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## Free volume effect on behavior of polymer liquids in shear flows<sup>\*)</sup>

**Summary** — Rheological properties of polymers such as non-Newtonian viscosity and non-zero normal stress differences during the shear flow of polymeric liquids were interpreted from the point of view of the free volume theory. It was shown that the shear viscosity variations result from the changes of the total free volume, while the normal stress differences stem from the anisotropy of the free volume distribution in a polymer liquid subjected to the shearing flow. Theoretical predictions were compared with literature data for PE-LD melt (known as IUPAC melt A) and polyisobutylene (PIB) solution in 2,6,10,14-tetramethylpentadecane (NIST standard reference material). Good agreement between theory and the experiment was found.

**Keywords:** free volume, shear flow, polymer liquids, viscosity, normal stress differences.

WPŁYW OBJĘTOŚCI SWOBODNEJ NA ZACHOWANIE CIECZY POLIMEROWYCH W PRZEPŁYWACH ŚCINAJĄCYCH

**Streszczenie** — Reologiczne właściwości polimerów, w tym lepkość nienewtonowską oraz niezerowe różnice naprężeń normalnych w przepływie ścinającym zinterpretowano na gruncie teorii objętości swobodnej. Wykazano, że zmiany lepkości wynikają ze zmian całkowitej objętości swobodnej, podczas gdy niezerowe różnice naprężeń normalnych są wywołane anizotropią rozkładu objętości swobodnej w cieczy polimerowej poddanej przepływowi ścinającemu. Teoretyczne przewidywania porównano z danymi literaturowymi dotyczącymi stopionego PE-LD (znanego jako stop IUPAC A) i roztworu poliizobutyleny (PIB) w 2,6,10,14-tetrametylopentadecanie (wzorcowy materiał odniesienia NIST). Stwierdzono dobrą zgodność między teorią a doświadczeniem.

**Słowa kluczowe:** objętość swobodna, przepływ ścinający, ciecze polimerowe, lepkość, różnice naprężeń normalnych.

### INTRODUCTION

The most fundamental features of polymeric liquids subjected to shear deformation are variable viscosity and the existence of two non-zero normal stress differences leading to various external flow phenomena, *i.e.* Weissenberg effect, extrudate swell, *etc.* The non-Newtonian viscosity and the normal stress differences, which reflect the viscoelasticity of polymeric systems, are predicted by most of constitutive equations resulting from both continuum and molecular theories [1, 2].

However, there are some other theories which present a quite different approach to the behavior of polymeric systems. One of them is the free volume theory. This theory assumes that rheological properties of any system depend on both the occupied volume ( $V_0$ ) defined as a total

volume of atoms or molecules and the free volume ( $V_f$ ) considered as an additional empty space between molecules, resulting from their motions and steric effects.

According to the free volume theory the quantities  $V_0$  and  $V_f$  are related to the specific volume ( $V$ ) and viscosity ( $\eta$ ) of the system by equations:

$$V = V_0 + V_f \quad (1)$$

$$\ln \eta = K + B \frac{V_0}{V_f} \quad (2)$$

where:  $K, B$  — material constants.

Eq. (2) was first formulated on empirical way by Doolittle [3] and then theoretically confirmed by Cohen and Turnbull [4]. It was found [5] that for many polymeric systems the material constant  $B$  is close to 1.

The free volume theory was successfully used to explain various polymer phenomena, *e.g.*: temperature and pressure dependence on viscosity [6], plasticization mechanism [5], effect of molecular weight [7] and of gas addition [8, 9] or dependence of solid filler (*e.g.* natural

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fibers) addition [10, 11] on viscosity and flow behavior of polymers. Rheological properties of polymer blends were also interpreted from this point of view [12, 13].

The aim of these considerations is to extend the free volume theory in order to explain the temperature, pressure and shear stress/rate dependence on viscosity and the existence of the non-zero normal stress differences during the shear flow of polymer systems. In contrast to the continuum and molecular theories the non-Newtonian viscosity and non-zero normal stress differences are interpreted here in terms of the free volume changes.

### THEORETICAL APPROACH

From the point of view of the free volume theory any intensive variable  $q_i$ , such as temperature ( $T$ ), pressure ( $p$ ) or shear stress/shear rate ( $\tau/\dot{\gamma}$ ), acting on a given polymer system causes some changes of  $V_0$  and of  $V_f$ . It can be assumed, that the changes of  $V_0$  are negligibly small as compared with  $V_f$  changes. It is due to the fact that the atomic forces, which mainly determine the changes of  $V_0$ , are very large in comparison with intermolecular forces which in turn determine the free volume. For this reason  $V_0$  can be treated as constant for any  $q_i$ . Assuming  $B \approx 1$  [5] in eq. (2) and denoting:

$$\theta = \frac{V_0}{V_f} \quad (3)$$

one obtains from eq. (1) and (2):

$$\frac{\partial \ln V}{\partial q_i} = -\frac{\partial \ln \eta}{\partial q_i} \frac{1}{\theta(1+\theta)} \quad (4)$$

Eq. (4) presents the general relationship between volumetric and viscometric properties of polymer systems as a function of any intensive variable  $q_i$ , e.g.:  $T$ ,  $p$  and  $\tau/\dot{\gamma}$ . This relationship enables the determination of various properties of polymer melts, such as compressibility and thermal expansion coefficients, from viscometric measurements. It can be seen from eq. (4) that  $V$  of any Newtonian liquid in the shear flow should be constant, since the viscosity is independent of shear rate/stress.

By means of eq. (2) and (3)  $\ln \eta$  can be eliminated from expression (4) to obtain:

$$\frac{\partial \ln V}{\partial q_i} = -\frac{\partial \theta}{\partial q_i} \frac{1}{\theta(1+\theta)} \quad (5)$$

Eq. (5) implies that  $V$  is a unique function of the parameter  $\theta$ . The change of  $V$  resulting from the  $q_i$ -variations can be determined by integrating eq. (5):

$$\frac{V}{V_0} = \frac{\theta_0}{1+\theta_0} \frac{1+\theta}{\theta} \quad (6)$$

where: the subscript „0” corresponds to a reference state.

The functional relationship between  $\theta$  and  $\theta_0$  results from eq. (2) and (3):

$$\theta = \theta_0 + \ln \frac{\eta}{\eta_0} \quad (7)$$

For the analysis of the flow behavior at a constant temperature the best reference state corresponds to  $p = 0$

and  $\dot{\gamma} = 0$ , i.e. in practice to atmospheric pressure and Newtonian flow region. This definition of the reference state is used in further considerations.

Eqs (4)–(7) are valid for any value of  $q_i$ . To determine a functional dependence of  $\theta$  on  $q_i$  additional assumptions should be taken into account.

It is known from experiments [6] that the specific volume of many polymer systems is a linear function of temperature or pressure in relatively wide intervals, i.e.:

$$\frac{\partial^2 V}{\partial q_i^2} = 0 \quad (8)$$

After differentiation of eq. (5) and using the assumption given by eq. (8) one obtains:

$$\frac{\partial^2 V}{\partial q_i^2} - 2 \left( \frac{\partial \theta}{\partial q_i} \right)^2 = 0 \quad (9)$$

This nonlinear differential equation of second order (if  $i = 1$ ) or a system of partial differential equations of second order (if  $i > 1$ ) can be easily integrated.

For  $q_1 = T$  (temperature) and  $q_2 = p$  (pressure) the integration of the system of two eqs (9), after a few simple algebraic transformations results in the following formula:

$$\theta = \frac{A}{T - T_0} \frac{1 - Cp}{1 - Bp} \quad (10)$$

where:  $A$ ,  $B$ ,  $C$  and  $T_0$  — suitably defined integration constants.

Eq. (10) corresponds to the well known Vogel equation [1] with pressure dependent material constants. Some experimental data on the pressure dependence on these constants for different polymer melts are given by Privalko [14]. It can be shown that for suitably chosen constants  $B$  and  $C$  eq. (10) very well describes these data.

Assuming  $T_0 = 0$  and  $A = E/R$  in eq. (10) one obtains the pressure dependent form of the Arrhenius equation. The activation energy of flow  $E$  or the constants in Vogel equation allows calculating the parameter  $\theta$  as a function of shear stress from viscosity measurements.

For many polymer systems the mean values of  $\theta$  are about 10–15. Hence, it follows from eq. (4) that the volumetric changes of a polymer system evoked by the variations of  $q_i$  should be at least 100 times smaller than the corresponding viscometric changes.

The effect of shear stress/shear rate on specific volume of polymers can be estimated from eqs (6) and (7). Assuming for polymer melts the typical value of  $\theta_0$  to be 15–16 and the viscosity ratio ( $\eta/\eta_0$ ) for very high  $\dot{\gamma}$  to be  $10^{-3}$  one obtains the extreme  $V/V_0$  value to be around 1.05, i.e.  $\dot{\gamma}$  value increase by 5–6 orders of magnitude increases the specific volume no more than 5 % (usually 2–3 %). This result is not consistent with one of the main assumptions of continuum mechanics, i.e. the shear deformation does not change the volume of the system. However, polymer liquids do not consist of zero-dimensional material points but of macromolecules with considerable

dimensions and relatively low mobility. In such case it is possible that the collisions of molecules during shear flow increase the mean distance between them. Additional  $V_f$  created this way is not able to relax quick enough due to the low mobility of macromolecules in contrast to the mobile molecules of low molecular liquids, which are as a rule Newtonian.

It is noteworthy that volume increase accompanied by reduction of internal friction is also observed on macroscopic level during the shear of particulate systems.

In the first approximation it can be assumed that the additional free volume is created at the rate proportional to the shear intensity described by some (awhile unknown) function of the shear stress ( $\tau$ ), which is denoted for convenience as  $|\tau|^*$ . Simultaneously this volume vanishes with the rate proportional to its instantaneous value. Both assumptions lead to the following kinetic equation describing variability in time of the excess free volume ( $V_{fe}$ ):

$$\frac{dV_{fe}}{dt} = k \cdot |\tau|^* - \frac{1}{\lambda} V_{fe} \quad (11)$$

$$V_{fe} = V_f - V_{f0} \quad (11a)$$

where:  $V_f$  – instantaneous free volume under shear,  $V_{f0}$  – free volume without shear (or in Newtonian flow region),  $\lambda$  – relaxation time of the free volume,  $k$  – proportionality constant.

Generally,  $|\tau|^*$  is an even function, because the volume changes should be independent of shear direction. On the other hand, the shear intensity can also be expressed in terms of  $|\dot{\gamma}|^*$  or of the product  $(\tau\dot{\gamma})^*$ , which is the even function. It seems that the assumption of shear stress dependent shear intensity provides the most accurate description of experimental data for various polymer systems that will be shown below.

It follows from eqs (11) and (11a) that under steady shear  $V_f$  is given by the following expression:

$$V_f = V_{f0} + k\lambda |\tau|^* \quad (12)$$

Introducing this value into eq. (2) and denoting:

$$\ln \eta_0 = K + \theta_0 \quad (13)$$

one obtains:

$$\ln \frac{\eta}{\eta_0} = -\theta_0 \frac{\alpha |\tau|^*}{1 + \alpha |\tau|^*} \quad (14)$$

$$\alpha = \frac{k\lambda}{V_{f0}} \quad (14a)$$

It can be seen that eq. (14) predicts the existence of both lower (for  $|\tau|^* \rightarrow 0$ ) and upper (or  $|\tau|^* \rightarrow \infty$ ) viscosity limits, *i.e.*  $\eta_0$  and  $\eta_\infty = \eta_0 \exp(-\theta_0)$ . It was mentioned above that for polymer melts  $\theta_0 > 10$ , therefore the upper viscosity limit is practically equal to zero, in contrast to dilute polymer solutions which have much lower  $\theta_0$  values.

For small and very mobile molecules typical of Newtonian fluids (*e.g.* water, organic solvents) the free volume

relaxation time in eq. (11) is very short in comparison with macromolecules (*i.e.*  $\lambda_{\text{Newt}} \approx 0$ ). For this reason the created excess volume vanishes almost at once, and the total free volume does not change, *i.e.* the viscosity is constant.

Considering the flow behavior of polymeric liquids from the point of view of the free volume theory one should also answer the question whether the shear induced increase of free volume (or equivalently of the specific volume), which leads to the viscosity lowering, is the same in all directions. It will be shown below that the assumption of an anisotropic distribution of the free volume during the shear flow of polymer liquids leads to the non-zero values of normal stress differences. In the case of low molecular compounds, the free volume is uniformly distributed in space due to their high mobility. For this reason they show zero normal stress differences, which is typical of Newtonian behavior.

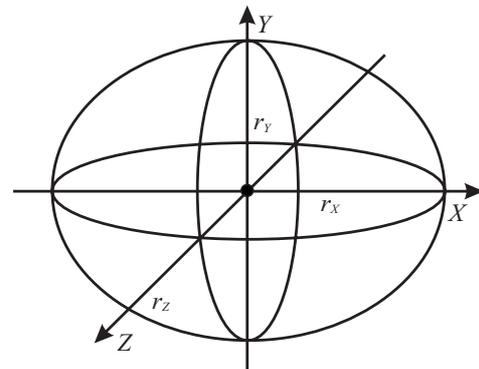


Fig. 1. Schematic illustration of the free volume distribution in shear flow

Figure 1 presents a schematic representation of the specific volume of a polymer liquid. In the reference (shear free) state the mean distance between the central macromolecule (marked as full circle) and the adjacent macromolecules is the same in all directions, *i.e.* the distribution of the free volume is isotropic. In this case  $r_x = r_y = r_z = r_0$ , and the specific volume is represented by a sphere with the radius  $r_0$  (half distance between adjacent molecules). The specific volume is the sphere volume described by expression:

$$V_0 = \frac{4}{3} \pi r_0^3 \quad (15)$$

During the shear flow (*e.g.* in  $x$ -direction with the velocity gradient in  $y$ -direction) the mean distance between molecules is changed from reasons mentioned above, and it becomes dependent on the direction of space, *i.e.* the free volume distribution becomes anisotropic. It can be represented by an ellipsoid with various radii  $r_x$ ,  $r_y$  and  $r_z$ .

The specific volume during simple shear flow is represented by the ellipsoid volume described by equation:

$$V = \frac{4}{3} \pi r_x r_y r_z \quad (16)$$

The relative volume change resulting from eqs (15) and (16) can be expressed with logarithmic measure as:

$$\ln \frac{V}{V_o} = \ln \frac{r_x}{r_o} + \ln \frac{r_y}{r_o} + \ln \frac{r_z}{r_o} \quad (17)$$

The quantitative description of the free volume anisotropy during shear flow relies on the assumption that the right hand-side components in eq. (17) fulfill the conditions:

$$\ln \frac{r_x}{r_o} = (1-\mu) \ln \frac{r_y}{r_o} \quad (18)$$

$$\ln \frac{r_z}{r_o} = (1-\nu) \ln \frac{r_y}{r_o} \quad (19)$$

where:  $\mu, \nu$  – small positive parameters, which should be treated as material constants.

The quantities  $(1-\mu)$  and  $(1-\nu)$  play somewhat similar role as the Poisson ratios in the mechanics of elastic solid (in this case such „Poisson ratios“ are negative!).

Defining:

$$V_i = \frac{4}{3} \pi r_i^3 \quad i = x, y, z \quad (20)$$

as the apparent specific volume in the  $i$ -th direction of space one obtains from eqs (17)–(20):

$$\frac{V_x}{V_o} = \left( \frac{V}{V_o} \right)^{\frac{3(1-\mu)}{3-\mu-\nu}} \quad (21)$$

$$\frac{V_y}{V_o} = \left( \frac{V}{V_o} \right)^{\frac{3}{3-\mu-\nu}} \quad (22)$$

$$\frac{V_z}{V_o} = \left( \frac{V}{V_o} \right)^{\frac{3(1-\nu)}{3-\mu-\nu}} \quad (23)$$

The anisotropic free volume increase during the simple shear flow can be treated as a result of the action of an internal stress represented by a tensor with normal components  $p_x, p_y, p_z$ . It is evoked by the shear deformation according to the described mechanism (collisions of molecules). Assuming the flow in  $x$ -direction and the velocity gradient in  $y$ -direction, the first and second normal stress differences can be defined in the following way:

$$N_1 = p_x - p_y \quad (24)$$

$$N_2 = p_y - p_z \quad (25)$$

In the first approximation (for a relative low shear intensity) it can be assumed that the free volume expansion in  $i$ -th direction of space is a linear function of the  $i$ -th normal component of the extrastress tensor. It can be treated as a „mirror behavior“ with respect to the compression with relative low pressure, which leads to a linear volume decrease. In such case the  $i$ -th component of the extrastress tensor  $p_i$  can be described by the result of integration of eq. (9) assuming  $q_i = p_i$  and  $\theta = \theta_i$ :

$$\theta_i = \frac{A}{D - p_i} \quad (26)$$

The integration constants  $A$  and  $D$  result with the use of eqs (6) and (26) for the reference state from the system:

$$\beta_o = \left( -\frac{\partial \ln V}{\partial p} \right)_o = \frac{1}{A + D} \quad (27)$$

$$\theta_o = \frac{A}{D} \quad (28)$$

where:  $\beta_o$  – the compressibility coefficient in the shear free state and under atmospheric pressure.

Taking into account eqs (26)–(28) one gets:

$$p_i = \frac{1}{\beta_o (1 + \theta_o)} \left( 1 - \frac{\theta_o}{\theta_i} \right) \quad (29)$$

The ratio  $\theta_o/\theta_i$  can be determined from eq. (6). Hence, expression (29) takes the form:

$$p_i = \frac{1}{\beta_o} \left( 1 - \frac{V_i}{V_o} \right) \quad (30)$$

The normal stress differences as functions of the specific volume can be now calculated from eqs (21)–(25) and (30):

$$N_1 = \frac{1}{\beta_o} \left[ \left( \frac{V}{V_o} \right)^{\frac{3}{3-\mu-\nu}} - \left( \frac{V}{V_o} \right)^{\frac{3(1-\mu)}{3-\mu-\nu}} \right] \quad (31)$$

$$N_2 = \frac{1}{\beta_o} \left[ \left( \frac{V}{V_o} \right)^{\frac{3(1-\mu)}{3-\mu-\nu}} - \left( \frac{V}{V_o} \right)^{\frac{3}{3-\mu-\nu}} \right] \quad (32)$$

Eqs (31) and (32) can be easily expanded into power series of  $\ln(V/V_o)$ . Since  $\ln(V/V_o)$  is small, only the first and second terms of the expansion can be taken into account. For small  $\mu$  and  $\nu$  values one gets the expressions:

$$N_1 = \frac{\mu}{\beta_o} \left[ \ln \left( \frac{V}{V_o} \right) + \ln^2 \left( \frac{V}{V_o} \right) \right] \quad (33)$$

$$N_2 = -\frac{\nu}{\beta_o} \left[ \ln \left( \frac{V}{V_o} \right) + \ln^2 \left( \frac{V}{V_o} \right) \right] \quad (34)$$

It follows from eqs (33) and (34) that the first normal stress difference is positive, while the second normal stress difference is negative according to experimental data [1]. For small values of  $\mu$  and  $\nu$  eqs (33) and (34) show that the ratio of both normal stress differences is constant, *i.e.*:

$$\frac{N_2}{N_1} = -\frac{\nu}{\mu} \quad (35)$$

This result is also confirmed by experimental data. The mean value of the  $N_2/N_1$  ratio for different polymers is found to be about -0.1 [2].

## NUMERICAL CALCULATIONS AND DISCUSSION

The experimental verification of theoretical predictions is based on data for a low density polyethylene (PE-LD) melt known in the rheological literature as melt

A. This melt taken as an example was widely characterized within a special IUPAC research program along with very similar melts B and C and some results are published elsewhere [15]. The second example is the solution of polyisobutylene (PIB) in 2,6,10,14-tetramethylpentadecane used as the NIST standard reference material [16].

**Table 1. Properties of melts A and PIB solution corresponding to Newtonian flow region**

Polymer liquid	Viscosity ( $\eta_0$ ), Pa · s	Flow activation energy ( $E_0$ ) kJ/mole	Compressibility coefficient ( $\beta_0$ ), Pa <sup>-1</sup>
PE-LD melt A at 130 °C	84 000	57.8	8.54·10 <sup>-10</sup>
PE-LD melt A at 150 °C	55 000	57.8	—
PIB solution at 25 °C	98.75	34.0	—

Table 1 presents as examples the values of the viscosity  $\eta_0$ , the flow activation energy  $E_0$  and the compressibility coefficient  $\beta_0$  for melt A at 403 and 423 K and for PIB solution at 298 K in the Newtonian flow region. The parameter  $\theta_0$  was calculated from the Arrhenius equation as:

$$\theta_0 = \frac{E_0}{RT} \quad (36)$$

The compressibility coefficient  $\beta_0$  for melt A was calculated according to formula (27) from the empirical Tait's equation of state using the data of Rodgers [17].

The rearrangement of eq. (14) shows the proportionality between the quantities:

$$X = \frac{1}{|\tau|^*} \quad (37a)$$

$$Y = \frac{\theta_0}{\ln(\eta_0 / \eta)} - 1 \quad (37b)$$

where the proportionality constant is equal to  $\alpha^{-1}$ .

Careful evaluation of viscosity data for very low shear stresses (shear rates) indicates that the most proper choice for the unknown function in eq. (14) is:

$$|\tau|^* = \tau^2 \quad (38)$$

Figure 2 obtained for viscosity data of melt A at 130 °C proves that eq. (14) with  $|\tau|^*$  defined by eq. (38) holds very well in the region of small shear stresses <3 kPa (shear rates <0.05 s<sup>-1</sup>). Qualitatively similar results shown in Figure 3 are obtained for PIB solution at 25 °C for small shear stresses <20 Pa (shear rates <0.2 s<sup>-1</sup>). In this case corresponding logarithmic quantities were applied. It can be seen that the calculated exponent (~2.06) is very close to the value of 2 assumed in eq. (38).

However, assumption taken in eq. (38) is not valid in the region of higher shear stresses (or rates). In this case an excellent correlation with experimental data provides the assumption:

$$|\tau|^* = |\tau|^n \quad (39)$$

in eq. (14), where  $n < 2$ .

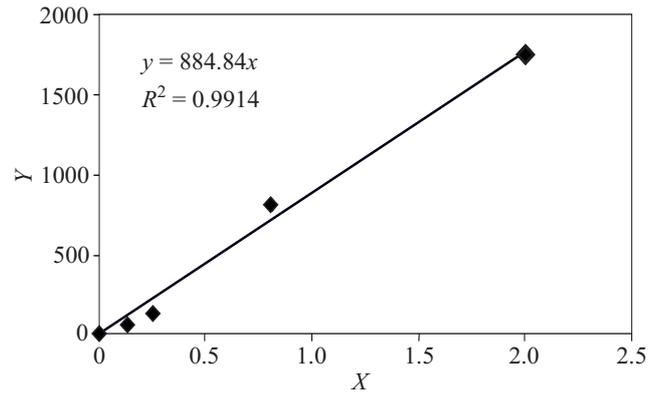


Fig. 2. Viscosity characteristics of melt A at 130 °C for low shear stresses

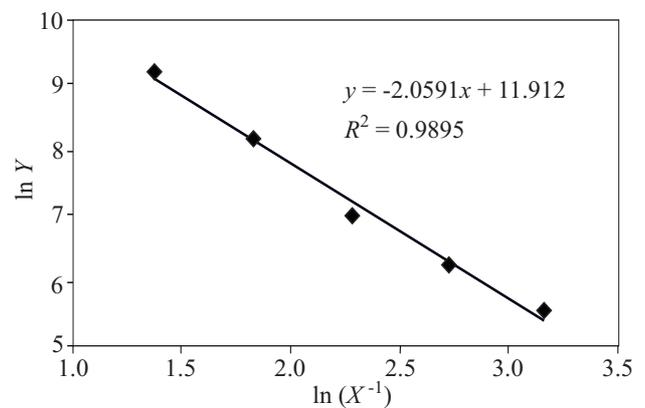


Fig. 3. Viscosity characteristics of PIB solution at 25 °C for low shear stresses

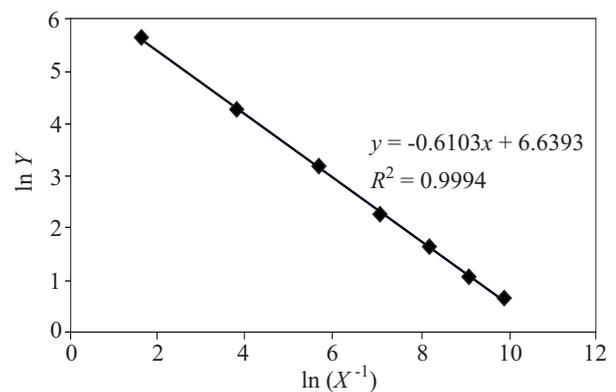


Fig. 4. Viscosity characteristics of melt A at 150 °C for high shear stresses

This relation for melt A at 150 °C and high shear stresses up to 20 MPa (shear rates up to 1000 s<sup>-1</sup>) is shown in Figure 4 as an example (measurements at 130 °C were restricted to shear rates below 1 s<sup>-1</sup>). Almost perfect description of experimental data ( $R^2 \approx 0.999$ ) is obtained for  $n = 0.610$ , which differs slightly from the value of 2, appropriate for low shear stress region. Qualitatively very similar behavior is shown in Figure 5 for PIB solution in the region of high shear stresses up to 720 Pa (shear rates

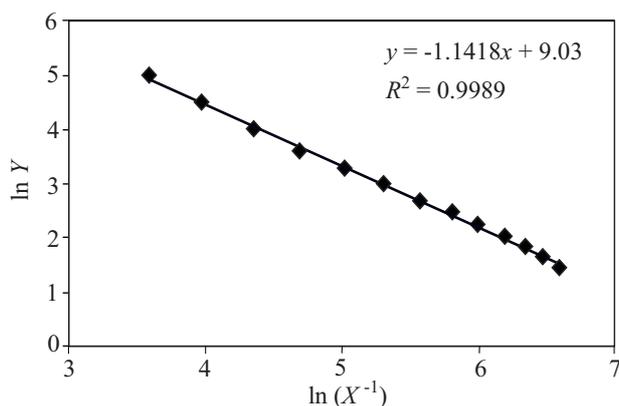


Fig. 5. Viscosity characteristics of PIB solution at 25 °C for high shear stresses

up to  $100 \text{ s}^{-1}$ ). In this case the experimental data are correlated with the same accuracy as in the previous case ( $R^2 = 0.999$ ) for  $n = 1.142$ . Because parameter  $\alpha$  in eq. (14) is very small, the viscosity curve can be also described quite well by the simplified formula obtained by neglecting the term  $\alpha |\tau|^n$  in the denominator of eq. (14).

It should also be noted, that in the general case as the first approximation of the power series expansion of the simplified eq. (14) the generalized form of the well known empirical equation of Ellis type [2] can be obtained ( $\delta = \alpha \theta_o$ ):

$$\frac{\eta}{\eta_o} = \exp(-\delta |\tau|^*) = \frac{1}{\exp(\delta |\tau|^*)} \approx \frac{1}{1 + \delta |\tau|^*} \quad (40)$$

In similar way a generalized equation of Ellis type predicting the upper viscosity limit ( $\eta_{\infty}$ ) can be derived as the first approximation from eq. (14).

Moreover, taking into account eqs (13), (14) and (36) one obtains the following formula for the flow activation energy as a function of shear stress:

$$E_{\tau} = \frac{E_o}{1 + \alpha |\tau|^*} \quad (41)$$

It can be generalized to include the pressure effect similarly as in the case of eq. (10).

The various flow behaviors at low and high shear stresses (shear rates) can be unified on a semi-empirical way by assuming that the rate of creation of the excess free volume in eq. (11) is proportional to:

$$|\tau|^* = \frac{\tau^2}{[1 + (c\tau)^2]^{\frac{2-n}{2}}} \quad (42)$$

This function (one of the possible forms) should be introduced into eq. (14).

Experimental verification of the formula (33) for the first normal stress difference requires the calculation of the volume ratio. The  $V/V_o$  ratio was calculated from eqs (6) and (7) for known value of the  $\eta$ , which corresponds to the same shear stress (shear rate) as the suitable value of the first normal stress difference  $N_1$ . The above data (some of them were also used for verification of the theoretical viscosity curve) can be found in [1, 15].

Eq. (33) suggests that the dependence of  $\beta_o \cdot N_1$  on  $\ln(V/V_o)$  should be described by a parabola having the zero-free term and the same coefficient  $\mu$  at the first and the second powers of  $\ln(V/V_o)$ . The plots created for melts A, B and C at 130 °C showed that the postulated parabolic relationship holds very well in all cases ( $R^2 > 0.98$ ). The

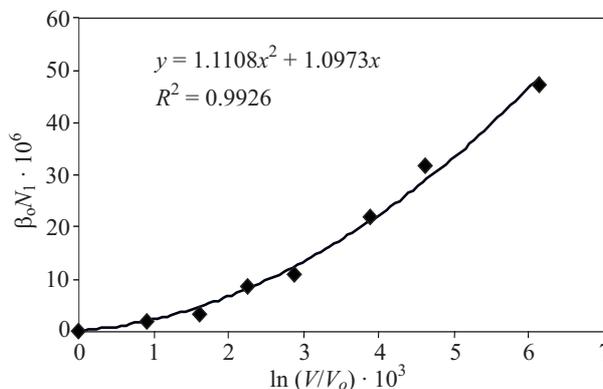


Fig. 6. Characteristics of the first normal stress difference of melt A at 130 °C

calculated values of  $\mu$  were very small ( $\sim 1 \cdot 10^{-3}$ ) and very similar for various powers of  $\ln(V/V_o)$ . For this reason only the plot for the melt A is shown in Figure 6 as an example. Because the values of  $\mu$  are of order  $1 \cdot 10^{-3}$  and the values of  $v$  are probably ten times smaller, the anisotropy of the free volume distribution during the shear flow, which results in the presence of the non-zero normal stress differences, is also very small.

Eq. (14) allows simplifying the representation of  $N_1$  (or  $N_2$ ) as a function of shear stress. With the use of eqs (6), (7) and (14) it follows:

$$\frac{V}{V_o} = 1 + \frac{\alpha |\tau|^*}{1 + \theta_o} \quad (43)$$

Introducing this result into eq. (33) and expanding logarithm function into power series restricted to the small first order term one obtains finally:

$$N_1 = \frac{\mu}{\beta_o} \left[ \frac{\alpha |\tau|^*}{1 + \theta_o} + \frac{1}{2} \left( \frac{\alpha |\tau|^*}{1 + \theta_o} \right)^2 \right] \quad (44)$$

Because in the region of small shear stresses  $|\tau|^* = |\tau|^2$  it can be seen from eq. (44) on neglecting the small second order term that  $N_1$  is proportional to  $|\tau|^2$  according to the predictions of other (continuum and molecular) theories [1, 2]. It is also easy to verify that the limiting value of the first normal stress coefficient can be expressed as:

$$\psi_1(0) = \lim_{\dot{\gamma} \rightarrow 0} \frac{N_1}{\dot{\gamma}^2} = \lim_{\tau \rightarrow 0} \frac{N_1}{(\tau/\eta)^2} = \frac{\mu \alpha \eta_o^2}{\beta_o (1 + \theta_o)} = 2J_e \eta_o^2 \quad (45)$$

where:  $J_e$  – equilibrium compliance.

The value of  $\psi_1(0)$  calculated from eq. (45) for melt A at 130 °C is equal to  $5.6 \cdot 10^5 \text{ Pa} \cdot \text{s}^2$ .

Eqs (14) and (44) make possible to find the correlation between the first normal stress difference and viscosity by eliminating the term  $\alpha|\tau|^*$  from both equations. For small shear stress values the second order term in eq. (44) can be neglected. This assumption simplifies the correlation equation to:

$$\frac{1}{N_1} = \frac{\beta_o \theta_o (1 + \theta_o)}{\mu} \frac{1}{\ln(\eta_o/\eta)} - \frac{\beta_o}{\mu} \quad (46)$$

Figure 7 shows the dependence (46) for melt A in the region of small shear stresses. It can be seen, that the linear correlation of experimental data is very good ( $R^2 > 0.99$ ). Moreover, the negative value of the free term predicted by eq. (48) is also obtained. However, the first regression coefficient and the ratio of both regression coefficients are somewhat too small.

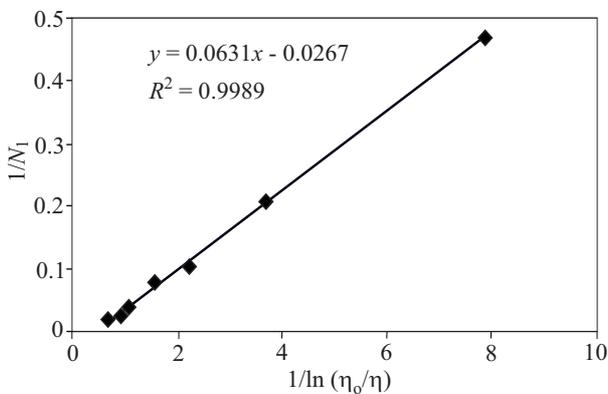


Fig. 7. Dependence I of first normal stress difference on viscosity for melt A at 130 °C

Eqs (14) and (44) lead also to other simple correlation between first normal stress difference and viscosity after eliminating the common term  $\alpha|\tau|^*$ . Because the typical values of the ratio  $\ln(\eta_o/\eta)/\theta_o$  are small in very wide shear stress interval the obtained expression can be expanded

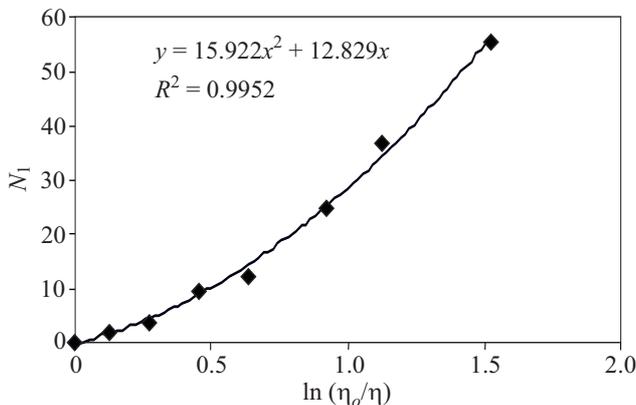


Fig. 8. Dependence II of first normal stress difference on viscosity for melt A at 130 °C

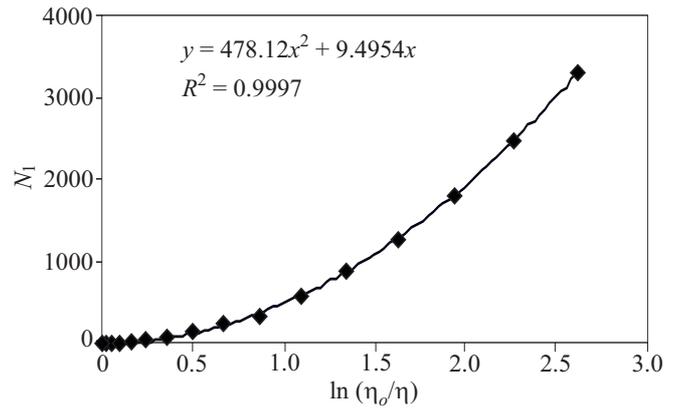


Fig. 9. Dependence I of first normal stress difference on viscosity for PIB solution at 25 °C

into power series of  $\ln(\eta_o/\eta)/\theta_o$  restricted to the second order terms. In this way one obtains:

$$N_1 = \frac{\mu}{\beta_o \theta_o (1 + \theta_o)} \left[ \ln \frac{\eta_o}{\eta} + \frac{3 + 2\theta_o}{2\theta_o (1 + \theta_o)} \left( \ln \frac{\eta_o}{\eta} \right)^2 \right] \quad (47)$$

Relations described by eq. (47) for melt A at 130 °C and PIB solution at 25 °C are shown in Figures 8 and 9. It can be seen that algebraic equation of second order with positive coefficients according to eq. (47) describes perfectly experimental data in both cases. However, the coefficient at second order term is considerably larger than that at the first order term in contrast to theoretical predictions. The reason of such behavior is not quite clear. One of the possible explanations is a dependence of the anisotropy coefficients ( $\mu, \nu$ ), which in these considerations was assumed to be constant, on the free volume changes  $\ln(V/V_o)$ .

Another very simple correlation between viscosity and the first normal stress difference results from the generalized Ellis eq. (40) and the eq. (44) after neglecting the small term of second order. Eliminating the term  $\alpha|\tau|^*$  from both equations one obtains:

$$N_1 = \frac{\mu}{\beta_o \theta_o (1 + \theta_o)} \left( \frac{\eta_o}{\eta} - 1 \right) = \frac{2J_e}{\delta} \left( \frac{\eta_o}{\eta} - 1 \right) \quad (48)$$

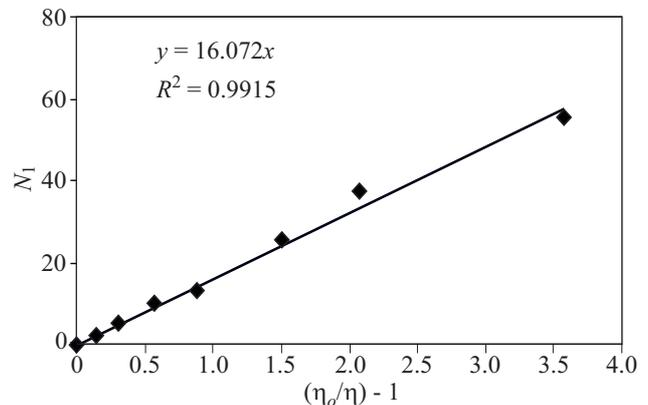


Fig. 10. Dependence III of first normal stress difference on viscosity for melt A at 130 °C

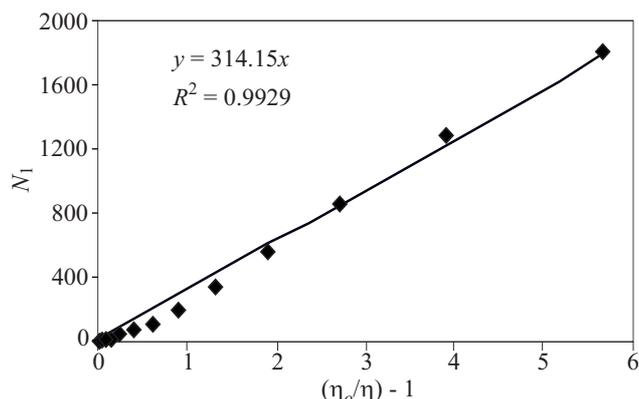


Fig. 11. Dependence of first normal stress difference on viscosity for PIB solution at 25 °C

In eq. (48) the definition of compliance  $J_e$  according to expression (44) was used.

It can be seen in Figures 10 and 11 that the relation (48) is very well fulfilled for both melt A at 130 °C for relative small  $\tau$  values and for PIB solution at 25 °C. However, the obtained value of the proportionality constant for melt A is higher than the theoretical value resulting from eq. (48). The examination of eq. (48) using experimental data for many other polymer systems has shown that it works as a rule very well in unexpectedly wide intervals of  $\tau$  or  $\dot{\gamma}$ .

The correlation predicted by eq. (48) suggests, that in the power law region the product of the viscosity and the first normal stress difference is represented by:

$$\eta \cdot N_1 = \text{Const} \quad (49)$$

It can be shown that eq. (49) is very well fulfilled in many systems. Since in very low  $\dot{\gamma}$  (or  $\tau$ ) region this product is proportional to the second power of  $\dot{\gamma}$  (or  $\tau$ ) the general shape of this function should be of the form:

$$\eta \cdot N_1 = \eta_0 \cdot \psi_1(0) \frac{\dot{\gamma}^2}{1 + (\xi \dot{\gamma})^2} \quad (50)$$

The same result predicts an integral constitutive eq. (18), which leads to the following simple expression for the first normal stress difference as the function of viscosity:

$$N_1 = 2 \frac{\eta_0}{\lambda_0} \frac{\partial \left( \frac{\eta_0}{\eta} - 1 \right)}{\partial \ln \dot{\gamma}} \quad (51)$$

where:  $\eta_0, \lambda_0$  – parameters of the Carreau viscosity equation:

$$\eta = \frac{\eta_0}{\left[ 1 + (\lambda_0 \dot{\gamma})^2 \right]^{\frac{1-n}{2}}} \quad (52)$$

Eqs (48) and (51) can be also used for calculations of the first normal stress difference from oscillatory measurements if the known Cox-Merz rule is applicable.

It should also be noted, that from the point of view of the free volume theory both normal stress differences are independent material functions, since they result from the anisotropic distribution of the free volume (characte-

rized by the coefficients  $\mu$  and  $\nu$ ), while the viscosity variation results from the changes of the total free volume described by the free volume relaxation mechanism. The presented mechanism can be generalized by introducing the relaxation time spectrum to account for various relaxation courses of different parts of the free volume. The predictions based on the free volume theory are qualitatively very similar to the continuum and molecular theories, which also predict the independence of normal stress differences and viscosity function, *i.e.* any of these functions cannot be derived from measurements of any other function. The principal difference between continuum or molecular theories and the free volume theory consists in the assumption that according to the latter theory the free volume, *i.e.* also the specific volume, of polymer liquids may change under shear, while the other theories assume no volume changes during shear. However, it was pointed out previously, that the volume changes in a real polymer system consisting of the three-dimensional molecules (but not of zero-dimensional points or one-dimensional springs) are very small, at least two orders of magnitude smaller than corresponding changes of the rheological functions, such as viscosity. For this reason the potential volume changes during shear flow of polymers are extremely difficult to measure. One of the possible ways would be the simultaneous, precise measurements of the volume and mass flow rates in tube (capillary) flow with various shear stresses (shear rates) taking into account possible temperature and pressure effects. A very good approximation describing the possible fluid density changes in the tube flow is the expression:

$$\frac{\rho_w}{\bar{\rho}} = \frac{d \ln \dot{m} / d \ln \tau_w + 3}{d \ln Q / d \ln \tau_w + 3} \quad (53)$$

where:  $\rho_w, \bar{\rho}$  – fluid density at the tube wall and mean fluid density in flow, respectively;  $\dot{m}$  – mass flow rate,  $Q$  – volume flow rate,  $\tau_w$  – shear stress at the tube wall.

Eq. (52) relies on the quite apparent assumption that the fluid density gradient in flow is negligibly small in comparison with the corresponding velocity gradient (shear rate).

## CONCLUSIONS

Based on the free volume theory, the presented considerations have shown that there are two fundamental factors affecting the rheological behavior of polymer liquids in the shear flow, *i.e.* the amount of total free volume and its spatial distribution in the flowing system. The first one determines the viscosity changes of the system while the second one is responsible for the existence of the first and second normal stress differences. Therefore, all systems which show neither free volume changes nor anisotropic distribution of the free volume during flow should be treated as Newtonian. Unfortunately, the measurements of very small changes of specific volume

during flow, which would confirm directly the above assumptions, are an extreme difficult task, and probably such measurements are not available for this reason. This problem is especially important taking into account the fact that the continuum and molecular theories do not require the flow induced changes of specific volume (density) to predict the typical non-Newtonian phenomena in shear flow of polymer liquids. In closing conclusion it should be also mentioned that calculations of „internal stress” components based on other principles, e.g.  $P$ - $V$ - $T$  equations or  $L$ - $J$  potential, bring qualitatively similar results for  $N_1$  and  $N_2$  as those based on the free volume theory presented in this paper.

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