + 50 phr DAP (dialphanyl phthalate).[9]

CONCLUSIONS

Empirical correlations appear to offer a useful method of approximately correlating the wide variety of experimental measurements at different temperatures, molecular weight, and shear rates. Correlations can be established for unplasticized PVC and plasticized PVC as well by incorporating the concentration term into the reduced variable.

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