

## Universality of the Temperature-Independent Viscosity Characteristic of Polymer Melts and Some of Its Consequences

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### Synopsis

It is shown that some results of recent publications (of Longworth and Piesky and of Bartoš) can be treated as particular consequences of the principle of universality of temperature-independent viscosity characteristics of polymer melts, earlier found by these authors. This concerns the method of determination of molecular weight by means of melt index measuring and supposition that the definite value of apparent viscosity to initial Newtonian viscosity ratio can be considered to be a criterion of elastic turbulent flow emerging.

It has been found<sup>1</sup> that the temperature-independent viscosity characteristics of the melts of various polymers, obtained as described in a previous publication<sup>2</sup> differ little from one another. This made it possible to formulate the principle of universality of the temperature-independent viscosity characteristics of polymer melts. Later, this principle was generalized for the relaxation spectra and other viscous and elastic properties of these systems.<sup>3</sup>

According to the results of Vinogradov et al.,<sup>1</sup> the ratio of the apparent viscosity  $\eta_a$  to the initial Newtonian viscosity  $\eta_0$  for polymer melts is a universal function of the product of the rate of shear by  $\eta_0$ . Later, it was pointed out<sup>4</sup> that  $\eta_a/\eta_0$  is a single-valued function of the shear stress  $\tau$ . The representation of this function is shown in averaged form in Figure 1 plotted from several decades of flow curves of different polymers, ranging from elastomers to plasticized ethyl cellulose. It follows from the universality of the function  $\eta_a/\eta_0 = f(\tau)$  that the initial Newtonian viscosity can be found simply by determining the apparent viscosity at a given shear stress. Hence it follows, in particular, that  $\eta_0$  can be found from measurements of the melt index, because this is precisely determination of the apparent viscosity at a given (constant) shear stress. Evidently, the papers of Vinogradov et al.<sup>1-4</sup> were unknown to Longworth and Pieski, who discuss in a recent paper<sup>5</sup> the possibility of determining  $\eta_0$  and molecular weights on the basis of melt index measurements. At the same time this paper,<sup>5</sup> which convincingly demonstrates this possibility, is an independent particular confirmation of the more general results of Vinogradov et al.<sup>1</sup>

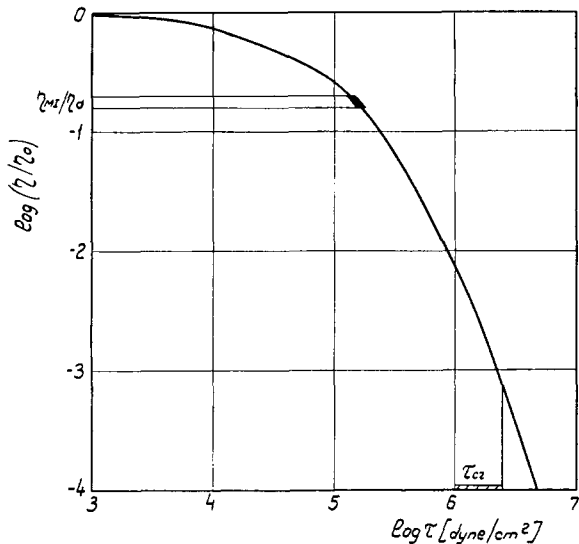


Fig. 1. Universal temperature-independent dependence  $\eta_a/\eta_0 = f(\tau)$  for polymer melts. Marked is the range of stresses at which the melt index is determined by the standard procedure.

Determination of the melt index by the standard procedure is carried out, without taking into account the entrance effect correction, at a shear stress (on the capillary wall) of  $2 \times 10^5$  dyne/cm.<sup>2</sup>. However  $L/R$  for the standard capillary with which the determination is made is not large, being only 8 units. It is therefore advisable to take into account the end corrections, which equal about  $(2-4)R$  for polyolefins. Then the true values of the stresses at which the melt index is determined are  $(1.35-1.6) \times 10^5$  dyne/cm.<sup>2</sup>. According to the data of Figure 1 (marked region of the curve) such stress values correspond to  $\eta_a/\eta_0 = (0.165-0.20)$ . Obviously, the theoretically obtained values of the ratio  $\eta_{MI}/\eta_0$  at a stress corresponding to the conditions at which the melt index was determined agree well with the  $\eta_{MI}/\eta_0$  values found by Longworth and Pieski.<sup>5</sup> The fluctuations of the value of  $\eta_{MI}/\eta_0$  are due to deviations of the properties of individual polymers from the averaged temperature-independent viscosity characteristic and to possible differences in the end correction values.

Of great importance for the rheology of polymer melts is determination of the conditions at which a state of elastic turbulence begins, this state being known sometimes also as "melt fracture." It is known from a large number of papers that the  $\tau$  value at which the state of unsteady flow occurs for the melts of many polymers is  $(1-2.5) \times 10^6$  dyne/cm.<sup>2</sup>. It follows, hence, that elastic turbulence should begin within a definite interval of  $\eta_a/\eta_0$  values. Careful examination of a great number of experimental data led to the finding<sup>6</sup> that elastic turbulence sets in at  $\eta_F/\eta_0$  from 0.006 to 0.0838,  $\eta_F$  being the effective viscosity value at which elastic turbulence appears. The value

0.025 was accepted by Bartoš<sup>6</sup> as the average critical value of the above viscosity ratio. It can be seen from Figure 1 that a sharp change in the viscosity ratio corresponds to the range of critical shear stress values, the change in this  $\tau$  interval being approximately proportional to  $\tau^{-2.45}$ . Therefore the  $\eta_F/\eta_0$  values from  $1 \times 10^{-2}$  to  $1 \times 10^{-3}$  correspond to  $\tau$  values of  $(1-2.5) \times 10^6$  dyne/cm.<sup>2</sup>. This interval partly overlaps the range of  $\eta_F/\eta_0$  values found by Bartoš,<sup>6</sup> but the average value of  $\eta_F/\eta_0$  accepted in that paper is clearly too high, because at  $\eta_F/\eta_0 = 0.025$ ,  $\tau = 6.5 \times 10^5$  dyne/cm.<sup>2</sup> i.e., much lower than the critical  $\tau$  values actually observed.

The criterion  $Re_{e,cr}$  for the set-in of elastic turbulence suggested,<sup>7,8</sup> is equal to the value of elastic shear deformation and is determined by the relation between the elastic and viscous resistance forces in the flow. The critical value of  $Re_{e,cr}$  is 5-7. For the above range of critical shear stress values, it is easy to estimate the value of the high elasticity modulus  $G_{e,cr} = Re_{e,cr}/\tau_{cr}$  corresponding to the occurrence of elastic turbulence. Obviously,  $G_{e,cr} = (1.4-5) \times 10^5$  dyne/cm.<sup>2</sup>. Although, as is clear from the above discussion of the question, the criterion  $\eta_F/\eta_0$  may be used for estimating the conditions of occurrence of elastic turbulence, the use of the criterion suggested<sup>7,8</sup> is to be preferred to  $\eta_F/\eta_0$  for the following three reasons: (1) the range of stresses wherein elastic turbulence occurs corresponds to the region of sharp change of the effective viscosity, and therefore a slight inaccuracy in determining the critical stresses (or in  $Re_{e,cr}$ ) will cause major deviations in estimating  $\eta_F/\eta_0$ ; (2) the  $G_{e,cr}$  values for melts of different polymers may differ slightly from one another; (3) the value of  $\eta_F/\eta_0$  depends on how much the properties of the concrete polymer deviate from the averaged values  $f(\tau)$  by which the curve in Figure 1 was plotted. Moreover, owing to what was mentioned in item (1), these deviations should have an essential effect on the estimation of  $\eta_F/\eta_0$ .

Therefore, physically the conditions of occurrence of elastic turbulence depend precisely on the value of  $Re_{e,cr}$ . Meanwhile, the conditions  $\eta_F/\eta_0 \approx$  constant is due to constancy of  $Re_{e,cr}$ , but is fulfilled only within the limits set by the above-mentioned circumstances.

Now, a warning should be made regarding the use of the dependence  $\eta_a/\eta_0 = f(\tau)$ , which was obtained from  $\eta_a/\eta_0 = F(\dot{\gamma}\eta_0)$ . When the dependence  $\eta_a/\eta_0 = F(\dot{\gamma}\eta_0)$  is plotted for different polymers the result is a band through which is drawn a middle line which we have called the universal temperature-independent viscosity characteristic. The dependence  $f(\tau)$  calculated from this averaged characteristic is actually a strictly single-valued universal function, but it must be taken into account that the universality of the function  $F(\dot{\gamma}\eta_0)$  is valid only to the deviations of the properties of individual polymers from the averaged dependence. Moreover, the form of the function  $F(\dot{\gamma}\eta_0)$  is essential in this respect. Owing to the non-linearity of this function the deviations of individual temperature-independent viscosity characteristics from the universal dependence  $F(\dot{\gamma}\eta_0)$  may differ substantially from the deviations of the individual  $f(\tau)$  dependences from the averaged dependence shown in Figure 1. It is essential here that

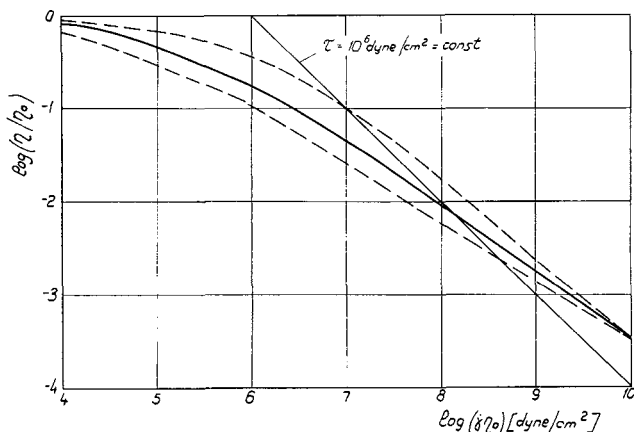


Fig. 2. Universal temperature-independent dependence  $\eta_a/\eta_0 = F(\dot{\gamma}\eta_0)$  for polymer melts. Marked is the range of  $\eta_a/\eta_0$  values observed for different polymers at given values of  $\dot{\gamma}\eta_0$ .

the function  $f(\tau)$  falls off much more sharply than  $F(\dot{\gamma}\eta_0)$ . Indeed, according to Vinogradov et al.,<sup>1,3</sup> in the range of shear rates wherein the viscosity anomaly is the most distinct, the value  $d \log(\eta_a/\eta_0)/d \log(\dot{\gamma}\eta_0) = -0.71$ , i.e., is close to  $-1$ , and the line with  $d \log(\eta_a/\eta_0)/d \log(\dot{\gamma}\eta_0) = -1$  corresponds to a constant shear stress value, i.e., to the condition  $\tau = \text{constants}$ . Therefore, inasmuch as there exists a band of  $\eta_a/\eta_0$  values (however narrow) the condition  $\tau = \text{constant}$  has rather a wide range of corresponding  $\eta_a/\eta_0$  values. It is essential that the dependence  $f(\tau)$  becomes the least definite in the range  $\tau \approx 10^6 \text{ dyne/cm}^2$ , i.e., precisely in the stress range wherein elastic turbulence might be expected. This is illustrated by the data in Figure 2.

Thus, a universal dependence  $f(\tau)$  can, as a matter of principle, be plotted, as shown in Figure 1, but its use for calculations is less reliable than the use of the initial  $F(\dot{\gamma}\eta_0)$  dependence.

This is just the reason for the substantial fluctuations of the value of  $\eta_F/\eta_0$  observed by Bartoš.<sup>6</sup> According to Bartoš, the ratio  $\eta_F/\eta_0$  may vary for different polymers over more than a tenfold range, which is much greater than the scattering of the critical values of the criterion suggested by Vinogradov, Malkin, and Leonov.<sup>7,8</sup>

Thus, the use of the universal temperature-independent viscosity characteristic of polymer melts (see Fig. 1) makes it possible to determine  $\eta_0$  values from the apparent viscosities measured at known shear stresses and to forecast correctly the conditions at which elastic turbulence will set in.

The existence of a universal viscosity characteristic for polymer melts makes it possible to indicate the differences in the dependences of  $\eta_a$  on the shear rate  $\dot{\gamma}$  for fractions of the same polymer with different molecular weights  $M$ . Obviously, the  $\eta_a(\dot{\gamma})$  curves are similar in shape but are displaced with respect to one another, because deviation of  $\eta_a$  from  $\eta_0$  begins at

different  $\dot{\gamma}$  values for polymers with different  $M$  (but at approximately equal  $\tau$  values). The shear rate at which this happens,  $\dot{\gamma}_a$ , depends on the viscosity of the system, and this dependence is described by a simple relation:  $\dot{\gamma}_a \eta_0 = \text{constant}$ . Hence, the shear rate values at which the viscosity anomaly effect should be displayed by polymers of different viscosities can be calculated. On the other hand the process of destruction of supermolecular structures in melts, which is possibly responsible for the viscosity anomaly, begins at approximately the same shear stress value. It is precisely the differences in the rate of change of the function  $\eta(\dot{\gamma})$ . at  $\dot{\gamma} = \text{constant}$  for polymers with different  $M$  values that determine the nature of change of the  $\eta(M)$  dependence at  $\dot{\gamma} \neq 0$ .<sup>4</sup>

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### Résumé

Les auteurs de la présente communication montrent que les résultats de plusieurs recherches expérimentales récemment publiées (Longworth et Piesky; Bartoš) peuvent être interprétés comme les conséquences du principe d'universalité des caractéristiques de viscosité des polymères fondus invariables avec la température qui a été établi auparavant par les auteurs de la présente communication. Cela concerne le procédé de calcul de la masse moléculaire d'après les résultats de mesure de l'indice du polymère fondu (melt index) et l'hypothèse que la valeur définie et constante du rapport de la viscosité apparente des polymères fondus à la viscosité newtonienne initiale peut servir de critère d'avènement du régime d'élasticité turbulente.

### Zusammenfassung

Es wird gezeigt, dass einige Ergebnisse vor kurzem veröffentlichter Arbeiten (Longworth und Piesky; Bartoš) als Sonderfälle des von den Autoren schon früher aufgestellten Prinzips der universellen, temperaturinvarianten Viskositätscharakteristik von Polymerschmelzen behandelt werden können. Dies bezieht sich auf die Methode der Molekulargewichtsbestimmung aus Schmelzindexmessungen sowie auf die Annahme, dass ein festgelegter Wert des Verhältnisses der effektiven Viskosität der Schmelze zu ihrer Newtonschen Anfangviskosität als Kriterium für den Beginn des elastischen, turbulenten Fließens gelten kann.

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