BIREFRINGENCE MEASUREMENT OF NORMAL AND TANGENTIAL STRESSES IN POLYMER FLOWS

V. I. Brizitskii, A. I. Isaev,
Yu. Ya. Podol'skii, and G. V. Vinogradov

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A study is made of the transition of polymers from the viscous to the forced highly elastic state. It is shown that this transition is accompanied by a sharp growth of the first difference in the normal stresses.

The flow of polymers through capillary dies can be accompanied by a transition of the polymer from the viscous state to a forced highly elastic state, when flow occurs at temperatures much higher than the glass point. This transition manifests itself as "flow separation," i.e., as a manyfold increase in the volumetric flow rate at a certain critical value of the shearing stress [1, 2]. One would expect that at shearing stresses exceeding the transition of the polymer to the forced highly elastic state the relationship between the tangential and normal stresses would change considerably. However, the experimental determination of the first difference in the normal stresses in the region close to flow separation runs up against a number of difficulties. For example, this sort of measurement is not possible with the methods of rotation viscometry, since the polymer detaches from the walls of the working unit at shearing stresses much less than those recorded in capillary viscometry as critical [3]. The difficulties are no less with the methods of capillary viscometry, in particular, in connection with the measurement of the normal stresses using pressure sensors distributed along the channel [4-6]. It is essential with this method to utilize very sensitive pressure sensors that, in addition, do not perturb the flow.

The normal stresses and the character of their distribution in the flow of polymers at high shear rates can be determined by the rheooptical method. This method exploits the birefringence effect exhibited by high-molecular-weight compounds under deformation in conjunction with the stress optical laws [7]. Indications that the latter are valid over a wide range of shearing stresses [8-15] favor the choice of this method, although the applicability of these laws to viscoelastic media in the general case has not been established [16]. The rheooptical investigations were made on the experimental setup briefly described in [17] and comprising a constant-pressure gas viscometer and an optical system for visualizing the flow. The measurements were on polymer flows through a die in the form of a rectangular slit for which L/H could be varied in the range from 8 to 35; the ratio W/H equalled 3.

The investigated objects were samples of polybutadienes and polyisoprenes of narrow molecular-weight distribution ($M_W/M_n = 1.1$) synthesized by the anionic polymerization technique with a butyllite catalyst. The viscosity-average molecular weights MWD; and the isomeric composition of the samples are given in Table 1.

Besides the samples listed in the table we also investigated a system modelling industrial polybutadiene and consisting of a 16-component mixture of equal quantities of narrow MWD polybutadiene samples with molecular weights from 65,000 to 320,000 ($M_W/M_n = 3.0$).

Such objects were chosen because, on the one hand, narrow MWD polymers exhibit the phenomenon of separation particularly sharply [1-3], while, on the other hand, the region of viscosity anomaly is clearly expressed with broad MWD polymers.

All the experimental results detailed below were obtained at 25°C.

Figure 1 shows the flow curves (dependence of velocity gradient on shearing stress) of the investigated

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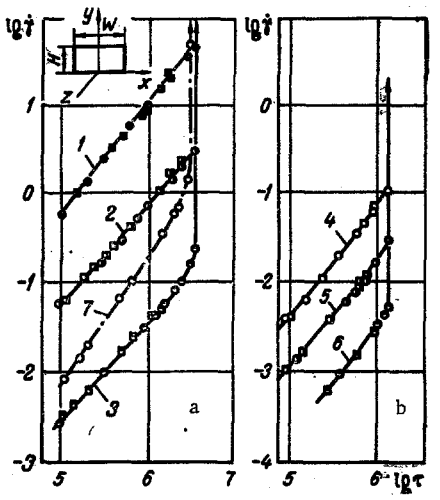

Fig. 1. Flow curves for polybutadiene (a) and polyisoprene (b) (squares relate to rectangular slit, circles to circular capillary). Numbers 1-6 correspond to the sample numbers in the table. Number 7 corresponds to a model broad-MWD polybutadiene sample with $M_V = 2.4 \cdot 10^5$; $\dot{\gamma}$ is in sec^{-1}, τ in dyn/cm^2.

TABLE 1. Brief Description of Investigated Elastomers with Narrow Molecular Weight Distribution $M_W/M_n = 1.1$

Sample No.	Name	$M_V \cdot 10^{-4}$	Isomeric composition			
			cis-1,4	trans-1,4	1–2	3–4
1	Polybutadiene	0,80	46	45	9	—
2	»	1,35	47	44	9	—
3	»	3,20	45	46	9	—
4	Polyisoprene	3,75	79	15	—	6
5	»	5,75	69	25	—	6
6	»	8,30	85	10	—	5

elastomers. For narrow MWD samples a comparison is made here of the results obtained in polymer flows through a rectangular slit (the squares) and through a circular capillary (the circles). In the first case the measurements were made using slits of various lengths so that allowance could be made for the entrance corrections by the two-capillary method [18]. Calculation showed that the entrance corrections are not more than 5 H for polybutadienes and 3 H for polyisoprenes in the entire investigated range of shear rates.

It can be seen from Fig. 1 that over quite a wide range of shear stresses narrow MWD polymers behave like Newtonian fluids. Accordingly, in the case of flows of such polymers through a rectangular slit, the velocity gradient and the tangential stresses can be calculated on the basis of the general solution of the problem of the isothermal steady flow of an incompressible Newtonian fluid [19].

For coordinate axes oriented as in Fig. 1, the equation of motion can be written in the following manner:

$$\frac{\partial P}{\partial z} = \eta \left(\frac{\partial^2 V_z}{\partial x^2} + \frac{\partial^2 V_z}{\partial y^2} \right). \tag{1}$$

Assuming complete attachment of the liquid to the channel walls, the boundary conditions can be written

$$V_z(x,\ 0) = 0;\quad V_z(x,\ H) = 0;\quad V_z\left(\pm \frac{W}{2};\ y\right) = 0. \tag{2}$$

The solution of Eq. (1), obtained by Boussinesq by separation of variables, has the form

$$V_z = \frac{1}{\eta} \cdot \frac{\partial P}{\partial z} \left[\frac{y}{2}(y-H) + \frac{4H^2}{\pi^3} \sum_{n=1,3\ldots}^{\infty} \frac{1}{n^3} \sin \frac{n\pi y}{H} \cdot \frac{\operatorname{ch} \frac{n\pi x}{H}}{\operatorname{ch} \frac{n\pi W}{2H}} \right]. \tag{3}$$

From this expression we readily obtain for the velocity gradient in the y direction and its maximum values $\dot{\gamma}_W$ on the walls of the slit in the plane x = 0:

$$\frac{\partial V_z}{\partial y} = \frac{1}{\eta} \cdot \frac{\partial P}{\partial z} \left[y - \frac{H}{2} + \frac{4H}{\pi^2} \sum_{n=1,3\ldots}^{\infty} \frac{1}{n^2} \cos \frac{n\pi y}{H} \cdot \frac{\operatorname{ch} \frac{n\pi x}{H}}{\operatorname{ch} \frac{n\pi W}{2H}} \right], \tag{4}$$

$$\dot{\gamma}_W = \frac{1}{\eta} \cdot \frac{\partial P}{\partial z} \cdot \frac{H}{2} \left[1 - \frac{8}{\pi^2} \sum_{n=1,3\ldots}^{\infty} \frac{1}{n^2} \cdot \frac{1}{\operatorname{ch} \frac{n\pi W}{2H}} \right] = \pm \frac{1}{\eta} \cdot \frac{\partial P}{\partial z} \cdot \frac{H}{2} K_1. \tag{5}$$

On the other hand, the volumetric flow rate Q of the polymer is given by

$$Q = \int_{-W/2}^{+W/2} \int_{0}^{H} V_z dx dy = -\frac{1}{\eta} \cdot \frac{\partial P}{\partial z} \cdot \frac{WH^3}{12} \left[1 - \frac{192H}{W\pi^5} \sum_{n=1,3\ldots}^{\infty} \frac{1}{n^5} \operatorname{th} \frac{n\pi W}{2H} \right] = -\frac{1}{\eta} \cdot \frac{\partial P}{\partial z} \cdot \frac{WH^3}{12} K_2. \tag{6}$$

On eliminating $(1/\eta) \cdot (\partial P/\partial z)$ from Eqs. (5) and (6) and setting $\tau_W = \eta \dot{\gamma}_W$, we obtain the following theoretical formulas for the velocity gradient and the tangential stress on the walls of the slit in the plane x = 0:

$$\dot{\gamma}_W = \mp \frac{6Q}{WH^2} \cdot \frac{K_1}{K_2}; \quad \tau_W = \pm \frac{H}{2} \cdot \frac{\partial P}{\partial z} K_1. \tag{7}$$

Equations (7) are analogous in form to the corresponding formulas for the calculation of $\dot{\gamma}_W$ and τ_W in the case of a flow of Newtonian fluid through a rectangular slit of infinite width [19] with corrections for the perturbing effect of the front and back walls. An estimate of the terms of the series entering into coefficients K_1 and K_2 shows that they decrease rapidly. Thus, for W/H = 3, the ratio of the second term of the series to the first is less than 10^{-2} and 10^{-5}, respectively, for the coefficients K_1 and K_2. Accordingly, retaining only the first term of the series, we obtain finally

$$\dot{\gamma}_W = \mp 1{,}246 \frac{6Q}{WH^2}; \quad \tau_W = \pm 0{,}985 \frac{H}{2} \cdot \frac{\partial P}{\partial z}. \tag{8}$$

In this manner, the correction to the shear rate and the shear stress due to the effect of the front and back walls amounts to 25 and 1.5% respectively.

It can be seen from Fig. 1 that plots of $\dot{\gamma}_W(\tau_W)$, calculated allowing for the aforementioned corrections indeed coincide well with the experimental data for a circular capillary in those cases when the behavior of the polymer is close to Newtonian. The flow curve for polydisperse polybutadiene shown in this figure was obtained solely with the use of a circular capillary, since the above-considered methods of treating the results of measurements using a rectangular slit are invalid in this case due to the strong viscosity anomaly.

Let us now go on to calculate the normal stresses in the flow in the region of high shear stresses. It is known that the first difference in the normal shear stresses σ equals [11]

$$\sigma = \frac{2\tau}{\operatorname{tg} 2\varkappa}. \tag{9}$$

It follows from this that for a known tangential stress distribution the first difference in the normal stresses is most simply calculated from the curve of the extinction angle distribution, which can be determined by the method of isoclines. However, for all the objects investigated by us, the isocline of any parameter in the region of developed flow takes the form of a dark fringe spread over the greater part of the height of the rectangular slit. It was, accordingly, impossible to ascribe the isocline of a given parameter to any definite point or to the

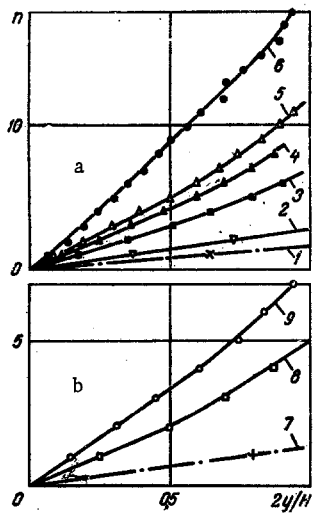

Fig. 2. Isochrome distribution over height of rectangular slit (L/H = 14.3) in region of developed flow for polyubutadiene with $M_V = 1.35 \cdot 10^5$ (a) and polyisoprene with $M_V = 3.75 \cdot 10^5$ (b) for various pressure drops ΔP (kg/cm^2): 1) 9; 2) 16; 3) 36; 4) 48; 5) 60; 6) 100; 7) 16; 8) 45; 9) 65.

narrow region of the cross section of the rectangular slit. As the extinction angle could not be determined experimentally, it became necessary to calculate it.

It is known [10] that

$$\sin 2\varkappa = \frac{\tau}{\tau_{max}} . \tag{10}$$

Thus, to calculate the first difference in the normal stresses, it is necessary and sufficient to know the magnitude of the tangential stresses and the maximum tangential stresses at each point of the flow.

The tangential stresses τ were calculated via the formula [19]

$$\tau = \frac{\Delta P \cdot y}{2L} . \tag{11}$$

As for the maximum tangential stresses, their distribution over the height of the flow was obtained directly from the isochrome pattern [20], since

$$\tau_{max} = \frac{n\lambda}{2CW} . \tag{12}$$

The fringe distribution over the height of the slit was recorded on a photographic film with subsequent photometric measurement of the negative.

Figure 2 shows the isochrome distribution over the height of the slit for polybutadiene (a) and polyisoprene (b) with molecular weights 135,000 and 375,000, respectively, for various pressures. It can be seen from the figure that at low pressures the fringes are distributed linearly over the cross section of the slit. With increasing pressure, i.e., with increasing shear stress, the character of the fringe distribution deviates more and more from linear, the distance between fringes decreasing near the channel walls.

It is evident from (12) that the maximum stresses over the channel height must be distributed exactly in accordance with the fringe distribution pattern. The stress-optical coefficient C entering into this formula was determined experimentally at low values of the tangential stresses, when it is sufficiently accurate to take $\tau = \tau_{max}$. For the investigated polymer homologous series the value of C at 25°C worked out to be $3.3 \cdot 10^{-10}$ and $1.9 \cdot 10^{-10}$ cm^2/dyn, respectively, for the polybutadienes and the polyisoprenes. This value of C for polybutadiene is close to results cited in the literature [21, 22].

In this manner, the visual representation of a polymer flow in a capillary of rectangular cross section can be used to determine the tangential stresses and the maximum tangential stresses at each point of the flow. By way of example we show in Fig. 3 the distribution of the maximum tangential stresses and the tangential stresses over the height of the slit for polybutadiene with molecular weight 135,000 for a pressure drop in the slit $\Delta P = 100$ kg/cm^2.

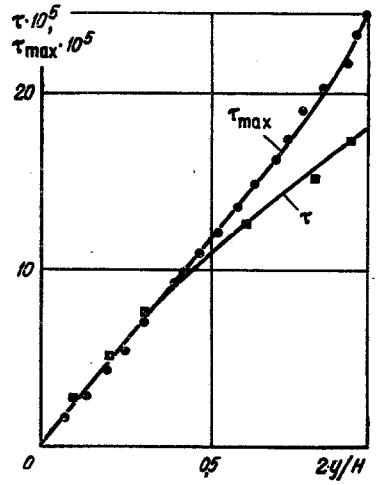

Fig. 3

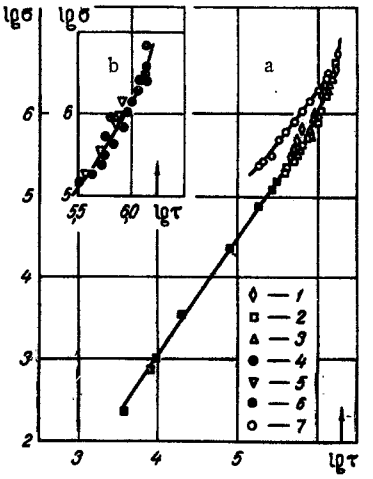

Fig. 4

Fig. 3. Distribution of maximum tangential stresses τ_{max} over height of rectangular slit (L/H = 14.3) in region of developed flow for pressure drop $\Delta P = 100$ kg/cm^2 for polybutadiene with $M_V = 1.35 \cdot 10^5$; τ and τ_{max} in dyn/cm^2.

Fig. 4. Dependence of first difference in normal stresses on tangential stresses for polybutadiene (a) and polyisoprene (b) (solid points obtained with cone-and-plate instrument, open points obtained with polarization-optical apparatus). Numbers 1-6 correspond to sample numbers in Table 1; No. 7 corresponds to model broad-MWD polybutadiene sample with $M_V = 2.4 \cdot 10^5$; σ and τ are in dyn/cm^2.

As is to be expected, these quantities coincide in the central part of the flow (i.e., at low shear stresses), whereas on approaching the walls the amount by which τ_{max} exceeds τ becomes increasingly significant. It is the relationship of these quantities for a known velocity profile that makes it possible to calculate the dependence of the first difference in the normal stresses on the shear stresses or the shear rate. It can be seen from the figure that this sort of calculation can be made only in the region of high shear stresses, which is simultaneously both an advantage and a limitation of the method.

The results of calculations of this sort are shown in Fig. 4 for polybutadiene and polyisoprene. In this figure we also show for comparison the dependence of the first difference in the normal stresses on the tangential stresses determined by Plotnikova and Malkin using a cone-and-plate viscometer in the region of low shear stresses for polybutadiene with a molecular weight 135,000.

It can be seen from the cited data that the values of the first difference in the normal stresses calculated by the method proposed above is in good agreement with the corresponding values found at low shear stresses by direct measurements. Furthermore, the dependence of the normal stresses on the tangential stresses for narrow MWD polymers of the same homologous series does not depend on the molecular weight of the polymer.

In the case of polybutadienes and polyisoprenes with a narrow molecular-weight distribution, the rate of growth of σ with increasing shear stress increases sharply on approaching the separation region (denoted by the vertical arrows on the axis of abscissas), and their value may exceed the shear stress corresponding to separation. This means that the phenomenon of flow separation is connected to a significant extent with the appearance of the highly elastic properties of the polymer. Furthermore, it follows from this that one must proceed with caution when extrapolating parameters characterizing the highly elastic properties of polymers into regions of stresses at which separation is observed.

The situation is different with polydisperse polybutadiene, for which the rate of growth of the normal stresses is weaker compared with monodisperse polybutadiene. This can be seen from a comparison of Figs. 1 and 4. Indeed, as can be seen from Fig. 1, a viscosity anomaly appears in the flow of the broad MWD polybutadiene sample, whereas the plot of $\sigma(\tau)$ in double logarithmic coordinates remains practically linear (Fig. 4).

In this manner the obtained results, in conjunction with known data in the literature on polymer systems, lead to the important conclusion that the components of the stress tensor are interrelated. It is known [23] that at low shear stresses $\sigma \sim \tau^2$. As can be seen from the data of Fig. 4 the dependence $\sigma(\tau)$ departs significantly from quadratic with increasing shear stress, the exponent of this dependence gradually decreasing. However,

for narrow MWD polymers, the exponent of the function $\sigma(\tau)$ begins to increase on approaching critical values of the shear stresses, and may become greater than 2; for a polydisperse polymer, on the other hand, the slope of the dependence of the normal stresses on the tangential remains effectively constant in the range of those shear stresses.

NOTATION

τ, τ_W, tangential stress in flow and wall stress, respectively; $\dot{\gamma}$, $\dot{\gamma}_W$, shear rate in flow and on wall, respectively; σ, first difference in normal stresses; η, effective viscosity; $\partial P/\partial z$, pressure gradient; V_z linear velocity along z axis; W, H, L, width, height, and length, respectively, of rectangular slit; Q, volumetric flow rate; $\varkappa$, extinction angle; n, interference fringe number; λ, wavelength of light source; C, stress-optical coefficient; τ_{max}, maximum tangential stress; ΔP, pressure drop.

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