

LIQUIDS

3.1 NEWTONIAN AND NON-NEWTONIAN LIQUIDS. DEFINITIONS

Rheology deals with materials in liquid and solid states. However, as can be derived from its name, liquids (or flowing media) attract the main attention of rheologists. This is why the information in this chapter is the backbone of rheology.

The quantitative approach to the flow properties of liquids began with “*Theorem XXXIX*” of the classical monograph of Newton, where he introduced such terms as “*defectus lubricitatus*” and “*attritus*”, which are equivalent to the modern terms “*internal friction*” and “*viscosity*”. He proposed that resistance appearing due to internal friction is proportional to the relative velocity of fluid particles. This is the fundamental hypothesis. However, he argued about the circular movement. Later, the analogous supposition was formulated by Navier¹ and then by Stokes,² who gave the modern form to the Newton hypothesis.

Liquid with flow properties obeying the Newton hypothesis is called *Newton-Stokes liquid*, or *Newtonian liquid*. These properties can be formulated in a standard form as:

$$\sigma = \eta \dot{\gamma} \quad [3.1.1]$$

where σ is the shear stress, $\dot{\gamma}$ is the shear rate, and the constant coefficient of proportionality, η , is called viscosity (or shear viscosity).³

This equation suggests that the shear stress is proportional to the deformation rate (the shear rate, in this case), and such liquid is a *linear* rheological medium.

If the shear stress is not proportional to the shear rate, such liquid is called *non-Newtonian* and the ratio $\sigma/\dot{\gamma}$ is called *apparent viscosity*, which is not necessarily constant.

The three-dimensional formulation of the basic rheological law for Newtonian liquid is

$$\sigma_{ij} = 2\eta D_{ij} \quad [3.1.2]$$

where σ_{ij} is the stress tensor and D_{ij} is the deformation rate tensor.

As a rule, it is assumed that Newtonian liquid is incompressible. Therefore, the spherical component of the rate of the deformation tensor is absent. The spherical component of the stress tensor (which represents the hydrostatic pressure) can exist but it is immaterial for rheological behavior of liquid.

In a simple shear

$$\dot{\gamma} = \frac{1}{2}D_{ij} = \frac{\partial u_1}{\partial x_2}$$

and therefore Eq. 3.1.2 refers to the standard definition of Eq. 3.1.1.

The basic Eq. 3.1.2 is the *rheological equation of state* (or a *constitutive equation*) of Newtonian, incompressible liquid. It is used for formulating the dynamic equilibrium equations, known as the *Navier-Stokes equations*, describing the mechanics of such liquids in any situation. These equations are the basis of formulating and solving any applied boundary problems.

The definition of Newtonian liquid can be easily extended to the uniaxial extension. It is evident that in this case there is only one component of the stress tensor – normal stress, σ_E . This stress tensor can be decomposed into spherical and deviatoric parts in the following manner:

$$\sigma = \begin{bmatrix} \sigma_E & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \frac{\sigma_E}{3}\delta_{ij} + \frac{\sigma_E}{3} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad [3.1.3]$$

where the first term is a spherical part (i.e., negative hydrostatic pressure) and the second term is a deviator of the stress tensor.

The rate of deformation tensor for a uniaxial extension of an incompressible medium is given by:

$$\dot{\gamma} = \frac{1}{2}\dot{\gamma}_{11} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad [3.1.4]$$

If a general definition of Newtonian liquid is applied and compared with the deviatoric parts of both tensors, the following equation is obtained:

$$\sigma_E = 3\eta\dot{\gamma}_{11} \quad [3.1.5]$$

The coefficient in this equation, η_E ,

$$\eta_E = 3\eta \quad [3.1.6]$$

is known as the coefficient of *extensional viscosity* or the *Trouton viscosity*, and the Eq. 3.1.6 is the *Trouton law*⁴.

The same calculations can be done for a two-dimensional or biaxial extension. In this case the coefficient of biaxial extensional viscosity, η_B , equals 6:

$$\eta_B = 6\eta \quad [3.1.7]$$

These two examples (uniaxial and biaxial extension) demonstrate that the results of different experiments can be treated as the consequences of the same basic rheological

equation of state establishing the general, tensor relationship between components of the stress and deformation rate tensors. Therefore the elongational viscosity appears not to be an independent constant (property) of material but only another image of the same Newtonian viscosity.

It is also useful to formulate the rheological equation of state of Newtonian liquid in an invariant form. Liquid is defined here as a medium for which all work done by deformation dissipates. The intensity of dissipation, A, is expressed as

$$A = \sum_{i,j} \sigma_{ij} \dot{\gamma}_{ij} \quad [3.1.8]$$

Then it is easy to show that the rheological equation of state Eq. 3.1.2 is equivalent to the following relationship:

$$A = -4\eta D_2 = -4\eta \sum_{i,j} \dot{\gamma}_{ij} \dot{\gamma}_{ij} \quad [3.1.9]$$

where D_2 is the second invariant of the deformation rate tensor.

Eq. 3.1.9 can be considered as the invariant definition of the Newton-Stokes liquid. Simple relationships between the stresses and the deformation rates for different deformation modes, such as Eq. 3.1.1 or Eq. 3.1.5, are obtained as consequences of this definition.

The coefficient of Newtonian viscosity, η , is a single characteristic of flow properties of liquid if its rheological behavior is determined by Eq. 3.1.2 or Eq. 3.1.9. Here are examples of ranges of viscosities of some liquids:

	viscosity range in Pa*s
Gases	0.00001
Water (at 20°C)	0.001
Sulfuric acid	0.03
Lubricating oils	0.1-3
Glycerin	2
Oligomers	0.010-10
Glues, paints	1-200
Melts of thermoplastics	100-100,000
Rubber compounds	10,000-10,000,000
Bitumens	100,000-100,000,000
Melted inorganic glasses	1,000,000-100,000,000,000
Glassy liquids	> 100,000,000,000

It is apparent that viscosity of liquids varies in a wide range of values exceeding 15 decimal orders.

If an experiment shows that apparent viscosity is not constant, then Eq. 3.1.2 becomes invalid and it is necessary to formulate some rheological equation of state for non-Newtonian liquid. In this case it is necessary to distinguish between two cases of non-Newtonian purely viscous liquid and viscoelastic liquid. In the first case, the work of deformation dissipates completely. In the second case, a part of deformation work is stored in the form of elastic energy and returned as elastic deformation.

The rheological equation of state for a purely viscous liquid can be written in the following general tensor form:

$$\sigma_{ij} = 2\eta(D_2)\dot{\gamma}_{ij} \quad [3.1.10]$$

or in the invariant form:

$$A = -4\eta(D_2)D_2 \quad [3.1.11]$$

The apparent viscosity is some function of the second invariant of the deformation rate tensor. The function $\eta(D_2)$ can be found experimentally in simple flow experiments, for example in simple shear or uniaxial extension, when only one non-zero component of the deformation rate tensor exists. However, it is necessary to confirm that the experiments performed in different geometries give the same function $\eta(D_2)$. If this principal condition is not fulfilled, it means that the rheological equation of state, taken for fitting one set of experimental data, is chosen incorrectly. Thus, it should not be used for any arbitrary flow geometry.

Example

For any purely viscous liquid it is possible to prove that the Trouton law is always valid if one compares the shear viscosity, η , and the elongational viscosity, η_E , at the following condition:

$$\dot{\gamma}_{11} = \frac{1}{\sqrt{3}}\dot{\gamma}_{12}$$

In this case, D_2 from Eq. 3.1.10 is the same for both simple shear flow and elongational flow. It is thus expected that if η is a decreasing function of the shear rate, then the elongational viscosity, η_E , should also be a decreasing function of the deformation rate. The first is frequently observed for various materials, but experiments demonstrate that the second statement is not true for many such liquids. It means that a model of a purely viscous liquid is not applicable to experiments in extension, and then it follows that such a model is of no general meaning for formulating an invariant rheological equation of state.

In discussion of non-Newtonian behavior in shear flow and, in fact, any rheological problem, there is no unique interrelation between stresses and deformation rates, but stresses are functions of both deformation rates *and* time (or deformations) simultaneously. Hence it is reasonable to distinguish between two cases:

1. If deformations continue for a sufficiently long time such that the *stationary* (or *steady*) *regimes* of flow have been reached, there is an unambiguous relationship between the shear stresses and shear rates. This relationship is called a *flow curve*.
2. If this stationary deformation regime has not yet been reached, the state of material continuously changes with time, and it is the function of deformation pre-history. In such a *transient deformation regime*, stresses are functions of deformation rate and deformation experienced by the material occurs from the beginning of flow.

It is usually assumed in *non-Newtonian shear flow* that the set of stationary deformation states is reached after material is subjected to deformations for a sufficiently long time to pass through all transient states.

Experimental results of viscosity measurement in stationary deformation regimes may be presented as the relationship between shear stress, σ , and shear rate, $\dot{\gamma}$, or opposite, as the relationship between shear rate and shear stress. For Newtonian liquid this dependence is always linear. The *apparent viscosity* of non-Newtonian liquid, defined as the ratio, $\sigma/\dot{\gamma}$, can be evaluated as a function of either σ or $\dot{\gamma}$. This ratio is constant for Newtonian liquid but not for non-Newtonian liquid.

Non-Newtonian behavior may appear at different ranges of stresses. Therefore, it is useful to measure the $\sigma(\dot{\gamma})$ dependence in a wide range of variables. This dependence, graphically presented in log-log coordinates, reveals peculiarities of a flow curve in different ranges of the shear stress.

If the shear stress is proportional to the shear rate (Newtonian liquid), its graphic representation on the log-log scale is a straight line equally inclined to both coordinate axes. If the angle of a line is not 45° or experimental points do not lie on a straight line, it means that the material under study is non-Newtonian liquid.

3.2 NON-NEWTONIAN SHEAR FLOW

3.2.1 NON-NEWTONIAN BEHAVIOR OF VISCOELASTIC POLYMERIC MATERIALS

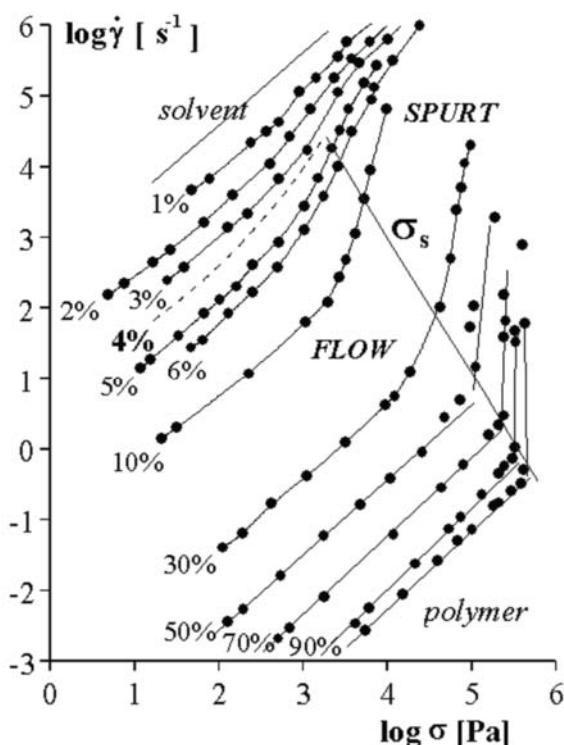


Figure 3.2.1. Flow curves of polybutadiene solutions in the full concentration range. $MM = 2.4 \times 10^5$; $\bar{M}_w/\bar{M}_n = 1.1$. Solvent: methyl naphthalene. $T = 25^\circ\text{C}$. [Adapted, with permission, from G.V. Vinogradov, A.Ya. Malkin, N.K. Blinova, S.I. Sergeyenkov, M.P. Zabugina, L.V. Titkova, Yu.G. Yanovsky, V.G. Shalganova, *Europ. Polymer J.*, **9**, 1231 (1973)].

(or *limiting viscosity at infinite shear rate*), η_∞ .

It is supposed that macromolecules in dilute solution are independent in their molecular movements and do not have permanent contacts with each other. Hence, non-Newtonian

Fig. 3.2.1 gives the results of viscosity measurements of solutions of monodisperse polymer in a wide concentration range. The left upper line is the representation of flow behavior of a low-molecular-weight solvent. This behavior is expressed by a straight line inclined at 45° in log-log coordinates. It means that the solvent is Newtonian liquid.

Adding any amount of high-molecular-weight, long-chain, flexible polymer radically changes the rheological behavior of the resultant liquid. Even 1% solution of polymer causes shear rate dependence of the *apparent viscosity*, η , ($\eta = \sigma/\dot{\gamma}$). However, the apparent viscosity is constant at very low shear rates. This is the so-called initial, or *zero-shear-rate Newtonian viscosity* (or *limiting viscosity at zero shear rate*),

η_0 . Then the apparent viscosity decreases with an increase of shear rate, and at higher shear rates the viscosity reaches its minimum value, which is called the *upper Newtonian viscosity*

nian behavior of the dilute polymer solution is explained by deformation of the individual molecules in the stream. Macromolecules change their shape, resulting in decrease of their resistance to flow due to streamlining at higher shear rates.

The increase of polymer concentration in solution (shift from upper left corner of Fig. 3.2.1 downwards) results in more frequent contacts of macromolecules and the formation of network of entanglements. Chains at the sites of contact may slide over each other and that is why the network is quasi-permanent. The contacts may have some “*lifetime*”. The intermolecular contacts causing formation of the entanglement network are believed to occur at some critical concentration, c^* , depending on the length of the chain. According to Debye,⁵ a criterion for “dilute” solution can be written as follows:

$$c[\eta] < 1$$

where $[\eta]$ is the intrinsic viscosity which can be treated as a measure of the size of a macromolecule.⁶

Non-Newtonian behavior becomes more and more pronounced with the increase of polymer concentration in solution. If one analyzes these graphs beginning from the lower right corner of the graph, the viscosity of polymer is constant until some critical shear stress, σ_s , is reached. At higher stresses flow becomes impossible: attempts to increase shear stresses result in loss of material fluidity and material begins to slide along the walls of the measuring device. This effect is called *spurt*.⁷ At high shear rates, the limit of flow is reached. This phenomenon is of principal importance for flow of viscoelastic liquids, though the outward appearance of this limiting state can be very different (see Section 3.6 specially devoted to this topic). Addition of solvent to melt does not change general behavior because material can only flow until some critical shear stress is reached and then it begins to slide when shear is further increased. The critical shear stress, σ_s , decreases with an increase in the content of solvent in solution. This is shown by a straight line in Fig. 3.2.1, which presents the limiting region of flow and corresponds to the transition from flow to spurt behavior of fluid. It is also worth mentioning that for dilute solution the region of decreasing apparent viscosity appears between the lower Newtonian branch of a flow curve and the spurt depicted by the vertical line on the graph. Such a region is absent in monodisperse polymer melts.

Experimental data in Fig. 3.2.1 are for a monodisperse polymer and its solutions. However, practically all real polymers are polydisperse, i.e., contain fractions of chains of different length. Hence they can be treated as mixtures of different substances. A typical flow curve of a polydisperse polymer is shown in Fig. 3.2.2 for polyethylene melt. The data points were obtained using various experimental techniques (geometric flow setups). This data shows that the apparent viscosity “at a point” is a real physical effect acting regardless of the geometry of flow or other peculiarities of the experimental methods used.

Fig. 3.2.2 shows exemplary non-Newtonian behavior of melt, the apparent viscosity of which decreases more than 1000 times. At low shear rates, the apparent viscosity reaches its initial Newtonian limit, η_0 . The upper Newtonian viscosity limit for concentrated solutions and melts is not reached due to the instability of the stream at high flow rates (see Section 3.6).

Non-Newtonian flow of melts of polydisperse polymers and their concentrated solutions depends on superposition of deformation of long flexible chains and mutual sliding

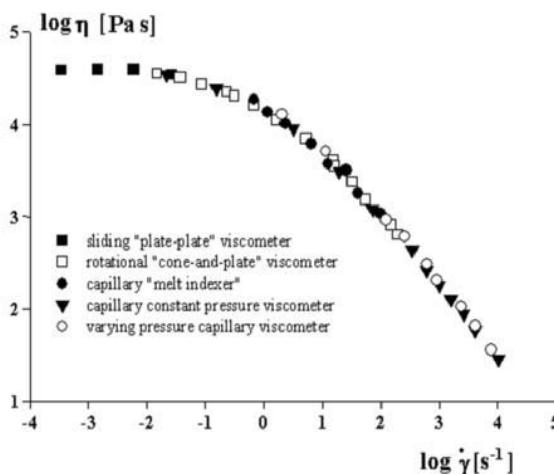


Figure 3.2.2. Flow curve obtained using different experimental techniques. LDPE with MI = 2 (ICI). 150°C. [Adapted, with permission, from G.V. Vinogradov, M.P. Zabugina, A.A. Konstantinov, I.V. Konyukh, A.Ya. Malkin, N.V. Prozorovskaya, *Vysokomol. Soedin.* (Polymers - in Russian), **6**, 1646 (1964)].

deformation of three-dimensional network in cured rubbers (which cannot flow). Then it is possible to think that there is a distribution of the lifetimes of entanglements and at some shear rate, some junctions behave as a stable (permanent) network, but some polymer chains may slide in the case of some entanglements. The shares of quasi-stable and disintegrating junction points depend on T_{def} . It means that resistance to flow and, consequently, apparent viscosity depends on shear rate. The range of deformation rates at initial Newtonian viscosity corresponds to a very slow flow when for all T_{ent} the condition $T_{\text{def}} \ll T_{\text{ent}}$ is fulfilled. Therefore, the value of η_0 is a parameter of material directly related to its molecular structure, which is not affected by deformation. Indeed, η_0 is a measure of molecular mass of polymer, which can be used for comparative purposes with different samples.

The concept based on the influence of shear rates (or stress) on stability of macromolecular entanglements explains non-Newtonian behavior of polymer systems. However, a quantitative description of non-Newtonian flow can be constructed only within the framework of viscoelastic behavior because the above mentioned physical events are related to different time effects.

3.2.2 NON-NEWTONIAN BEHAVIOR OF STRUCTURED SYSTEMS – PLASTICITY OF LIQUIDS

Fig. 3.2.3 shows non-Newtonian behavior of water suspension of bentonite. The relationship is composed of three parts:

1. a flow with very high viscosity at low shear stresses
2. an abrupt drop in the viscosity at some critical shear stress, σ_y (or at least in very narrow stress range)
3. non-Newtonian flow at stresses exceeding σ_y

of macromolecules in network entanglements. In dilute solutions (interchain interactions are practically absent), the mechanism of flow is controlled by deformation of individual macromolecular chains. The intermolecular contacts may be considered as the dominating cause of non-Newtonian behavior.

Qualitative explanation of non-Newtonian flow is based on analysis of the interrelation between the lifetime of entanglements, T_{ent} , and characteristic time of deformation, T_{def} (the latter can be defined as the reciprocal shear rate, $T_{\text{def}} = \dot{\gamma}^{-1}$). If $T_{\text{def}} \ll T_{\text{ent}}$, the entanglements behave as stable joining points. The polymer melt behavior is analogous to

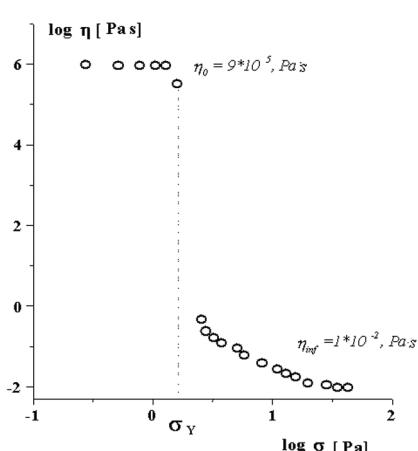


Figure 3.2.3. Complete flow curve, including the yield stress, of 5% bentonite dispersion in water. [Reconstructed from experimental data of L.A. Abduraghimova, P.A. Rehbinder, and N.N. Serb-Serbina (1955).]

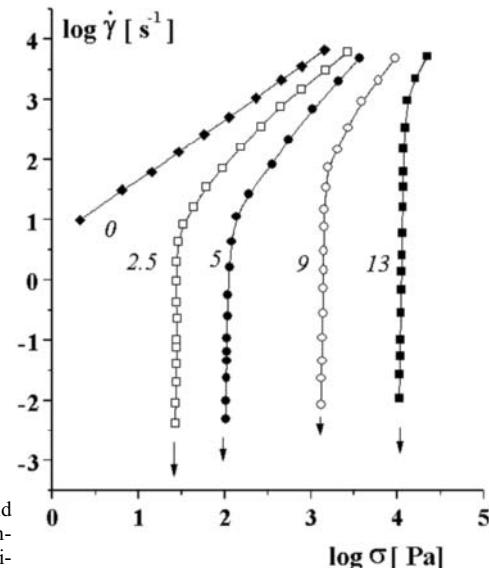


Figure 3.2.4. Flow curves of a filled low-MM polyisobutylene. Filler: active carbon black. Concentration of a filler in vol% is given on the curves. Arrows show σ_Y values.

Here, there is no gradual decrease in viscosity but a rapid drop in viscosity by several decimal orders. This is a case of solid dispersed phase organized in a continuous three-dimensional structure (*coagulated structure*) having some *strength*. At low shear stresses, flow takes place because of sliding of thin (possibly molecular size) layers between elements of a solid phase. The resistance to sliding is high and therefore the viscosity at low stresses is also high.

The strength of the coagulated structure is characterized by stress σ_Y called the *yield stress*. After destroying the coagulated structure of a solid phase (at stresses exceeding σ_Y) the dispersion flows like a low viscosity liquid, which does not contain residues of a solid phase. The viscosity of such a system is close (within the order of values) to the viscosity of a dispersion medium. This viscosity is several decimal orders lower than the viscosity of a system with undestroyed coagulated structure.

This type of rheological behavior is called *plasticity*, and the behavior is called *viscoplastic flow*. Plasticity is typical of many liquid-like media, such as greases, coal suspensions, concrete mixes, crude oil, mud, different pastes (toothpaste, cosmetic pastes, shoe polish, ice cream, and many other products), biological liquids, and so on.⁸

Superposition of viscoelastic and viscoplastic effects in non-Newtonian flow is often observed if a dispersion medium is a viscoelastic liquid. This is observed in filled polymers with an active (structure forming) filler. Fig. 3.2.4 shows flow curves of polyisobutylene filled with varying amounts of carbon black. The similarity of shapes of curves in Figs. 3.2.3 and 3.2.4 is pertinent.

Fig. 3.2.5 shows rheological behaviors of two polyisobutylenes having different molecular masses (viscosities differ with molecular mass) and the concentration of carbon black. The viscosity of materials with non-destroyed structure (very low shear stresses) is

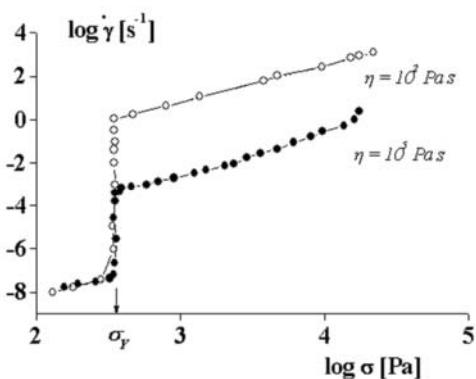


Figure 3.2.5. Complete flow curves of two filled polymers of different MM but with the same active filler concentration. Polymer: polyisobutylene. Filler: carbon black. The viscosity at $\sigma < \sigma_Y$ is $10^9\text{-}10^{10}\text{ Pa*s}$.

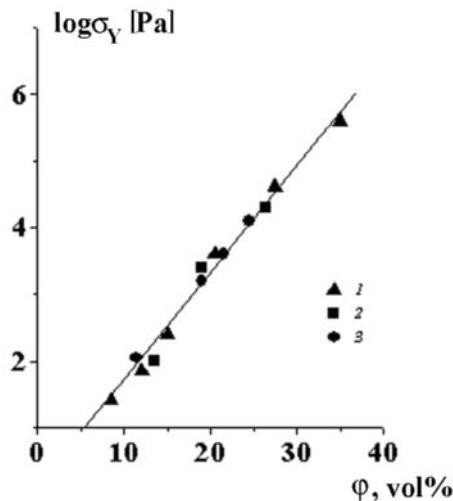


Figure 3.2.6. Concentration dependence of the yield stress for the same filler and different binders: Polybutadiene MM = 1.35×10^5 (1); Polybutadiene MM = 1×10^4 (2); Silicone oil - low viscosity liquid (3).

the same for both systems, because flow in this stress range does not depend on the viscosity of binder but it is determined by molecular forces and interaction between solid particles. The yield stress in both cases is the same, because the strength of the structure formed by carbon black does not depend on the nature of the liquid binder.

Flow of viscoplastic materials below the yield stress may occur and viscosity in this range ("upper Newtonian viscosity") is on a level of viscosity of coagulated materials or filled systems, typically in the range of $10^9\text{-}10^{10}\text{ Pa*s}$ regardless of the nature of a disperse liquid. This indicates that the resistance to deformation (i.e., "viscosity") at the low shear stresses is weakly related to the viscosity of a liquid medium in a structured system. Much lower values of the upper Newtonian viscosity are observed for weak gels formed by so called molecular colloids. The apparent viscosities at low shear stresses for these materials lie in the range $10^3\text{-}10^5\text{ Pa*s}$ clearly expressing the yield stress drop down by 7 decimal orders.⁸ Meanwhile, doubts always exist whether the observed apparent fall in viscosity is the homogeneous volume effect or is it the consequence of the separation of a medium into two zones with different rheological properties and flow proceeding in a low-viscous zone.

For an observer, the transition from the low shear stress ($\sigma < \sigma_Y$) to the higher stress ($\sigma > \sigma_Y$) looks like a transition from solid-like to liquid-like behavior. Materials at $\sigma < \sigma_Y$ flow so slowly that in many cases a very long observation time or special experimental methods and devices are needed to notice it. At higher stresses, "ordinary" liquid is tested, which flows like any other liquid.

The value of the yield stress mainly depends on the strength of the structure formed by solid filler. In particular, σ_Y depends on the concentration of filler but not on the nature of a liquid binder. Fig. 3.2.6 shows concentration dependence of σ_Y for different liquid binders containing the same filler. The concentration dependence of $\sigma_Y(\phi)$ is close to exponential (ϕ is concentration of filler in vol%). However, it is not always true, because

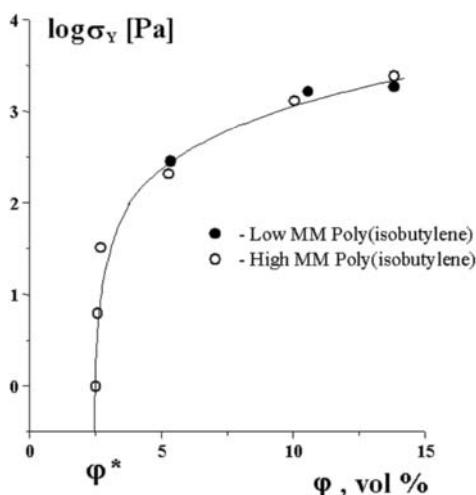


Figure 3.2.7. Concentration dependence of the yield stress showing the existence of a “critical” concentration of structure formation, ϕ^* . Filler: active carbon black. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, E.P. Plotnikova, O.Yu. Sabsai, N.E. Nikolaeva, *Intern. J. Polym. Mater.*, **2**, 1 (1972)].

affected by the same factors – structure and concentration of filler. At stresses exceeding σ_y , viscosity of systems depends on viscosity of liquid medium.

Some authors consider the “structure” (though this term is being treated as a generalized but not rigorously defined phenomenon) as a unique cause of non-Newtonian behavior. The apparent viscosity, depending on the shear rate, is then called the “structural viscosity” (e.g., *strukturviscosität* in German),⁹ and a relative decrease of the apparent viscosity in comparison with the initial Newtonian viscosity is treated as a measure of structure breakdown.

In reality, there is no strict separation of flow of materials into two different regimes exhibiting a low shear stress limit of Newtonian flow and viscoplastic flow with yield stress. However, it may be useful to define some limiting cases:

- yielding may develop in a wide stress range but not as an abrupt change in a flow curve. A continuous decrease in the apparent viscosity, as in Fig. 3.2.2, is sometimes called *pseudo-plasticity*
- one can always suspect that the observed low shear stress of a Newtonian branch is a pseudo-Newtonian region and it consists of part of a complete flow curve. It could be envisioned that at much lower stresses a yield point is reached and flow becomes impossible. It is possible to find real materials which are close in behavior to the described extreme cases of non-Newtonian flow, as well as materials whose behavior is intermediate and approaching the extreme cases.

The method of presentation of experimental data (“points”) can be illusive and lead to false conclusions. For example, Fig. 3.2.2 clearly demonstrates that there is low-shear-rate Newtonian limit on the flow curve of polyethylene melt. However, if one presents the

plasticity occurs only when concentration of filler is sufficiently high to form a continuous structure. This is demonstrated in Fig. 3.2.7, where a linear scale instead of a logarithmic scale is used for filler concentration. Plasticity of filled systems occurs when $\phi > \phi^*$.

The transition from the solid-like to liquid-like behavior with increasing stress may not be necessarily catastrophic but may proceed in a wide stress range. This happens when the structure of material is not “rigid” and there is a distribution of bond strength. In this sense it is not always correct to consider “the yield stress” or “yield point” as a “point” on the flow curve, but this term is only used as an approximate description of real rheological behavior of material.

Structured systems are *non-Newtonian viscoplastic liquids*. Their viscosity below the yield stress and yielding are

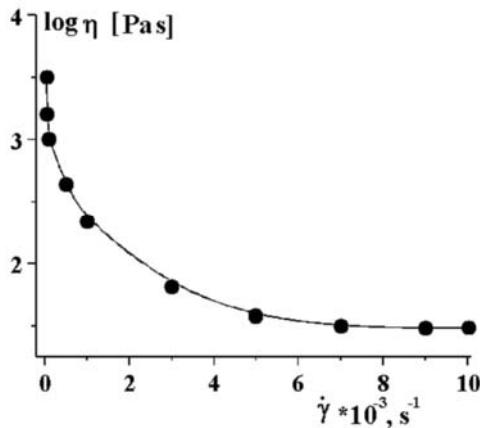


Figure 3.2.8. Flow curve of polyethylene as in Fig. 3.2.2, but presented in semi-log scale. Several points at low shear rates are arbitrarily taken from Fig. 3.2.2.

low shear rates are taken from Fig. 3.2.2), then the relationship looks different, showing unlimited growth of the apparent viscosity on approaching the yield point.

The answer to the question concerning such physical reality as the yield stress is the following: for some materials there is a more or less wide stress range in which their apparent viscosity decreases in a sudden manner; this stress range is treated as the yield stress. This is similar to the *strength* of solid materials. The majority of engineers believe that the values of strength given in handbooks are real physical characteristics of materials. At the same time, these reference values come from measurements made under some standardized conditions. The same material may break at different stress, depending on numerous factors, including duration of stress application.

The difference between two extreme cases of rheological behavior is reflected in the difference of definitions between “*solution*” and “*gel*”. The term “*solution*” is related to systems exhibiting the Newtonian branch of a flow curve at low shear stress, i.e., formally, by definition, it is a material which flows at any stress regardless of how low this stress is. At the same time, viscosity of the Newtonian region may be very high. Gels, on the contrary, are materials which, by definition, do not flow at low stresses because of the existence of a yield point, though their viscosity at higher stresses may be low. Moreover, the term *gel* is often used to characterize low-modulus (very soft) rubbery materials (stable gels) with a permanent molecular or supermolecular (crystalline) network. Such materials cannot flow at all because the lifetime of bonds in these materials is infinite, whereas the lifetime of network entanglements in flowing gels is limited. Then, the yield stress in stable gels equals their macroscopic strength.

The transition between solutions and gels can be continuous and sometimes it is impossible to give a self-evident definition of a matter. An example illustrating the last statement is presented in Fig. 3.2.9 where flow curves of emulsions with different concentration of an inner phase are presented.⁹

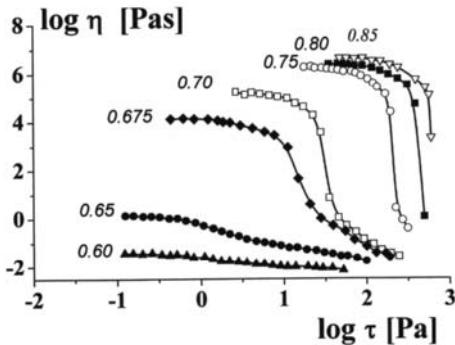


Figure 3.2.9. Flow curves of emulsions at different concentration of an inner phase (shown at the curves) [After R. Lapasin, A. Trevisan, A. Semenzato, G. Baratto, Presented at AERC, Portugal, Sept. 2003].

same experimental data in semi-log scale (as is done in Fig. 3.2.8, where several points at

It is seen that the flow curves of emulsions at a concentration range of 0.6-0.675 exhibits typical non-Newtonian behavior. However, the change in apparent viscosity as a function of shear stress is strongly affected by a slight increase of concentration from 0.65 to 0.675. A further increase of concentration till 0.70 creates a medium with clearly expressed yielding behavior. At concentrations of 0.75-0.85 a medium becomes gel-like which does not flow after the transition through the yield stress. So, even small changes in the concentration of an emulsion lead to radical changes in rheological behavior. The latter is explained as a result of the approach to the state of the closest packing of spherical liquid droplets and their compression after the transition through this threshold.

The term “plasticity” (and the concept of plastic behavior) is also widely used in mechanics of solids: there are materials which can be treated as purely elastic up to the yield point and they can be deformed unlimitedly at stresses exceeding the yield stress.¹⁰ In other words, such solids flow at high stresses. The term “flow” has a rather peculiar meaning for materials such as metals, but in reality these materials also flow, i.e., deform irreversibly at high stresses. Plastic flow of many “solid” materials is essential in different technological operations, such as punching of silver or golden articles (coins, jewelry), rolling of steel, pulling wire through dies, and so on.

The difference between viscoplastic and solid plastic materials is hidden in their behavior at $\sigma < \sigma_y$. In a formal approach, describing the mechanical behavior of material, this difference is not principal. In real technological practice, the yield stress value for viscoplastic liquid is much lower than the yield stress of solid plastic materials. It should be remembered that both concepts, viscoplastic liquid and plastic solid, are no more than a model presentation of rheological properties of real technological materials.

3.2.3 VISCOSITY OF ANISOTROPIC LIQUIDS

In many cases, viscosity is treated as a scalar value and it means that the viscosity does not depend on the flow direction (or the direction of its measurement). Meanwhile, there are liquid substances which have their inherent or stress induced structure, and not all directions in such liquids are equivalent. They are known as *anisotropic liquids*, which are analogous to anisotropic solids (see Eq. 4.3.1 with the change of deformation for rate of deformation and tensor of elastic modulus for tensor of viscosity). It means that the simplest Newtonian approximation does not have a general meaning. In a general case, viscosity must be considered as a parameter of a tensor nature.

The quantitative approach to the description of anisotropic viscosities was first formulated by Miesowicz.¹¹ He proposed to distinguish three coefficients of viscosity related, correspondingly, to direction of flow, direction of the velocity gradient and direction perpendicular to both these directions. Actually, his three coefficients are components of the complete viscosity tensor.

There are two main causes of anisotropy. First, there are liquid crystals,¹² which initially have a structure. Their viscosity depends on the direction of measurement in relation to the orientation of crystallographic axes. Indeed there are a lot of investigations of this phenomenon frequently treated in terms of the three Miesowicz coefficients.¹³ The main body of investigations in this field is devoted to viscosity anisotropy in nematic liquid crystals.¹⁴

Further development of the rheology of anisotropic nematic crystals was proposed by Leslie,¹⁵ Ericksen,¹⁶ and Parodi.¹⁷ They introduced a conception of the *director*, which

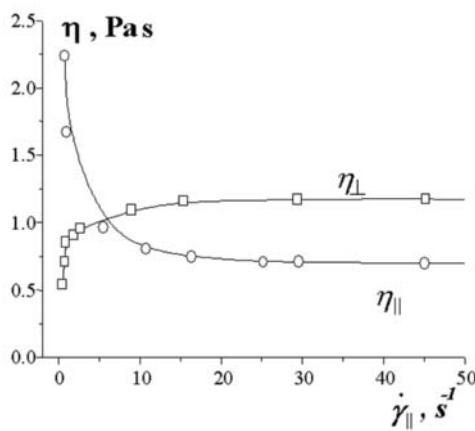


Figure 3.2.10. Anisotropic viscosity of liquid crystal solution of poly-p-benzamide in dimethyl acetamide: η_{\parallel} – viscosity measured in the direction parallel to shear; η_{\perp} – viscosity measured in the direction perpendicular to shear. [Adapted, by permission from A.Ya. Malkin, N.V. Vasil'eva, T.A. Belousova, V.G. Kulichikhin, *Kolloid. Zh.* (Colloid. J. – in Russian), **41**, 200 (1979)].

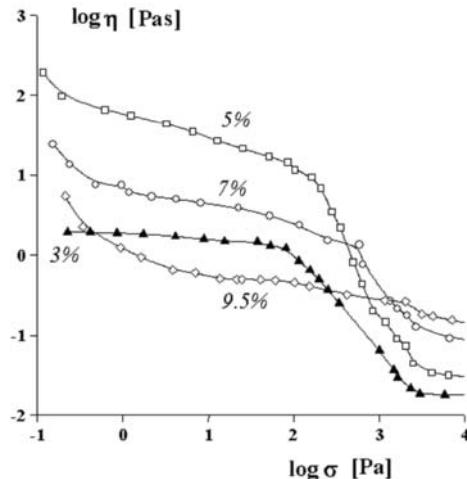


Figure 3.2.11. Flow curves of poly-p-benzamide solutions in dimethyl formamide. (1) – 3%; (2-4) – 5-9.5%. [Adapted, with permission, from S.P. Papkov, V.G. Kulichikhin, V.D. Kalmykova, A.Ya. Malkin, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1753 (1974)].

is a vector characterizing the average molecular orientation. The degree of order in structure orientation is described by the average deviation of long molecular axes from the director. The existence of a specified direction results in the anisotropy of all physical properties of a liquid including its viscosity.

Leslie considers five independent viscosity values, which characterize the behavior of the director (see also reviews).¹⁸ There are connections between three Miesowicz coefficients and Leslie coefficients of viscosity.

The second case is that of induced anisotropy. Deformations may lead to the dominating effect of orientation of structural elements in matter. This is typical of polymeric substances having macromolecules oriented in flow. Orientation also influences the results of measurement of elongation viscosity (see Section 3.7).

Methods of measuring different coefficients of anisotropic viscosity are described in the review.¹⁹ The fluid dynamics of nematic crystals includes the equation for orientation movement of the director in addition to all other equations of equilibrium.

First measurements of anisotropic viscosity of low molecular weight liquids were performed by Miesowicz and Tsvetkov and Mikhailov.²⁰

The viscosity of anisotropic liquids depends on direction of flow. Moreover, the effect of anisotropy depends on flow conditions. Therefore components of anisotropic viscosity are also shear rate dependent and contribute to non-Newtonian behavior of such systems. Anisotropic viscosity of polymer liquid crystal is given in Fig. 3.2.10. For one dimensional shear flow, the apparent viscosity was measured along two directions: parallel to flow lines and in perpendicular direction. Non-Newtonian behavior of the liquid crystal solution manifests itself in two ways:

- the initial viscosity values (at very low shear rates) are different, due to the anisotropic structure of liquid
- a shear rate dependence is observed for both components of the viscosity and it is due to the structure rearrangement induced by shear deformation: the viscosity decreases in the parallel direction due to sliding of aligned crystal layers, and it increases in the perpendicular direction, reflecting an increase in the resistance to penetration through regular layers of macromolecules.

Non-Newtonian behavior of liquid crystals combines different mechanisms of the phenomenon (Fig. 3.2.11). A flow curve of solution at low polymer concentration (3%), below the concentration threshold of phase transition, is typical of ordinary (isotropic) polymer solutions. The solutions containing sufficiently high polymer fractions have an inherent structure. So, it is reasonable to expect that they might have yield stress. It is proven by increase of apparent viscosity at very low shear stresses for solutions with high concentration of the polymer (curves at 5 to 9.5%). In the domain of higher shear stresses, the part of the flow curves is similar to that observed in isotropic polymeric materials. In this region, the regular shear rate dependence of the apparent viscosity is observed.

Concentration dependence of viscosity of LC polymers will be discussed in more detail in Section 3.3 (see Fig. 3.3.7). This dependence convincingly demonstrates the transition from isotropic to LC state.

The shear-induced anisotropy of viscosity in initially isotropic polymer solutions was observed in Ref.²¹ It was found that the velocity of falling ball in a gap between two coaxial cylinders depends on the rate of rotation of one cylinder i.e. on shear rate in flow of 10% solution of polyisobutylene in tetralin. The transverse apparent viscosity decreased in the increase of the primary shear rate. It is reasonable to think that this is caused by orientation of macromolecules in flow resulting in induced anisotropy of the solution.

Mechanical field induced structure anisotropy can appear even in a dispersion of spherical particles. As was first observed,²² initially random distribution of rigid spherical particles in a viscoelastic liquid tends to rearrange into regular necklace structure.

The tendency to alignment of disperse particles in flow has been confirmed by computer simulation.²³ The same effect was observed experimentally by the small-angle light scattering method.²⁴

It is quite possible that this effect is related not to inherent rheological properties of a continuous medium but to the influence of solid walls and the migration of particles because the structure formation definitely depends on the gap in flow between two parallel plates.²⁵

One can soundly expect that this effect might be expressed much stronger in dispersions of anisotropic particles. Indeed, it was found that viscosity anisotropy in discontinuous fibers suspended in a viscous fluid expressed as the ratio of the axial elongational viscosity to the transverse elongational viscosity and both axial and transverse shear viscosities appears to be as high as 10^4 - 10^6 .²⁶

Anisotropy of structure leading to the viscosity anisotropy can be easily created in magnetic liquids by application of a magnetic field.²⁷

The wide interest to the viscosity anisotropy is also related to the problem of geodynamics, because it is thought that strong anisotropy of the rheology exists in rocks and other earth substances.²⁸

The combination of various possible mechanisms of non-Newtonian behavior is typical of many real materials. Specific mechanisms are developed for model systems to describe particular functions of the model.

3.3 EQUATIONS FOR VISCOSITY AND FLOW CURVES

3.3.1 INTRODUCTION – THE MEANING OF VISCOSITY MEASUREMENT

Viscosity, or in a more general case, a flow curve, is a fundamental characteristic of mechanical properties of liquid. Hence, it is widely used in different applications. There are two principal ways of using viscometric (as well as other rheological) data in practice:

- As a physical method to characterize material; in this case it is necessary to choose one or several well-defined points on a flow curve or some constants in an equation used for fitting experimental data. The numerical values for these points or constants are compared with objective parameters of material (its chemical structure, contents of components in multi-component system, concentration, molecular mass, and so on). It is a physical method of material control and a method of control of its standardized parameters relevant in technological processes. In this case, the discussion of viscometric data includes correlation of the experimental constants with product specifications.
- As objective characteristics of mechanical properties of material; a stress-deformation rate relationship is used as the basis for solving various dynamic problems, such as transportation of liquid through pipelines, movement of solid bodies through liquid media, and so on. Experimental points can be approximated by different fitting equations, and the choice among them is a matter of personal preference or convenience in practical calculations.

In any case, it is useful to describe a set of experimental points with an appropriate equation which best fits a flow curve. If a flow curve is utilized as a method of material characterization, the most important point is to standardize the methods of finding typical data suitable for this purpose. It could be a “zero-shear-rate” (Newtonian) viscosity, yield stress, degree of non-Newtonian behavior, apparent viscosity at the specified (strictly defined) stress, and so on. In this case, the *standardized procedure* for measuring and treatment of experimental data is developed. The flow curve does not need to be measured in a wide shear rate range.

If the main interest concentrates on solving dynamic problems, it is necessary to measure and describe the flow (viscous) properties in the shear rate range covering the range of shear rates (or stresses) used in a specific application. It is frequently dangerous to use a fitting equation beyond the limits of direct viscometric measurements. Moreover, it is necessary to confirm that material, for which a dynamic problem is analyzed, is purely viscous, i.e., a flow curve is adequate presentation of its rheological properties. The equation describing a flow curve is the necessary part of formulation of any dynamic problem related to non-Newtonian liquids.

There are several general and commonly used approaches for fitting experimental data obtained in viscometric measurements. They are based on some typical models representing flow curves. As shown in Section 3.2, there are two characteristic types of flow curves dependent on behavior of material at low shear stresses – curves with the initial (“zero-shear-rate”) Newtonian viscosity limit and curves with the yield stress limit.

Neglecting intermediate situations, both types of flow curves require different approaches for their quantitative characterization.

It is possible to find dozens of analytical formulas proposed in literature for fitting flow curves. It is reasonable to distinguish a molecular approach intended to *explain* real flow curves of materials having non-Newtonian behavior and various fitting methods useful to *describe* flow curves only. The first approach usually leads to complicated analytical expressions, which are not convenient in applications to fluid mechanics, though they could be useful in the physics of matter. An example of this approach is discussed in Section 3.3.5. In the next section, usefulness of fitting equations are discussed for solving applied problems.

3.3.2 POWER-LAW EQUATIONS

Fitting experimental data to construct an equation for a flow curve requires that two conditions are satisfied:

- a wide range of stresses and shear rates data gives linear $\sigma(\dot{\gamma})$ dependence in log-log coordinates
- a low stress range exists in which the apparent viscosity is constant (range of zero-shear-rate or initial Newtonian viscosity).

The four-constant Carreau-Yasuda^{29,30} and the Cross³¹ equations, respectively, are used to fit experimental data:

$$\eta = \eta_0 [1 + (\lambda \dot{\gamma})^m]^{(n-1)/m} \quad [3.3.1a]$$

$$\eta = \frac{\eta_0}{1 + (\eta_0 \dot{\gamma} / \sigma^*)^{1-n}} \quad [3.3.1b]$$

where η_0 is the initial Newtonian viscosity, λ is a characteristic constant with the dimension of time, σ^* is the characteristic shear stress, m and n are empirical factors.

The mathematical peculiarities of these equations include: the dependence $\eta(\dot{\gamma})$ has the limit at low shear rates equal to η_0 and at high shear rates this equation transforms to:

$$\eta = \eta_0 (\lambda \dot{\gamma})^{n-1} \quad [3.3.2a]$$

$$\eta = \eta_0 (\eta_0 \dot{\gamma} / \sigma^*)^{n-1} \quad [3.3.2b]$$

Eqs. 3.3.1 satisfy the main conditions, which are necessary for fitting experimental data of non-Newtonian liquids. They can be generalized if there is need to include the upper Newtonian viscosity, η_∞ ($\eta_\infty \ll \eta_0$). This generalization is:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda \dot{\gamma})^m]^{(n-1)/m} \quad [3.3.3]$$

Simple analysis shows that at $\dot{\gamma} \rightarrow 0$, $\eta \approx \eta_0$ and at $\dot{\gamma} \rightarrow \infty$, $\eta \approx \eta_\infty$. In the intermediate shear rate range, the power-law dependence of $\sigma(\dot{\gamma})$ is predicted.

The intermediate range of stresses and shear rates is the most important range for practical applications, where Eq. (3.3.2) is valid. This equation is usually used in a form known as the “power law” model or the Ostwald-De Waele equation:³²

$$\sigma = k \dot{\gamma}^n \quad [3.3.4]$$

where k and n are empirical constants and $n < 1$.

In this case, the apparent viscosity is a decreasing function of shear rate expressed as

$$\eta = \frac{\sigma}{\dot{\gamma}} = k \dot{\gamma}^{n-1} \quad [3.3.5]$$

The value of exponent, n , in Eqs 3.3.4 and 3.3.5 lies between 0 and 1. This provides a decrease of the apparent viscosity with an increase in the shear rate or stress.

The power law, like all other above-discussed equations, is obtained in the experiments carried out in simple shear flows. However, for fluid mechanics applications it is necessary to formulate a three-dimensional generalization of the fitting one-dimensional equation because the majority of real dynamic problems deal with two- or three-dimensional flows. This task does not appear important for Newtonian liquid because viscosity of such liquid is its unique material constant, and from a mathematical point of view the viscosity is a scalar value.

A rheological equation for viscosity of a non-Newtonian liquid is formulated in invariant terms. The power law for three-dimensional flows is written as:

$$\eta = k \left(\frac{D_2}{2} \right)^{\frac{n-1}{2}} \quad [3.3.6]$$

where D_2 is the second invariant of the deformation rate tensor.

Such generalization is no more than an assumption. It is correct for various shear flows, but it is not proper for extensional flow: Eq. 3.3.6 predicts that the apparent viscosity decreases with an increase of D_2 , but it is not so in extension (see Section 3.7).

3.3.3 EQUATIONS WITH YIELD STRESS

Section 3.2 shows real materials which do not flow at low shear stresses, or their flow is negligible because their viscosity is so high at low shear stress. However, at higher shear stresses, these materials flow and they can be transported like any other liquid. Commercial materials of this kind include concrete and other construction products, greases, food products (yogurt, ketchup, tomato puree, ice cream, chocolate), pharmaceutical pastes, etc.

The yield stress, σ_Y , is one of their fundamental parameters. The most popular and simple equations reflecting viscoplastic behavior are as follows:

the Bingham equation³³

$$\sigma = \sigma_Y + \eta_p \dot{\gamma} \quad [3.3.7]$$

the Casson equation³⁵

$$\sigma^{1/2} = \sigma_Y^{1/2} + (\eta_p \dot{\gamma})^{1/2} \quad [3.3.8]$$

the Hershel-Bulkley equation³⁵

$$\sigma = \sigma_Y + K\dot{\gamma}^n \quad [3.3.9]$$

In these equations, σ_Y is the yield stress, η_p , is the “plastic” viscosity, and K and n are the experimental parameters.

A more general rheological equation with the yield stress was proposed to describe shear rate dependence of viscosity of filled elastomers:³⁶

$$\sigma = \sigma_Y + \frac{A\dot{\gamma}}{1 + B\dot{\gamma}^{1-n}} \quad [3.3.10]$$

where A and B are parameters. This equation is capable to describe rheological data for the carbon black filled NR, SBR, CR and EPDM compounds.³⁷ Also, this equation was further developed to incorporate the temperature and state of cure dependence of the apparent viscosity of rubber compounds during vulcanization process.³⁸

The “plastic” viscosity η_p is not equivalent to the apparent viscosity, η . By using a standard definition: $\eta = \sigma/\dot{\gamma}$, the apparent viscosity for the Bingham viscoplastic medium is:

$$\eta = \frac{\sigma_Y + \eta_p \dot{\gamma}}{\dot{\gamma}} = \eta_p + \frac{\sigma_Y}{\dot{\gamma}} \quad [3.3.11]$$

The apparent viscosity of the Bingham medium is a decreasing function of the shear rate ($\eta \rightarrow \infty$) at very low shear rates and it approaches the constant limit η_p at high shear rates. All such equations are valid, by definition, at stresses $\sigma > \sigma_Y$ only.

These equations predict that just above σ_Y , the apparent viscosity is high. But this does not exactly correspond to experimental data (see, e.g., Fig. 3.1.3). Hence, it is preferable to modify the Hershel-Bulkley equation in the following manner. Viscosity is assumed to be unlimitedly high at $\sigma < \sigma_Y$, and in the stress range $\sigma > \sigma_Y$, the flow curve is described by the power law, Eq. 3.3.5, without σ_Y value in formula for the apparent viscosity, but power law equation is correct only when $\sigma > \sigma_Y$. This model can be written as:

$$\eta = \begin{cases} \infty & \text{at } \sigma < \sigma_Y \\ k\dot{\gamma}^{n-1} & \text{at } \sigma > \sigma_Y \end{cases} \quad [3.3.12]$$

A three-dimensional generalization of any of the equations proposed for viscoplastic liquids is based on mechanical arguments representing a “critical” point σ_Y in the invariant form. The *Von Mises criterion of plasticity*³⁹ is the most popular and widely used for real materials. The state of plasticity is reached at the certain “critical” value of the second invariant of the stress tensor. This criterion can be written through the principal stresses as

$$K_{cr} = \left[\frac{(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2}{6} \right]^{1/2} \quad [3.3.13]$$

where σ_1 , σ_2 , and σ_3 are the principal stresses, and K_{cr} is some critical value of the second invariant of the stress tensor, corresponding to the yield point. In a simple shear flow, the

value K_{cr} can be easily expressed through σ_Y measures. In a simple shear flow, $\sigma_1 = -\sigma_2 = \sigma$, and then

$$K_{cr} = \frac{1}{\sqrt{3}}\sigma_Y \quad [3.3.14]$$

The equations proposed may be applied for approximation of the rheological properties of viscoplastic bodies in discussing three-dimensional deformation (flow) problems.

The determination of the yield stress in two (or three-) dimensional deformations is not trivial, especially for Hershel-Bulkley liquid, due to a non-linearity of viscous properties of viscoplastic liquids at $\sigma > \sigma_Y$.⁴⁰ In order to solve three-dimensional dynamic problems it is necessary to formulate an invariant critical condition of yielding and use the generalized form of this equation.⁴¹

As noted above, the equations for viscoplastic bodies (Eq. 3.3.7 to Eq. 3.3.11, as well as many others proposed by different authors) are based on the following assumptions:

- there are no deformations at stresses below σ_Y
- the transition from solid to liquid occurs just at one point, namely yield stress.

Both assumptions are no more than model approximations of the observed rheological behavior of real materials made by the “best” fitting of experimental points. The yield stress is found by the procedure of extrapolation of experimental points based on the specified fitting equation.

It is necessary to stress again that all equations discussed in Sections 3.3.2 and 3.3.3 are no more than an approximations applicable to a part of full flow curves of real materials. As was illustrated in Section 3.2, the general picture of non-Newtonian behavior can be richer. Indeed, measuring the rheology of different media demonstrated that their non-Newtonian properties are caused by the existence of two limiting

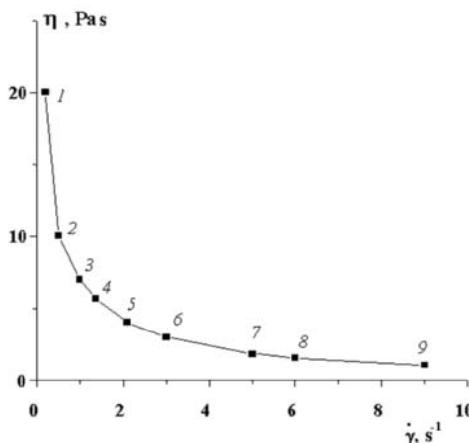


Figure 3.3.1. Illustration of the ambiguity in determination of yield stress.

values of Newtonian viscosity and the existence of an intermediate region of quasi-power law viscosity with more or less abrupt transition from the upper Newtonian viscosity to decreasing apparent viscosity. What an experimentalist see and how one approximates experimental data depends on the range of explored shear rates or stresses and analytical fitting of experimental points measured with some limited accuracy.

Example

Is it reasonable to say that it is possible to measure real yield point?

The following numerical example analyzes the situation. Fig. 3.3.1 gives an example of experimental data: nine marked points are measured values of the apparent viscosity at different shear rates. The flow curve indicates that the material under investigation has yield stress. Let us try to find the σ_Y value by approximation of the experimental data at the low shear rate region using linear equation (3.3.7). The set of three points will be used for linearization. First, these are points 1, 2 and 3. Then, it is supposed that only 8 points, starting from the point 2 are measured, and so on. The results are as follows:

Points used for approximation	1, 2, 3	2, 3, 4	3, 4, 5	4, 5, 6
Found σ_Y value, Pa	3.5	3.8	6.2	7.12

It is seen that the σ_Y value is no more than the result of approximation strongly dependent on the range of shear rates used for measuring and fitting. Then, if σ_Y values are used as a measure of material quality and to compare different media it is necessary to use a reproducible standardized method of searching for σ_Y value.

3.3.4 BASIC DEPENDENCIES OF VISCOSITY

In general, the viscosity of materials depends on their properties. This section is limited to dependencies of viscosity on the molecular mass in a homologous series and concentrations of fillers in dispersions.

3.3.4.1 Viscosity of polymer melts

It is commonly assumed⁴² that the dependence of Newtonian viscosity on the molecular mass, $\eta_0(M)$, consists of two parts: close to linear in the low molecular weight domain, expressed by a power law with the universal exponent, close to 3.4 in the high molecular weight domain. It is expressed as follows:

$$\eta_0 = \begin{cases} K_1 M^a & \text{at } M < M_c \\ K_2 M^b & \text{at } M > M_c \end{cases} \quad [3.3.15]$$

where K_1, K_2 are empirical constants, the exponent a is close to 1 and $b \approx 3.4$.

The boundary value of molecular mass, M_c , separating low and high molecular mass domains is called “critical molecular mass”. In the physics of polymers it is a boundary between low molecular weight products and polymers. For example, non-Newtonian flow begins at $M > M_c$. Activation energy of viscous flow becomes independent of length of a polymeric chain at $M > M_c$, and so on. The M_c value can be related to sufficiently long chains such that their parts behave independently and the spatial entanglement network is present. The “independent” part of chain is called a *chain segment*. The idea of a chain consisting of many independently moving segments is one of the fundamental suggestions in polymer physics. The characteristic length of chain is a statistical value, and it is meaningless to consider that individual segments may have some well defined “boundaries”. It is reasonable to treat M_c as a measure and reflection of the chain rigidity.

Examples

	M_c of polymer
Polyethylene	4,000
Polybutadiene	5,600
Polyisobutylene	17,000
Polymethylmethacrylate	27,500
Polystyrene	35,000

The origin of a segment can be attributed to the existence of the flexibility of a long macromolecule. This allows one part of molecule to move independent from the other part(s) of a chain. Macromolecules in molten state or in a concentrated solution contact each other and form a *network of entanglements*. Then it is reasonable to introduce the average length of chain between two neighboring physical junctions (nodes). The part of a chain between two neighboring junctions consists of several segments (if the chain is flexible enough). The entanglements (junctions) can be characterized by some lifetime and the

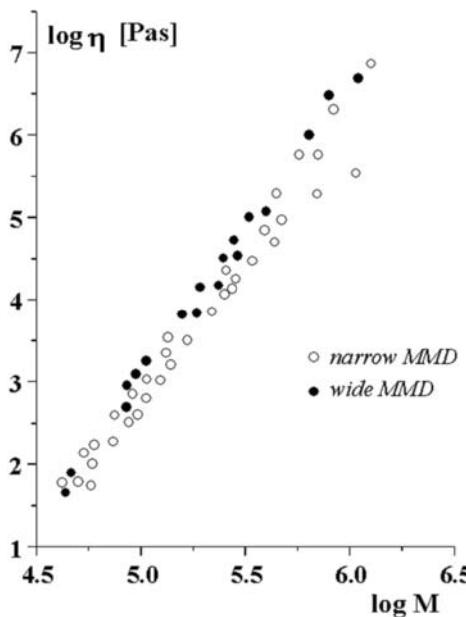


Figure 3.3.2. Zero-shear-rate viscosity of polystyrene melt as a function of molecular mass. $T = 200^\circ\text{C}$. This figure in the original publication summarizes the experimental data of 18 studies. Here, only a part of experimental points is reproduced. [Adapted, with permission, from A. Casale, R.S. Porter, J.F. Johnson, *J. Macromol. Sci., Rev. Macromol. Chem.*, C, 5, 387 (1971)].

These permanent chemical bonds prevent flow because chains cannot slide over each other. The shorter the distance between crosslinks, the more rigid a material becomes.

An example illustrating the dependence of $\eta_0(M)$ in high molecular mass domain is shown in Fig. 3.3.2. This dependence is represented by a power law with exponent close to 3.4 (the averaged value of the slope for the points in Fig. 3.3.2 is 3.3 ± 0.1). This dependence is also valid for polydisperse polymers, if one assumes that M in Eq. 3.3.15 means the *weight averaged molecular mass*, \bar{M}_w , i.e., the dependence $\eta_0(M)$ for high molecular mass polymers is given by:

$$\eta_0 = K_2 \bar{M}_w^b \quad [3.3.16]$$

where constants K_2 and b have the same values as in Eq. 3.3.15.

One can see that the viscosity of polystyrene, given in Fig. 3.3.2, as an example, changes in a very wide range exceeding 5 decimal orders. The same is true for any other polymer. Therefore, in contrast to low molecular weight substances, it is meaningless to put the question: which polymer is more or less viscous? The answers depend on the chain length.

measure of this lifetime is a characteristic relaxation time. If deformation proceeds slower than this relaxation time, the chains move without “noticing” these junctions, they can slide over each other, which means that the polymer can flow. If the deformation is sufficiently rapid, these junctions do not have sufficient time to disintegrate. In this case, they form stable (quasi-chemical) entities and polymer behaves similar to a cured rubber: it cannot flow and it assumes rubber-like physical (or relaxation) state. It is necessary to add that the lifetime is not a single constant of such a system, but a distribution of lifetimes of junctions (and consequently of relaxation times) always exists.

Chemical bonds between chains decrease the average length of chain between neighboring entanglements. This occurs in the process of curing (or cross-linking) of rubbers. It is possible to treat chemical bonds as having an infinite lifetime (even though it is not absolutely true: some cases are known when bonds break under stress at sufficiently long time).

3.3.4.2 Viscosity of polymer solutions

An example of viscous properties of polymer solutions in the whole concentration range is given in Fig. 3.2.1. Viscosity of solution, η , is higher than viscosity of solvent, η_s . In very dilute solutions, macromolecules move independently. One may postulate that there is a linear dependence of solution viscosity on concentration, c .⁴³ This linear dependence is written as

$$\eta = \eta_s(1 + c[\eta]) \quad [3.3.17]$$

where the constant $[\eta]$ is introduced as a coefficient of the first-order term. A more rigorous definition of this constant is:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_s}{c\eta_s} \quad [3.3.18]$$

The constant $[\eta]$ is called the *intrinsic viscosity* and its dimension is reciprocal to concentration. $[\eta]$ is a measure of influence of polymer dissolved in solvent on the viscosity of a polymer-solvent system. In various molecular theories, it was proven that $[\eta]$ depends on a size of the macromolecule. That is why $[\eta]$ directly correlates with the molecular mass of polymer and can be used as a simple measure of molecular mass. As a general rule, this correlation is expressed by the standard *Mark-Kuhn-Houwink equation*:

$$[\eta] = k\bar{M}_\eta^\alpha \quad [3.3.19]$$

where the parameters k and α are constants that are characteristics of polymer and solvent used. In many cases, at least for flexible-chain polymers, α lies between 0.5 and 0.8. Molecular mass related to $[\eta]$ is known as viscometric-averaged molecular mass which is intermediate between number-averaged, \bar{M}_n , and weight-averaged, \bar{M}_w , molecular mass.

The product $c[\eta]$ is a measure of volume occupied by macromolecules in solution. It is assumed that $c[\eta] < 1$ is typical of *dilute solutions*. In this case, one may neglect interactions between macromolecular chains. At $c[\eta] > 1$, intermolecular contacts influence viscous properties of solution.

The dependence $\eta(c)$ is also represented by the *Huggins equation*,⁴⁴ which can be written as:

$$\frac{\eta - \eta_s}{\eta_s} = c[\eta] + K_H(c[\eta])^2 \quad [3.3.20]$$

where the constant K_H is called the *Huggins constant*. The Huggins constant is a measure of interaction between polymer and solvent.

Many other approximations of $\eta(c)$, dependence can be formally constructed as the sum of higher order terms of concentration. Many fitting equations for $\eta(c)$ dependence were proposed. The *Martin equation*⁴⁵ is one of them:

$$\eta = \eta_s \exp(K_M c[\eta]) \quad [3.3.21]$$

where K_M is the *Martin constant*.

The *Kraemer equation*⁴⁶ is widely used in analytical practice:

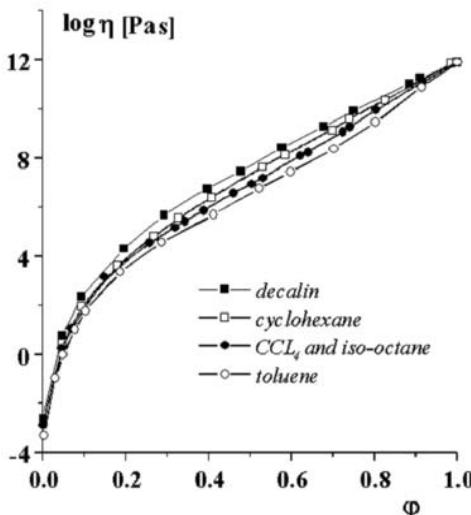


Figure 3.3.3. Concentration dependencies of viscosity of polyisobutylene solutions in different solvents in the whole concentration range. $T = 20^\circ\text{C}$. [Adapted, with permission, from V.E. Dreval, A.Ya. Malkin, G.V. Vinogradov, A.A. Tager, *Europ. Polym. J.*, **9**, 85 (1973)].

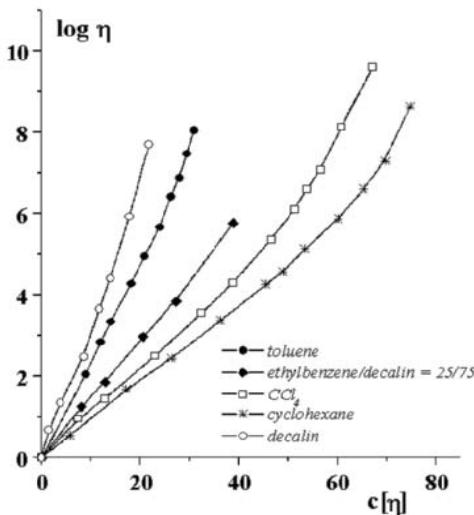


Figure 3.3.4. Concentration dependencies of viscosity of polystyrene in five different solvents. $T = 25^\circ\text{C}$. [Adapted, with permission, from V.E. Dreval, A.Ya. Malkin, V.O. Botvinnik, *J. Polym. Sci.: Polym. Phys. Ed.*, **11**, 1055 (1973)].

$$\ln(\eta/\eta_s) = c[\eta] - K_K(c[\eta])^2 \quad [3.3.22]$$

where K_K is the *Kraemer constant*.

In the range of low concentrations any non-linear equation is approximated by the simplest linear Eq. 3.3.17. The method of determination of $[\eta]$ depends on the equation used for approximation. If the Huggins equation is used for fitting experimental data, $[\eta]$ is found by presentation of the experimental data in coordinates $(\eta - \eta_s)/\eta_s c$ vs. c and extrapolation of this dependence to $c = 0$. The intercept gives the value of $[\eta]$ and the slope of the straight line is a measure of K_H . This dependence is linear.

The structure of equations commonly used for $\eta(c)$ dependence shows that they can be presented in a dimensionless form. The argument is expressed as $c[\eta]$, and the dimensionless viscosity as $\tilde{\eta} = (\eta - \eta_s)/\eta_s[c]$. These values are used in analysis of concentration dependencies of viscosity of different polymers. In presentation of viscometric data with these dimensionless variables for different polymer-solvent systems, the common initial reference point exists: $\tilde{\eta} = 0$ at $c[\eta] = 0$. This permits comparison of concentration dependencies of different polymer-solvent systems in reference to a common point.

Two polymers are further discussed: polyisobutylene (Fig. 3.3.3) and polystyrene (Fig. 3.3.4) solutions in different solvents. Polyisobutylene melts at the measurement temperature. This permits us to measure viscosity of its solutions in the whole concentration range. Polystyrene is in the glassy state at measurement temperature. Thus, its solution at a certain concentration will form a glassy state. In the first case, there is a single final point

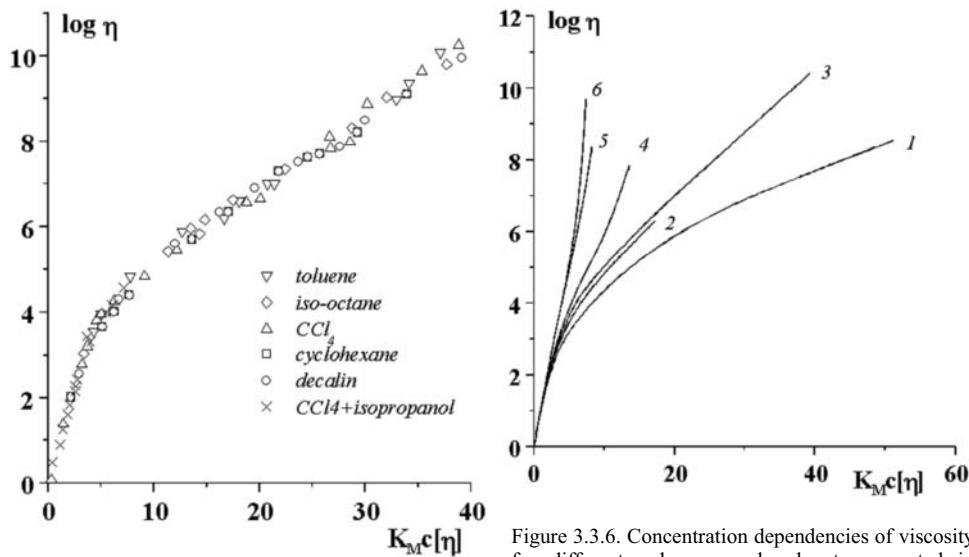


Figure 3.3.5. Concentration dependence of polyisobutylene solutions in different solvents using the reduced coordinates. [Adapted, with permission, from V.E. Dreval, A.Ya. Malkin, V.O. Botvinnik, *J. Polym. Sci.: Polym. Phys. Ed.*, **11**, 1055 (1973)].

corresponding to the polymer melt. The difference in viscosity of equi-concentrated solutions is not large in the whole concentration range.

Experimental data in Fig. 3.3.4 are represented by *reduced* (dimensionless) variables in order to have a common initial point. The viscosity grows unlimitedly when concentration approaches a certain value (different for various solvents). This corresponds to the glass transition of solution. Depending on the nature of solvent, the difference in viscosity of equi-concentrated solutions can reach several decimal orders.

The difference in the concentration dependence of viscosity for different polymers is determined by the relaxation state of polymer, i.e., whether the polymer is in melt or glass state at the temperature of viscosity measurements.

The influence of solvent on solution viscosity in the low concentration range is determined by the coefficients of the high-order term of the $\eta(c)$ dependence. The initial parts of these dependencies coincide if the reduced argument $K_M c[\eta]$ is used. This argument permits generalization of $\eta(c)$ dependence in the whole concentration range. This is illustrated in Fig. 3.3.5. The reduced coordinates are used to construct a unique viscosity vs. concentration dependence for all solvents in the *whole* concentration range. It means that the parameters $[\eta]$ and K_M representing the $\eta(c)$ dependence in the low concentration range are responsible for viscous properties of solutions up to the limit of very high concentrations.

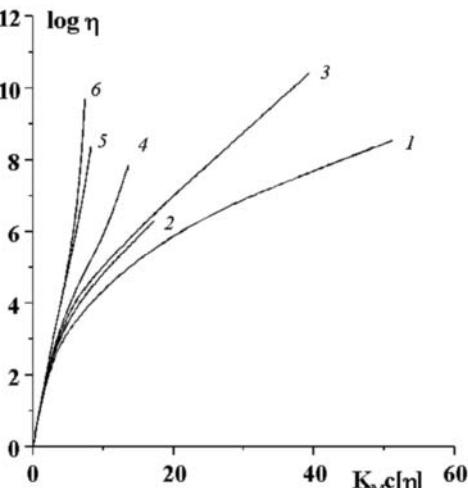


Figure 3.3.6. Concentration dependencies of viscosity for different polymers and solvents presented in reduced variables: 1 – polybutadienes of different molecular masses, $\phi = 0-1.0$; 2 – polydimethylsiloxanes, $\phi = 0-1.0$; 3 – polyisobutylenes of different molecular masses, $\phi = 0-1.0$; 4 – acetyl cellulose, $\phi = 0-0.35$; 5 – polyarylate, $\phi = 0-0.3$; 6 – polyvinyl acetate, $\phi = 0-0.7$; 7 – polystyrene, $\phi = 0-0.7$. Each curve contains data obtained for several different solvents. [Adapted, by permission, from V.E. Dreval, A.Ya. Malkin, V.O. Botvinnik, *J. Polym. Sci.: Polym. Phys. Ed.*, **11**, 1055 (1973)].

The last statement is valid for many polymer-solvent systems (see Fig. 3.3.6).⁴⁷ There is an initial universal part of the reduced dependence, η/c , common to all polymer-solvent systems. A universal character of this dependence for any polymer and different solvents in the whole concentration range exists with continuous shift in position of the curve of flexible and rigid polymer chains.

The $\eta(c)$ dependence in the high polymer concentration range can be represented by simple analytical equations. In many cases, the power-law equation is useful:

$$\eta = k_c c^m \quad [3.3.23]$$

The values of exponent are: $m = 5-7$.

Combination of Eqs. 3.3.16 and 3.3.23 gives:

$$\eta = k_{M,c} M^b c^m = k_{M,c} (M^{b/m} c)^m \quad [3.3.24]$$

Using ordinary values of constants ($b = 3.5$ and $m = 5-7$), the exponents ratio b/m is 0.5-0.7. The value of the ratio b/m coincides with exponent α in Eq. 3.3.19. Then, combining Eqs. 3.3.19 and 3.3.24, the following equation for solution viscosity is obtained:

$$\eta = K_c (c[\eta])^m \quad [3.3.25]$$

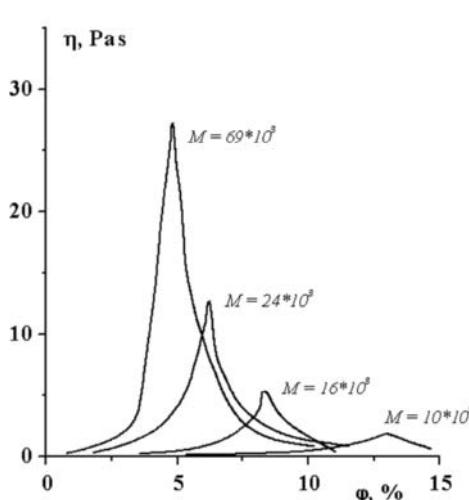


Figure 3.3.7. Concentration dependencies of viscosity of poly-p-benzamide solutions in dimethyl acetamide – transition to the LC state. Molecular masses of a polymer are shown on the curves. [Adapted, with permission, from S.P. Papkov, V.G. Kulichikhin, V.D. Kalmykova, A.Ya. Malkin, *J. Polym. Sci.: Polym. Phys. Ed.*, **12**, 1753 (1974)].

and viscosity of highly concentrated solutions is a function of the product $c[\eta]$ as in the low concentration range. The same factor also determines viscosity of concentrated solutions. There is no proof, but circumstantial evidence, that the structure of solvent does not change in the whole concentration range and that the macromolecular conformation (conformation of a statistical coil) continues to exist in the whole range of concentrations from dilute to concentrated solutions until the molten state. It means that solutions are homogeneous mixtures of polymer and solvent. It is not necessarily a general case. The opposite situation is met when polymer molecules in solution are arranged in a regular structure. It is especially typical of rigid-chain (rod-like) polymers, which transfer into *liquid crystalline* (LC) state.⁴⁸ This transition may take place at a certain temperature (for *thermotropic* polymer solutions) and in isothermal conditions at certain concentration (*lyotropic* solutions).⁵¹ The latter case is the most interesting for discussion of concentration dependence of viscosity. It is illustrated in Fig. 3.3.7.⁴⁹ The unexpected sudden decrease of viscosity at some critical concentration, c^* , is observed instead

certain concentration (*lyotropic* solutions).⁵¹ The latter case is the most interesting for discussion of concentration dependence of viscosity. It is illustrated in Fig. 3.3.7.⁴⁹ The unexpected sudden decrease of viscosity at some critical concentration, c^* , is observed instead

of continuous growth as in Figs. 3.3.3 to 3.3.6. It corresponds to a phase transition from a homogeneous solution to the LC state. Flory⁵⁰ has provided physical reasons for these transitions. He showed that a regular, parallel positioning of the rod-like molecules becomes thermodynamically preferable at some critical concentration. This critical concentration of LC phase transition corresponds to sharp maxima of viscosity in Fig. 3.3.7.

The monotonous viscosity growth given by the factor of volume filling $c[\eta]$ in the whole concentration range and the rapid phase transition into the LC state with a drop of viscosity at $c > c^*$ are extreme cases (though the first one is rather typical of many polymer-solvent systems). In practice, it is possible to observe various intermediate cases of intermolecular interaction (for example, hydrogen bonding, formation of colloid-like micelle clusters, and so on) leading to the appearance of various, more or less regular, structure aggregates of different sizes with various lifetimes. It results in different, sometimes very unusual anomalies of viscosity vs. concentration dependencies of real polymer solutions.

3.3.4.3 Viscosity of suspensions and emulsions

Suspensions and emulsions are multicomponent media consisting of continuous phase and dispersed particles. So, in discussion of viscosity of suspensions, it is important to answer the following question: should a dispersion of solid particles (in suspension) or liquid droplets (in emulsions) in a flowing medium be treated as a homogeneous system neglecting its concentration and structure distribution? The answer to this question is not always positive. It depends on the ratio of particle size and the dimensions of the flow channel. It is reasonable to neglect the inner inhomogeneity of the medium and to consider a flowing system as a continuum to calculate some of its averaged characteristics, such as viscosity. In this case, viscosity represents a measure of energy dissipated in the flow of such a multi-component system.

The same is also true for mixtures: the size of component particles may be large, but in many cases (with some caution), it is reasonable to calculate viscosity of such multi-component system as a measure of energy dissipation during flow.

It is well known that the concentration dependencies of viscosity of suspensions and emulsions in the range of dilute and semi-dilute dispersions are analogous.⁵¹ This is correct till approaching the close packing limit of particles of disperse phase in suspensions. However, in highly concentrated emulsions the concentration of the inner phase can exceed this limit. The latter case will be discussed at the end of this section.

Viscosity of liquid typically increases when concentration of dispersed particles in flowing medium increases. This is due to the additional energy loss for liquid to flow around solid particles. Einstein⁵² was the first who examined the problem of viscosity calculations of liquids containing small amounts of dispersed particles. He obtained the following relationship, which is a ground rule for all future studies in this field:

$$\eta = \eta_s(1 + 2.5\phi) \quad [3.3.26]$$

Here η is the viscosity of suspension, η_s is viscosity of a liquid phase and ϕ is the volume concentration of solid spherical particles.

This equation is the first, or *linear* approximation, valid for non-interacting particles. It means that the dynamics of flow around one particle does not influence the velocity field around any other particle.

Many publications were devoted to generalization of this equation for a range of higher concentrations. The complete form of expression for viscosity at higher approximations is a sum of concentrations with increasing power:

$$\eta = \eta_s(1 + 2.5\varphi + b\varphi^2 + c\varphi^3 + \dots) \quad [3.3.27]$$

The values of coefficients are different in various theories. The values cited for the coefficient b vary from 4.4 to 14.1. However, it is worth mentioning that the essential part in estimation of b is played by the number of terms in Eq. 3.3.27.

The other popular and convenient semi-empirical equation for the dependence $\eta(\varphi)$ was proposed by Mooney:⁵³

$$\eta = \eta_s \exp\left[\frac{2.5\varphi}{1 - (\varphi/\varphi^*)}\right] \quad [3.3.28]$$

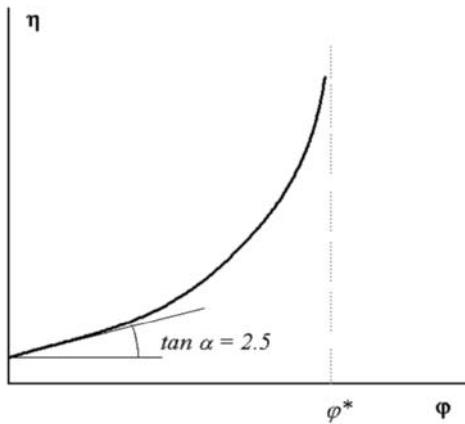


Figure 3.3.8. Typical concentration dependence of the viscosity of suspension of solid particles.

suspensions as unique functions of concentration⁵⁴

- non-spherical shape of particles
- presence of particles of different sizes and shapes
- non-Newtonian properties of a liquid medium
- deformability of filler particles which are not necessarily solid (e.g., liquid or gas)
- physical interaction between liquid and solid particles, leading to formation of stable surface layers
- interactions of various types between solid particles (for example, solid particles may mechanically touch each other, be charged, and so on).

Each of the effects on the list may have special importance for a particular system. For example, the deformability of solid non-spherical particles is especially important for the flow of blood. Physical interactions between solid particles is of special importance in

This equation is converted to the Einstein equation at low concentrations. It satisfies numerous experimental data in the intermediate concentration range, and it describes an important effect of unlimited viscosity increase when approaching some critical concentration, φ^* . The latter has the meaning of limiting the possible degree of filling a space with filler particles. For example, if a solid filler is composed of spherical particles arranged in a hexagonal or cubic-centred manner $\varphi^* = 0.74$.

Typical shape of the concentration dependence of viscosity of dispersion of solid particles is shown in Fig. 3.3.8.

Formulas of the power or exponential type, as discussed above, treat viscosity of

the following effects can lead to more

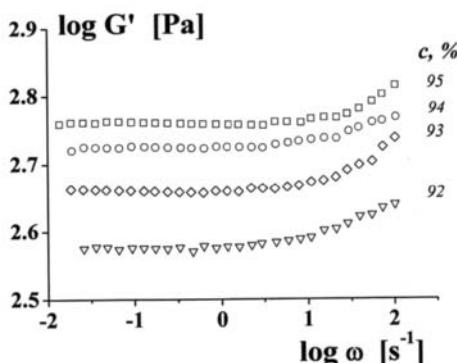


Fig. 3.3.9. Storage modulus in a wide frequency range for highly concentrated emulsions with different concentration of an inner phase (shown at the curves). After I. Masalova, A.Ya. Malkin, *Colloid J.*, **69**, 185 (2007).

occupy empty spaces between larger ones. Meanwhile the threshold of filling of solid particles does not much exceed this limit.

The situation with emulsion is different. They can be compressed leading to filling some space due to transformation of spheres to polygonal objects separated by thin interface films. Then, the volume degree of filling can be as high as 0.93. The transition to the highly concentrated emulsions significantly affects their rheological properties. First of all, they become gel-like or pastes. It means that they exhibit a solid-like behavior at low deformations or low stresses. This is illustrated in Fig. 3.2.9⁵⁵ (see also Fig. 2.8.12) where this effect is indicated by the absence of frequency dependence of the elastic (storage) modulus. It should be noted that in this frequency range the loss modulus exhibits low value.

The physical explanation of this kind of elasticity was proposed by Princen⁵⁶ and later developed in Ref.,⁵⁷ where elasticity of compressed droplets was treated as a consequence of the increases in the droplet surface under the osmotic pressure. However, the latest understanding of this phenomenon includes the input of interface interaction between compressed droplets.⁵⁸

3.3.5 EFFECT OF MOLECULAR WEIGHT DISTRIBUTION ON NON-NEWTONIAN FLOW

Various attempts to construct the flow curve equations are based on molecular models. For this approach the knowledge of mechanism of non-Newtonian behavior is required. Polymeric materials are characterized by their polydispersity, i.e., they are *mixtures of fractions* having different molecular mass. As demonstrated in Fig. 3.3.10, the viscosity of *monodisperse polymer* is constant, $\eta_0 = \text{const}$, until a critical stress, σ_s , after which no flow is possible. Formally, it can be written as:

$$\eta = \begin{cases} \eta_0 & \text{at } \sigma \leq \sigma_s \text{ or } \dot{\gamma} \leq \dot{\gamma}_s \\ \sigma_s / \dot{\gamma} & \text{at } \sigma > \sigma_s \text{ or } \dot{\gamma} \geq \dot{\gamma}_s \end{cases} \quad [3.3.29]$$

processing and applied properties of rubbers, and so on.

Taking into account any of these effects requires modification of equations for concentration dependence of viscosity. The modification has to include information about the content and structure of a flowing system. This is a problem that requires advanced and special investigations in the field of multi-component systems.

As was mentioned above, there is a close packing limit of spherical particles in continuum, which for monodisperse particles is close to $\varphi^* = 0.74$. The degree of filling can be higher for the polydisperse particles because small particles can

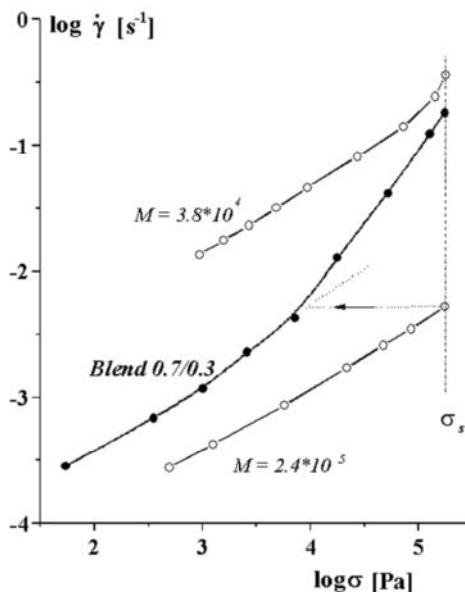


Figure 3.3.10. Non-Newtonian behavior of a polydisperse polymer sample. Flow curve of a blend (0.7/0.3) of two monodisperse polymers. Polyisoprenes. MM are shown at the curves. 25°C. Horizontal arrow shows the spurt shear rate for a high molecular weight fraction. [Adapted, by permission, from A.Ya. Malkin, N.K. Blinova, G.V. Vinogradov, M.P. Zabugina, O.Yu. Sabsai, V.C. Shalagova, I.Yu. Kirchevskaya, V.P. Shatalov, *Europ. Polym. J.*, **10**, 445 (1974)].

Newtonian liquids, and second, high molecular weight exceeding their (different for different fractions) critical values $\dot{\gamma}_s$ and behaving as non-fluid “filler”.

The rule of mixing may have different forms based on empirical or molecular arguments. In particular, it can be assumed that Newtonian viscosity of a polydisperse polymer, η_0 , is proportional to the weight-averaged molecular mass of a blend in the power b , as was discussed above (Eq. 3.3.16)

Based on the above-formulated suggestions, it is possible to write the following equation for a flow curve:

$$\eta(\dot{\gamma}) = \left[\int_0^{M(\dot{\gamma})} (K_2 M^\alpha)^{1/\alpha} f(M) dM + \left(\frac{\sigma_s}{\dot{\gamma}} \right)^{1/\alpha} \int_{M(\dot{\gamma})}^{\infty} f(M) dM \right]^\alpha \quad [3.3.30]$$

Here $f(M)$ is a molecular mass distribution function.

The structure of Eq. 3.3.30 demonstrates that non-Newtonian behavior results from polymer polydispersity. The first term in this equation is the input of “flowing” fractions, and the second term represents the input of high molecular mass fractions which do not flow at high shear rates. The boundary between these two terms is the function of shear

Let us mix two fractions of different molecular masses, each behaving like a Newtonian liquid until shear stress is σ_s . The results are shown in Fig. 3.3.10. The blend of two quasi-“Newtonian” liquids has non-Newtonian behavior. The deviation from the low shear rate Newtonian branch begins at a shear rate corresponding to a critical point, $\dot{\gamma}_s$, of the high molecular fraction, as shown by a horizontal arrow in Fig. 3.3.10. This means that there are two domains in the flow curve of the blend and each of them is characterized by different rheological properties. In the low shear rate range, the blend, similar to both components, is a Newtonian liquid. In the shear rate range above the critical shear rate of the high molecular mass component, this blend is a non-Newtonian liquid.

The following model of non-Newtonian behavior of a polydisperse polymer can be proposed.⁵⁹ Low shear rate viscosity of a polydisperse polymer is determined by some rule of mixing; non-Newtonian viscosity at the high shear rate range is calculated as the sum of inputs, first, low molecular mass components flowing as

rate. This boundary (the upper limit of the first integral and the lower limit of the second integral) is expressed as:

$$M(\dot{\gamma}) = \left(\frac{\sigma_s}{K_2 \dot{\gamma}} \right)^{1/\alpha} \quad [3.3.31]$$

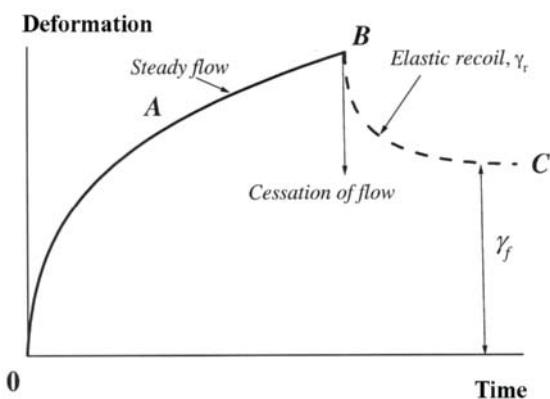


Figure 3.4.1. Deformation and elastic recoil.

The validity of this approach is confirmed by the results of calculations of the non-Newtonian branch of the flow curve of a blend (the solid symbols in Fig. 3.3.10). This method attracted the attention of many researchers because it permits solving the inverse problem – calculation of molecular weight distribution, function $f(M)$, based on rheological measurements. Though it is incorrect (ill-posed) problem,⁶⁰ various methods for solving it are widely discussed in modern rheological literature.⁶¹

3.4 ELASTICITY IN SHEAR FLOWS

3.4.1 RUBBERY SHEAR DEFORMATIONS – ELASTIC RECOIL

Results of continuous development of shear deformation after application of a constant shear stress are schematically shown in Fig. 3.4.1 by the 0AB part of the curve. The section 0A is an unsteady deformation range and the straight line AB represents the deformations corresponding to steady flow. At the point B stress is removed, flow ceases and elastic recoil takes place. The value of this *elastic recoil* is a measure of the *elastic (or rubbery) deformation*, γ_r stored before the regime of steady flow was reached. This value is also called the *recoverable strain*, or *recoil strain*. The limits of elastic recoil are elastic deformations stored during the steady flow called *ultimate recoil*, γ_∞ . The total shear deformation, γ , is the sum of γ_r and the irreversible (plastic) deformation of flow, γ_f :

$$\gamma = \gamma_r + \gamma_f \quad [3.4.1]$$

This sum reflects the superposition principle, which is valid in the linear viscoelastic behavior domain. However, it is not universal principle. It is possible to carry out the same measurements at high shear stresses (the non-linear domain). In this non-linear case the measured elastic recoil does not correspond to the elastic deformation stored at steady flow: if in the linear region there is no flow during elastic recoil, in the non-linear case, some flow (accompanied by partial dissipation of the stored elastic energy) can take place during elastic recoil, and the measured value of γ_r is lower than expected. Therefore, the values of γ_r measured in non-linear viscoelastic domain must be treated as relative (though

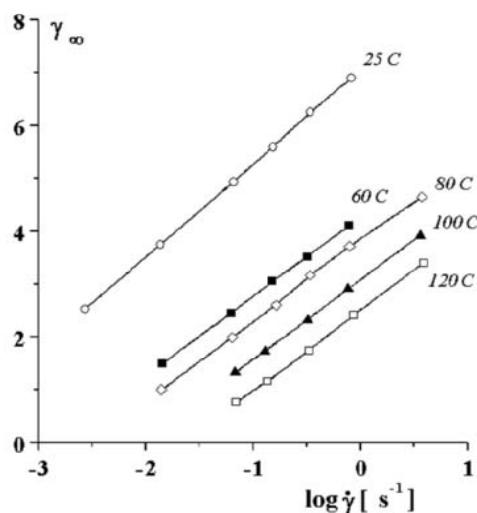


Figure 3.4.2. Elastic recoil as a function of shear rate for butyl rubber at various temperatures. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, M.P. Zubugina, V.F. Shumsky, *Vysokomol. Soedin. (Polymers – in Russian)*, **11A**, 1221 (1969)].

polymer-like structures, such as aluminum naphthanate colloid solutions, and some other materials.

Typical example of the $\gamma_\infty(\dot{\gamma})$ dependence is shown in Fig. 3.4.2. The real measured values of recoverable strains may reach several hundred per cent and they increase with increase in shear rate (or shear stress). Changes in the rubbery modulus (or shear compliance) as a function of shear rate do not exceed one decimal order, even in the range of shear rates exceeding 6 decimal orders.⁶² Measured values of the rubbery modulus in the non-linear domain have qualitative meaning only due to the noticed absence of superposition of elastic and flow deformations.

The initial (“linear”) value of shear compliance, J_s^0 , is an important rheological parameter (see Chapter 2). It is a factor related to the molecular structure of matter.

Many authors noticed that J_s^0 of the so-called “monodisperse” polymers does not depend on molecular mass (MM) of a polymer.

The following values of J_s^0 were obtained experimentally for “monodisperse” polymers (or at least polymers with very narrow molecular-mass distribution):^{63,64}

Polydimethylsiloxanes	$1.5 \times 10^{-3} \text{ Pa}^{-1}$
Polybutadienes	$1.6 \times 10^{-4} \text{ Pa}^{-1}$
Polyisoprenes	$1.4 \times 10^{-5} \text{ Pa}^{-1}$
Polystyrenes	$7.1 \times 10^{-6} \text{ Pa}^{-1}$

These values are only estimates because of difficulties in preparation of “monodisperse” polymers.

The elasticity of polymer melts depends on the width of molecular-mass distribution (MMD). Regularly, MMD is characterized by the \bar{M}_w/\bar{M}_n ratio. However, the \bar{M}_w/\bar{M}_n ratio is not a representative characteristic of MMD in its correlation with J_s^0 , because J_s^0 is

might be useful) characteristic of elasticity only but not as the absolute values of rubbery deformations in the state of steady flow.

Rubber elasticity is characterized by the *rubbery modulus*, G_e , or by the reciprocal value – *equilibrium shear compliance*, J_s , or (in non-linear domain of viscoelastic behavior) *ultimate recoil function*. These parameters are determined as:

$$G_e = J_s^{-1} = \frac{\sigma}{\gamma_\infty} \quad [3.4.2]$$

By definition, G_e and J_s , are constants in the linear viscoelastic domain and they become dependent on the shear stress in transition to the non-linear behavior domain.

Rubber elasticity is typical for all liquid polymeric materials – melts, solutions, dispersions, some colloid systems forming

determined primarily by higher averaged values of MMD, i.e., presence of even very small amounts of species with very high MM dramatically increases rubbery elasticity (quantitatively presented by the steady state compliance) of melt.

The J_s^0 values are determined by ratios of different average molecular weights, including higher moment of molecular weight distribution. Two of these relations are the most popular. As was mentioned above, many authors used the ratio \bar{M}_z/\bar{M}_w as the measure of molecular weight distribution determining J_s^0 . In this case the following equation is usually used:⁶⁵

$$J_s^0 = A \left(\frac{\bar{M}_z}{\bar{M}_w} \right)^{3.7}$$

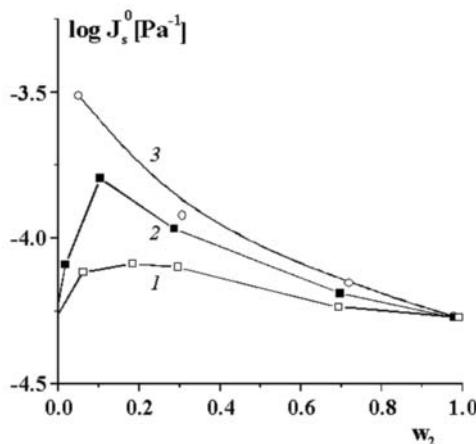


Figure 3.4.3. Shear compliance of mixtures of “monodisperse” polyisoprenes – influence of MMD. w_2 – concentration of a component with higher MM. 1 – MMs of components: $1.6 \cdot 10^5 / 5.75 \cdot 10^5$; 2 – MMs of components $6.5 \cdot 10^4 / 8.3 \cdot 10^5$; 3 – Solution of a polymer (MM = $7.3 \cdot 10^3$). [Adapted, by permission, from G.Zh. Zhangereyeva, M.P. Zabugina, A.Ya. Malkin, in *Rheology of polymers and disperse systems and rheo-physics*, *Inst. of Heat and Mass Transfer, Belorussian Academy of Sciences*, Minsk, 1, 161 (1975)]

are also sensitive to details of chain architecture and particularly to branching. Fig. 3.4.3 also shows that compliance of solutions increases when solvent content increases, and becomes much higher than J_s^0 of polymer melt.

The nature of recoverable deformations (elastic recoil) in polymer melts and solutions is the same as in the cured rubbers: conformational changes in chain configurations in space. The difference between linear and cured polymers is in the lifetime of junctions: in cured rubbers junctions can be treated as existing infinitely long; junction (entanglement) lifetime in flowing solutions and melts is limited and therefore the elastic recoil is accompanied by sliding in junctions, i.e., by flow.

The other equation is as follows:⁶⁶

$$J_s^0 = A \left(\frac{\bar{M}_z \bar{M}_{z+1}}{\bar{M}_n \bar{M}_w} \right)^{3.7}$$

Actually, it is rather difficult to make the choice between these equations. Both equations can successfully describe the same experimental data, as was demonstrated for high density polyethylenes.⁶⁷ At the same time the ratio \bar{M}_w/\bar{M}_n can be used for the rough correlation with J_s^0 , as was shown for polypropylenes.⁶⁸

The role of small fractions of high MM fractions is illustrated in Fig 3.4.3, where J_s^0 is presented as a function of the relative concentration in a mixture of two “monodisperse” polymers with different MM. The J_s^0 values of mixed polymers are the same, but blend has very different value of J_s^0 . Also, a very strong effect of small amounts of high MM fractions is observed.

Analogous experimental evidences are known for various polymers. The J_s^0 values

3.4.2 NORMAL STRESSES IN SHEAR FLOW

3.4.2.1 The Weissenberg effect

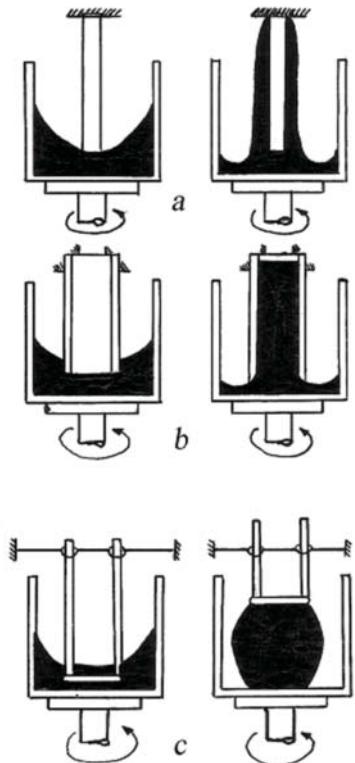


Figure 3.4.4. The Weissenberg effects (see text for details).

between the discs to the periphery of the discs, is pressed through the hole. Some other related observations were also made which demonstrate similar unusual behavior of “rheological” liquid.

The immediate impression appears that in the flow of “rheological” liquid some forces exist which compress liquid from outside normal to its surface, acting like a stretching elastic ribbon twining around a sample and forcing it to move to the center. Such *normal forces* act not only normal to the surfaces of the discs but also in the radial direction to the central axis as well.

Phenomena associated with the Weissenberg effect are very common in technological applications: reactors are supplied with rotating mixing elements (mixers) of different geometry and type. Such equipment is used in various branches of chemical, food, and pharmaceutical industries. Moreover, the last example of the Weissenberg effect shown in Fig. 3.4.4, case c was used to design a special type of machine for polymer processing, the so-called *screwless extruder*. In this design, a material is mixed between two discs and

Weissenberg described several abnormal observations from the point of view of classical fluid dynamics.⁶⁹ Saponified hydrocarbon colloid gels and polymer systems (solutions and gels) become the main materials for demonstrating the Weissenberg effect.⁷⁰

Some examples of the phenomena called the *Weissenberg effect* are shown in Fig. 3.4.4, where behavior of traditional viscous fluid and special “rheological” liquid are compared. The left pictures demonstrate what happens with an ordinary viscous liquid, whereas the pictures on the right side show the special phenomena observed in deformation of a “rheological” (or elastic) liquids. These are called the *Weissenberg effect*.

If a rod is rotating inside a “rheological” liquid, such liquid, instead of being displaced out of the rotor by the centrifugal forces towards the walls of a vessel, begins to climb around the rotor (Fig. 3.4.4, case a). In the case of two coaxial cylinders (inner hollow), the rotation of the outer cylinder forces liquid into the inner cylinder (Fig. 3.4.4, case b). Another characteristic example concerns the flow of liquid between two parallel discs. When the outer disc is rotated around a common axis, the inner disc is lifted up by the normal force generated due to rotation (Fig. 3.4.4, case c), and if a hole were made in the center of one of the discs, this “rheological” liquid, instead of being removed from the space

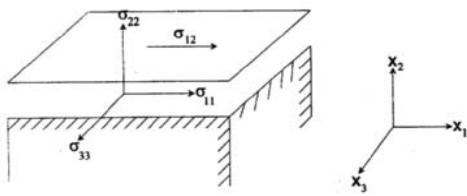


Figure 3.4.5. Stress tensor in shear between two parallel planes.

pressed through a nozzle by action of forces originated from the Weissenberg effect. Normal forces caused by rotation of parallel discs also give additional support in slide bearings if “rheological” (elastic) liquid is used as a lubricant. Some investigators think that the Weissenberg effect provides the ability of articulations in biological organisms and that deficiency in this phenomenon leads to illness (“squeak in joints”).

It is interesting to understand the rheological origin of this effect, i.e., what happens at the reference point. The common feature of all phenomena is the appearance of forces acting in the direction of shear and in the perpendicular direction. In the language of continuum mechanics it is equivalent to the appearance of the normal stresses in shear.

It can be anticipated that normal components of the stress tensor are related to the appearance of a diagonal component in the tensor of large elastic deformations. So, there is a common agreement that the Weissenberg effect is related to the existence of *normal stresses* in shear, and the latter can be explained by large elastic deformations developed in flow. (It may be argued whether this explanation is general, but undoubtedly the large elastic deformations lead to normal stresses).

3.4.2.2 First normal stress difference – quantitative approach

Stress combination in a simple shear is expressed by the stress tensor shown in Fig. 3.4.5. The tensor has the following structure:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix} \quad [3.4.3]$$

The stress tensor can be presented as the sum of hydrostatic pressure and the deviatoric components. If pressure is not high, it is possible to neglect the compressibility of liquid relevant in some real situations. Therefore, only the deviatoric part of the stress tensor is important for deformation of fluids. It means that if the hydrostatic pressure is superimposed, it will change all normal components of the stress tensor but would not influence flow. The direct consequence of this approach is that in order to characterize the effect of normal stresses in shear flow, it is not the absolute values of normal stresses but their *differences* that are important.

The differences of normal stresses are defined as follows:

the first (or primary) difference of normal stresses: $N_1 = \sigma_{11} - \sigma_{22}$

the second (or secondary) difference of normal stresses: $N_2 = \sigma_{22} - \sigma_{33}$

In rheological literature, N_1 and N_2 are not often used but their coefficients (analogous to the use of viscosity coefficient instead of the shear stress) are introduced.

The *first* and the *second normal stress coefficients* are defined as

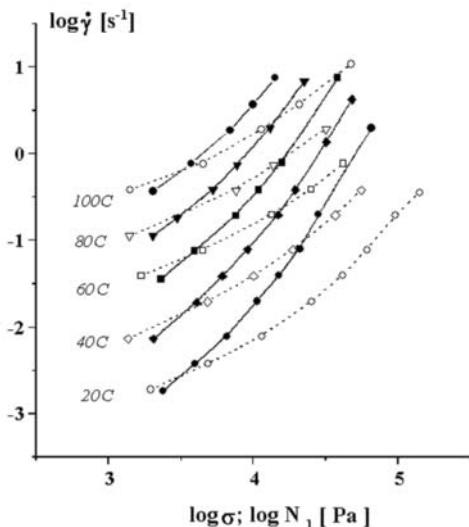


Figure 3.4.6. Shear and the first normal stress dependencies on shear rate in a steady flow at different temperatures. Polyisobutylene. $M = 1 \times 10^5$. Dotted lines – shear stresses; solid lines – normal stresses. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, V.F. Shumsky, *Rheol. Acta*, **9**, 155 (1970)].

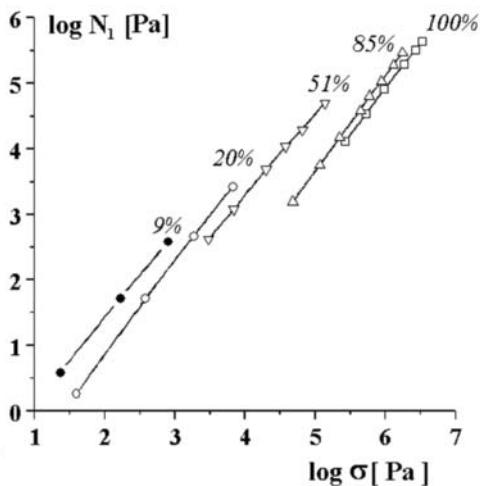


Figure 3.4.7. Relationship between the first difference of normal stresses and the shear stresses in a steady flow of butyl rubber solutions in cetane. $T = 20^\circ\text{C}$. Concentrations are labelled on the curves. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, G.V. Berezhnaya, *Vysokomol. Soedin. (Polymers – in Russian)*, **12**, 2797 (1971)].

$$\Psi_1 = \frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2} = \frac{N_1}{\dot{\gamma}^2} \quad [3.4.4]$$

and

$$\Psi_2 = \frac{\sigma_{22} - \sigma_{33}}{\dot{\gamma}^2} = \frac{N_2}{\dot{\gamma}^2} \quad [3.4.5]$$

It is interesting to compare the shear and normal stresses in a steady shear flow in order to understand the meaning and value of the normal stress effect. An example of experimental results is shown in Fig. 3.4.6 for the shear stress and the first normal stress difference. The normal stresses are smaller than the shear stresses at low shear rates but they are growing along with an increase of the shear rate much faster than shear stresses and they exceed the latter at high shear rates. The ratio between stress tensor components depends not only on the shear rate but on the nature of liquid, temperature, and so on.

The direct relationship between the first normal stress difference, N_1 , and the shear stress, σ , can be obtained after excluding the shear rate (see Fig. 3.4.7). N_1 is proportional to the square of the shear stress:

$$N_1 \propto \sigma^2$$

It means that the appearance of the first difference of normal stresses is the *second-order effect* in relation to shear stresses.

The coefficients of normal stress differences (and apparent viscosity) depend on shear rate. This is caused by a strong non-linearity of rheological properties of liquid. The initial values of the coefficients of normal stresses, Ψ_0 , as their limits at low shear rates, can be defined analogous to Newtonian viscosity.

The first normal stress difference is the second order effect in the whole shear rate range, including the range of non-Newtonian flow. The following relationship is valid:

$$\Psi(\dot{\gamma}) = \left(\frac{\Psi_0}{\eta_0^2} \right) \eta^2(\dot{\gamma}) \quad [3.4.6]$$

The first normal stress difference is the effect of the second order in comparison with viscous flow and this directly leads to the relationship between Ψ_0 and molecular mass of polymer (based on Eq. 3.3.15):

$$\Psi_0 = K_\Psi M^{2b} \quad [3.4.7]$$

where K_Ψ and b are constants.

However, normal stresses – contrary to shear stresses – are more dependent on higher moments of molecular mass distribution than viscosity, i.e., the M value in Eq. 3.4.7 for polydisperse polymers must be substituted not by \bar{M}_w but by higher averaged values of molecular mass.

3.4.2.3 Second normal stress difference

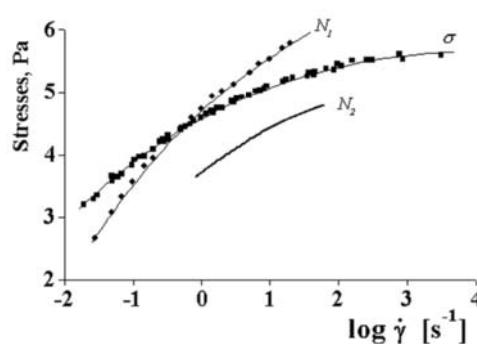


Figure 3.4.8. Shear and normal stresses in stationary flow of polyisobutylene [Adapted, by permission, from: N. Ohl and W. Gleissle, *Rheol. Acta*, **31**, 294 (1992)].

The *second normal stress difference* seems less important for practical applications because $N_2 \ll N_1$. However, the measurements of N_2 are important for constructing different rheological models and theories. The published experimental results of N_2 are controversial: in early publications zero, negative, and positive values of N_2 were found. However, careful analysis of possible experimental errors leads to the general conclusion that N_2 is negative ($N_2 < 0$) and its absolute value is close to $(0.1-0.3)N_1$.⁷¹ Some shear rate dependencies of all components of the stress tensor are presented in Fig. 3.4.8.

3.4.3 NORMAL STRESSES AND ELASTICITY

The common agreement that the normal stresses are related to elasticity of liquid is quantitatively expressed by the Lodge equations valid for “linear” elastic liquids (see also Section 2.5.2):

$$J_s^0 = \frac{N_1}{2\sigma^2} \quad [3.4.8]$$

or

$$\gamma_\infty = \frac{N_1}{2\sigma} \quad [3.4.8a]$$

These equations can also be written as a relationship between coefficients:

$$G_e = J_s^{-1} = \frac{2\eta_0^2}{\Psi_1} \quad [3.4.9]$$

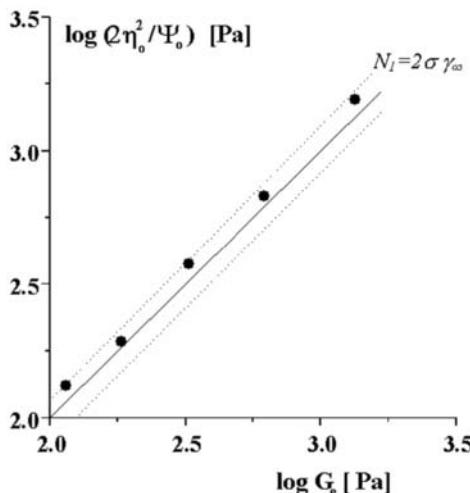


Figure 3.4.9. Comparison of independently measured values of G_e and the ratio (η_0^2/Ψ_0) . Polystyrene solutions in decalin. $T = 25^\circ\text{C}$. Dotted lines – limits of 25% experimental error. [Adapted, by permission, from A.Ya. Malkin, G.V. Berezhnaya, G.V. Vinogradov, *J. Polym. Sci., Symposia*, **42**, 1111 (1973)].

be used as a direct measure of the stored elastic energy in flow. The expression for the stored elastic energy, W , per unit volume can be obtained from the Lodge equation for an elastic liquid:

$$W = \frac{N_1}{4} \quad [3.4.10]$$

This equation permits estimation of stored elastic energy in non-linear regimes of steady flow.

Fig. 3.4.10 compares concentration dependencies of rheological characteristics of solutions, such as viscosity, normal stresses, and elastic modulus using the reduced concentration, $c[\eta]$, as an argument.

These equations demonstrate that the normal stresses are second-order effects with respect to the shear stresses.

Eq. 3.4.9 is for Newtonian liquid capable of exhibiting elastic deformations. Therefore this equation contains coefficients for Newtonian viscosity, η_0 , and zero-shear-rate coefficient of the first normal stress difference, Ψ_1 . The applicability of Eq. 3.4.9 is illustrated by experimental data in Fig. 3.4.9. The elastic modulus, G_e , and the coefficients η_0 and Ψ_0 were measured independently. The values of G_e and $(2\eta_0^2/\Psi_0)$ are equal.

Eq. 3.4.8 is not valid in the nonlinear range of viscoelastic flow, primarily because the directly measured elastic recoil does not correspond to the elastic energy stored at the steady flow regime (because of the absence of superposition of elastic and flow deformations in the nonlinear domain). However, the normal stresses can

The Debye criterion, $c[\eta] = 1$ helps to establish a boundary of dilute solutions. This concentration range is on the left side of Fig. 3.4.10. There are two separate concentration ranges. In the low concentration range, at $c[\eta] < (c[\eta])_{cr}$, where $(c[\eta])_{cr} \approx 5-7$, η_0 is a weak function of concentration and ζ_0 is proportional to the square of viscosity (the second-order effect). In the high concentration range, i.e., at $c[\eta] > 7$, η_0 is proportional to c^5 and ζ_0 is proportional to c^{10} (again, the second-order effect). It is worth mentioning that concentration dependencies of the “apparent” modulus pass through a minimum at the same concentration $(c[\eta])_{cr}$.

Thus, there are *three* concentration domains in polymer solutions:

- domain of *dilute* solutions at $c[\eta] < 1$; in this concentration range, macromolecules deform independent of one another
- domain of *semi-dilute* or *semi-concentrated* solutions at $1 < c[\eta] < 7$; in this concentration range contacts between different macromolecules are possible but a continuous three-dimensional entanglement network is still absent
- domain of *concentrated solutions* at $c[\eta] > 7$; in this concentration range, a special entanglement network exists throughout the whole volume of solution.

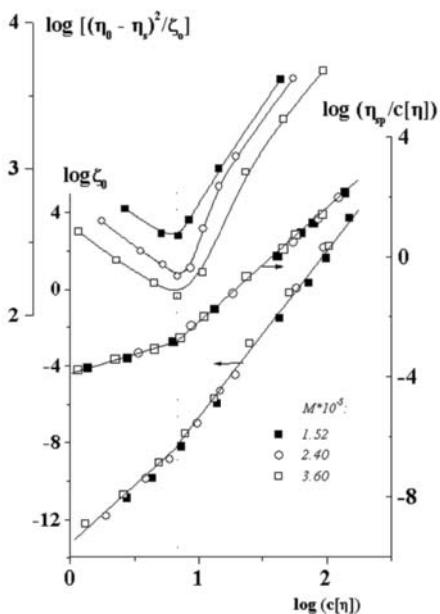


Figure 3.4.10. Comparison of concentration dependencies of Newtonian viscosity, η_0 , coefficient of the first difference of normal stresses, ζ_0 , and elastic modulus, G_e , calculated as $(\eta_0 - \eta_s)^2/\zeta_0$. In this Figure: $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$ and η_s is the viscosity of a solvent. Coefficient of normal stresses, ζ_0 , used in the original publications equals $\zeta_0 = \Psi_0/2$. Polybutadiene solutions in methyl naphthalene. $T = 25^\circ\text{C}$. [Adapted, by permission, from A.Ya. Malkin, G.V. Berzhnaya, G.V. Vinogradov, *J. Polym. Sci.: Symposia*, 42, 1111 (1973)].

Rubberly (large) deformations in solution happen in the range of concentrations in which macromolecular chains form a temporary network, i.e., at $(c[\eta]) > (c[\eta])_{cr}$. Fig. 3.4.10 shows that normal stresses and “apparent” modulus can be measured in the low concentration range, $(c[\eta]) < 7$. This means that the elastic energy can be stored not only by the molecular network but also by individual macromolecules, changing their conformation under shear deformation in solution. It becomes increasingly more “difficult” (modulus increases) to deform a macromolecule by diluting its solution.

It can be predicted that normal stresses always appear if the shear deformation results in a three-dimensional (3D) reaction of structural elements in a flowing medium. The deformation of polymer liquid (either melt, solution, or cured rubber) inevitably results in changes of the macromolecular conformations. The deformation or relaxation – due to statistical reasons – always proceeds in 3D space. Macro- one-dimensional shearing leads to 3D micro-reaction and this is the reason for appear-



Figure 3.4.11. Extrudate swell in post extrusion of polyethylene melt. (Original photo of the authors).

ance of normal stresses in a simple shear flow. This is also true for dilute polymer solutions where the 3D network is absent, but individual macromolecules deform in 3D space in any geometry of macro-deformations. The same effect, not related to the elasticity of medium, can be expected in the shear flow of suspensions of non-spherical particles (e.g., fiber in a Newtonian matrix). The micro-reaction is 3D and it results in a relaxation process restoring statistical distribution of particle orientation in space and normal stresses in shear flow.

3.4.4 DIE SWELL

When a stream of viscoelastic liquid leaves a die, the diameter of an extrudate increases, and the ratio of the extrudate diameter to the die diameter is called the *swell ratio*, S_R . Calculations based on the kinetic equations of classical fluid dynamics predict that the jet diameter changes for Newtonian liquid do not exceed 13% and an extrudate contracts at high Reynolds numbers. However, Barus⁷² demon-

strated that there are liquids (e.g., marine glue) for which a large swelling of a stream was observed. Later, analogous experimental results were published by Merrington⁷³ who experimented with rubber solutions and soap-thickened mineral oils and directly explained this effect by the elastic nature of materials used.

The typical example of *die swell* (or post-extrusion swelling) is shown in Fig. 3.4.11 for a polymer melt. The values of S_R for real technological materials can reach several units and they provide a measure of the elasticity of these materials. The observed values of S_R depend on the preceding kinematics of deformation – the shear rate at the capillary and the length of the channel. Also, S_R depends on the nature of material, reflecting its capability to store elastic deformations.⁷⁴

Elastic deformations in the post-extrusion stage of polymer processing are caused by the release of elastic energy stored during deformations inside a channel. However, the die swell occurs in the nonlinear viscoelastic behavior domain and the elastic deformations of a free stream are accompanied by a partial dissipation of the stored elastic energy. This is why it is not easy to establish direct quantitative relationships between S_R and the rheological parameters of material. However, S_R can be used as an important and useful estimation of the elasticity of material.

The extrudate swell distorts the shape of extruded articles in comparison with the sizes of calibrating devices (of a die). It gives an especially undesirable effect in extrusion of complicated profiles, because the elastic swell appears differently in different parts of a cross-section. The production of calibrating dies in extrusion of such profiles is expensive, and it gives a good chance to develop numerical methods for calculation of S_R in the flow through channels of various cross-sections.

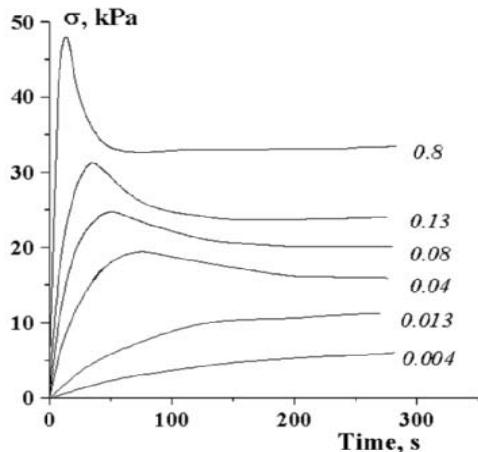


Figure 3.5.1. Transient shear stress evolution at startup of shear flow at different shear rates. Values of shear rate are shown at the curves (in s^{-1}). Polyisobutylene, MM = 1×10^5 . T = 0°C. [Adapted, by permission, from E. Mustafayev, A.Ya. Malkin, E.P. Plotnikova, G.V. Vinogradov, *Vysokomol. Soedin.* (Polymers – in Russian), **6**, 1515 (1964)].

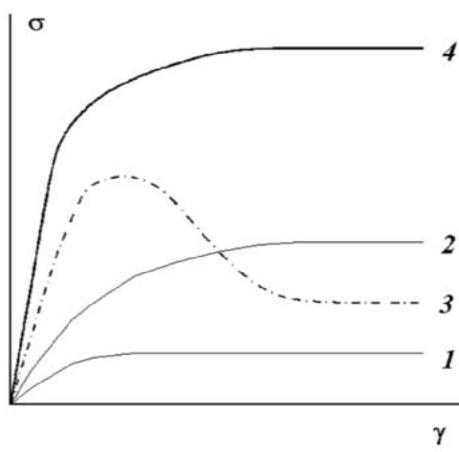


Figure 3.5.2. Transient shear stress evolution at startup of shear flow of a grease at different shear rates. Increasing shear rates: $\dot{\gamma}_1 < \dot{\gamma}_2 < \dot{\gamma}_3 < \dot{\gamma}_4$. Curves 1 and 2 – creeping flow of a material with undestroyed structure; curve 3 – deformation in the yielding range (transition through the maximum of the structure strength); curve 4 – flow of material with destroyed structure. [Adapted, by permission, from V.P. Pavlov, G.V. Vinogradov, *Dokl. AN SSSR* (Reports of the Academy of Sciences of the USSR – in Russian), **122**, 646 (1958); *Kolloid. Zh.* (Colloid J. – in Russian), **28**, #3 (1966)].

3.5 STRUCTURE REARRANGEMENTS INDUCED BY SHEAR FLOW

3.5.1 TRANSIENT DEFORMATION REGIMES

In steady flows of liquids, there is a unique relationship between shear stress, σ , and shear rate, $\dot{\gamma}$. In transient deformation regimes such an unambiguous relationship is absent. It means that at $\sigma = \text{const}$, the shear rate continuously changes until it reaches its steady level, and *vice versa*.

A transient deformation regime also exists for Newtonian liquid, however, it is due to inertial effects alone. In contrast, inertial effects are negligible for highly viscous liquids. The reasons for the transient behavior of non-Newtonian viscous liquids are:

- development and storage of elastic (rubbery) deformation, superimposed on flow
- structure changes induced by shearing.

Both reasons may exist simultaneously.

The transient behavior is observed for $\dot{\gamma} = \text{const}$. In this case a pre-stationary evolution of shear stress is observed. Typical relationships are shown in Fig. 3.5.1 for an elastic polymer melt and in Fig. 3.5.2 for an inelastic grease. Formally both sets of curves are similar: at low shear rates, a monotonic growth of shear stress, σ , is observed; at higher shear rates, a maximum, σ_m , on stress-vs.-time curve, $\sigma^+(t)$, appears. This phenomenon is usually called an *overshoot*. In both cases the steady state stress, σ_{st} , is reached at $t \rightarrow \infty$. There are some principal peculiarities in both sets of experimental data, and the transient

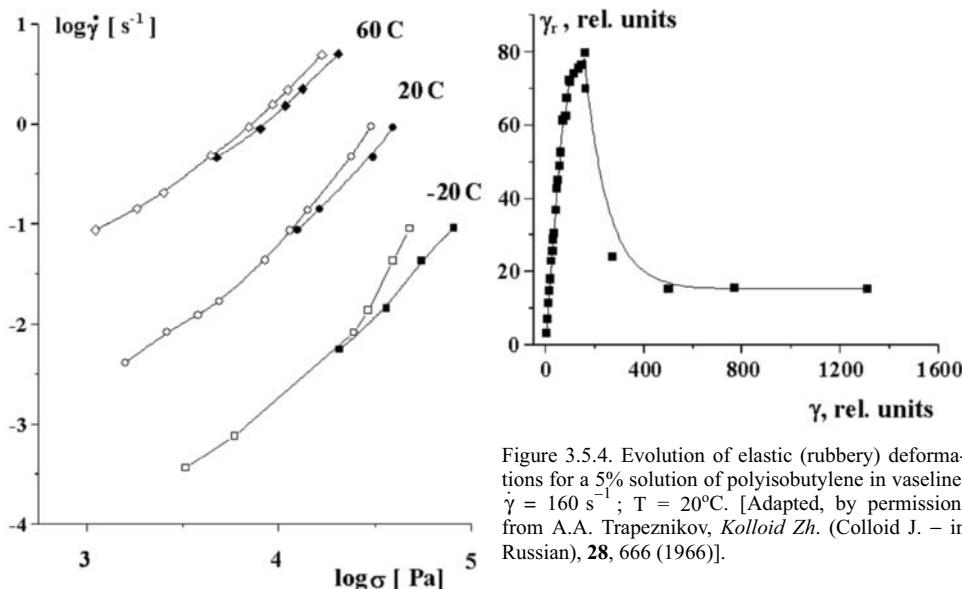


Figure 3.5.3. Shear rate dependence of stresses at steady-state flow, σ_{st} (open symbols) and at maxima of the transient stage of deformations, σ_m (solid marks), Polyisobutylene. $MM = 1 \times 10^5$. [Adapted, by permission, from G.V. Vinogradov, A.Ya., Malkin, E.P. Plotnikova, V.A. Kargin, *Dokl. AN SSSR* (Reports of the Academy of Sciences of the USSR – in Russian), **154**, 1421 (1964)].

the transient deformation regimes of polymer systems compares $\sigma^+(t)$ curves with development of elastic (recoverable) deformations, γ_r , stored during the *transient deformation range*. The dependence $\gamma_r(t)$ at $\dot{\gamma} = \text{const}$ is shown in Fig 3.5.4 for 5% solution of polyisobutylene in vaseline. Analogous dependencies are observed for many polymer solutions and melts as well as for some colloid systems; for example, for aluminum naphthanate dispersions.⁷⁵

The following observations were made. At the beginning of shearing the total deformation is mainly elastic. Hence, the material in this deformation range is primarily “stretched” but does not flow. The elastic deformation can be as large as 60-80 units (6,000-8,000%). These are very large values. They are typically observed in materials such as aluminum naphthanate, some gels, egg-white, and others. Typical elastic deformations of synthetic polymer melts do not exceed several units. Similar to the $\sigma^+(t)$ dependence, the $\gamma_r(t)$ dependence passes through a maximum. It is caused by the elastic deformation of the entanglement network, the knots of which are temporary bonds between macromolecules or polymer-like colloid particles. If the time of deformation is shorter than the characteristic lifetime of these junctions, they behave as permanent bonds and the material mechanical behavior is similar to that of rubber. At longer times, macromolecular chains slip in junctions, partly destroying the network. It results in the begin-

Figure 3.5.4. Evolution of elastic (rubbery) deformations for a 5% solution of polyisobutylene in vaseline. $\dot{\gamma} = 160 s^{-1}$; $T = 20^\circ\text{C}$. [Adapted, by permission, from A.A. Trapeznikov, *Kolloid Zh.* (Colloid J. – in Russian), **28**, 666 (1966)].

behavior in both cases reflects two different mechanisms of this effect.

Analysis of the $\sigma^+(t)$ curves for polymer solutions and melts shows that both σ_{st} and σ_m are shear rate dependent and they increase monotonously with increase in $\dot{\gamma}$. Fig. 3.5.3 shows the $\sigma_{st}(\dot{\gamma})$ dependencies and the $\sigma_m(\dot{\gamma})$ dependencies. Analysis of

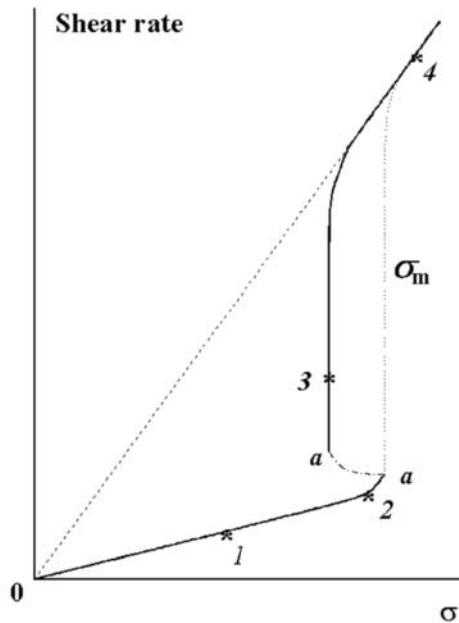


Figure 3.5.5. Complete rheological curve of a viscoplastic liquid (grease). 1-2 – creeping flow of material with undestroyed structure; aa – range of unsteady deformation regimes; 3 – range of yielding; σ_m – stress limit (strength) of structure; 4 – flow of liquid with destroyed structure. [Adapted, by permission, from G.V. Vinogradov and V.P. Pavlov (see Refs. in Fig. 3.5.2)].

stress value is lower than that of curves 1 and 2. At very high shear rates (curve 4), the maximum on the $\sigma^+(t)$ curves disappears, the apparent steady value of the stress, σ_{st} , increases again, and the viscosity at these shear rates is low, corresponding to the viscosity of a dispersion phase (oil). It is also important to mention that the steady state stress, σ_{st} , in flow of plastic greases is constant in a wide range of shear rates and therefore it must be regarded as the yield stress, σ_y , typical of any viscoplastic materials. The stress values at the maximum of the $\sigma^+(t)$ curves, σ_m are also constant in the same shear rate range.

The rheological behavior of this material is generalized in Fig. 3.5.5, where the dependencies of σ_{st} and σ_m on shear rate are shown, and the numbers at the points 1, 2, 3, and 4 correspond to the number of the curves in Fig. 3.5.2. It is evident that the material is viscoplastic, and the following features are characteristic for such materials in addition to the existence of the yield stress.

First, if one follows the $\sigma_{st}(\dot{\gamma})$ dependence, a multi-valued branch of the flow curve appears in the transition region from the range of very low shear rates to the central part of the flow curve. This branch is shown in Fig. 3.5.5 by the dashed line aa. Possibly, this part of the flow curve is not reached experimentally and the attempts to “measure” the apparent viscosity of this branch of a flow curve results in sudden increase in flow rate.

ning of flow and decrease in the stored elastic deformations. Part of the entanglements (with lifetime longer than $\dot{\gamma}^{-1}$) continue to exist even in a steady flow and therefore some elasticity can also be found in the flowing liquid.

The existence of a very sharp maximum on the $\gamma_f(t)$ curves suggests that the maximum on the $\sigma^+(t)$ curves reflects elastic deformation in shear: at short times material deforms predominantly as a rubber-like, and, only after partial disintegration of entanglements, the transition to viscous flow occurs. This physical reason explains the shapes of curves in Figs. 3.5.1.

The physical effects responsible for transient behavior of greases (as well as numerous other technological materials) are different. At very low shear rates (curves 1 and 2 in Fig. 3.5.2), the transient $\sigma^+(t)$ curves are analogous to curves depicted in Fig. 3.5.1. These curves correspond to very high viscosity values, typical of structured materials with the yield value. An increase in the shear rate (curve 3) leads to the appearance of a maximum on the $\sigma^+(t)$ curves. However, the steady state

Second, the difference in viscosity values between the lower part (straight line 012 in Fig. 3.5.5) and the upper part (straight line 04 in Fig. 3.5.5) of the flow curve are very large and reach many decimal orders (the graphs in this figure are not presented in the same scale). The initial low shear rate branch of the flow curve is characterized by high viscosity values, which are typical of viscoplastic materials with solid structured filler (see Section 3.2.2). Viscosity at the final high shear rate branch of the flow curve is low and close to the viscosity of a dispersion medium.

Third, the difference between σ_m and σ_{st} values shows that the properties of material depend on its pre-history. The yield stress varies depending on whether the shear rate increases or decreases in the cycle of measurements: if the shear rate is decreased and measurements started, after the initial structure of material is destroyed, it is possible not to “notice” the high yield stress value corresponding to σ_m . It is a reflection of thixotropic behavior of material, which will be discussed in more detail in the next section.

Systems such as greases, toothpaste, and other analogous viscoplastic materials are not rubbery at all. Rheological properties, as presented in Fig. 3.5.5, are attributable to structure effects and partial damage to their inherent structure caused by deformation. In this sense the stress at the maximum σ_m of the $\sigma^+(t)$ curve can be treated as the strength of this structure.

The transient time dependence of stresses and the transitions through the stress maximum in materials of any type is generally explained by the “structure effects”, though this structure is different. For polymer and polymer-like colloid systems it is the network of rubbery chains, which can store large elastic deformations and slip in temporary entanglements at low deformation rates. For plastic materials it is a rigid coagulated structure that is formed by solid particles. This structure is characterized by a certain strength and it is destroyed at the yield stress. Then, the difference in Figs. 3.5.1 and 3.5.2 shows the difference in flow curves of elastic and plastic materials as discussed in Section 2.1. It is possible to find intermediate situations since the structure of the real natural or synthetic materials can be formed in various ways.

3.5.2 THIXOTROPY AND RHEOPEXY

The term “*thixotropic*”⁷⁶ means “sensitive to touching” and the effect of thixotropy is commonly regarded as slow changes in viscosity, or in a more common sense, any rheological properties induced by deformation and rest after deformation. The difference between “non-Newtonian” and “thixotropic” behavior is in the time-scale: by definition, it is supposed that the apparent viscosity of non-Newtonian liquid changes immediately along with the change in the shear rate, whereas the viscosity of the thixotropic medium changes slowly. This difference is evident in some cases, but it may not be easy to establish the time-scale of changes and in some cases it may be reasonable to treat thixotropy as a cause of non-Newtonian behavior and *vice versa*. Deformation destroys the inherent structure of structured liquids, leading to non-Newtonian behavior, and recovery of structure requires time, resulting in thixotropic effects. The difference between thixotropy and other rheological properties is not always clear for viscoelastic materials, because time effects due to elasticity are superimposed on structure rearrangements and can proceed within the same time-scale. Moreover, the question whether the relaxation phenomenon (which is also caused by structure rearrangements, e.g., molecular chain movements and/or disappearance of fluctuation) can be treated as “thixotropy” or not, can be discussed.

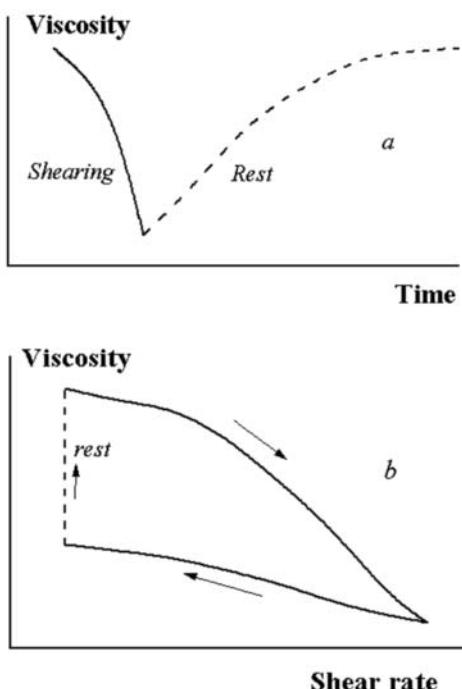


Figure 3.5.6. Typical thixotropic effects. a: viscosity decrease in deformation at constant shear rate and viscosity increase at rest; b: viscosity decrease as a function of ascending shear rate at steady flow and delayed restoration of viscosity at descending shear rate.

There is a large number of commercial materials which are thixotropic in nature. They include:⁷⁷

- paints, inks and coatings
- sealants and adhesives
- detergent systems
- clay suspensions
- oils and lubricants
- coal suspensions
- metal slushes
- rubber solutions, specially filled with different fillers
- food and biological systems (including blood)
- creams and pharmaceutical products.

Viscosity decrease of many food products (yogurt, cream, pastes, gels), pharmaceuticals, or concrete as a result of their mixing encountered everyday are typical and technologically important cases of thixotropic behavior. A typical example is shown in Fig. 3.5.7 for a body lotion: a decrease in viscosity on shearing, followed by a slow increase at rest. It is pertinent that the quality (or performance properties) of products are determined by a

Structure processes in some cases may be thought to be similar to chemical reactions leading to the formation of chemical bonds with unlimited (or at least very long) lifetime. In this sense thixotropy is a part of a more general field of rheokinetic effects, i.e. rheological transformations taking place in the synthesis and reactions of different materials, primarily oligomers and polymers (see Section 6.3).

Thixotropy is understood in two ways (Fig. 3.5.6): first, as a slow viscosity decrease due to deformations (at constant shear rate), together with a reverse process of complete or partial restoration of the initial viscosity at rest after deformation ceases (Fig. 3.5.6a); second, as a decrease of steady-state values of the apparent viscosity at different shear rates accompanied by delayed restoration of the viscosity values with decreasing shear rates (Fig. 3.5.6b). Both cases are treated as the kinetic reactions of structure rearrangements induced by deformations and it is commonly accepted that thixotropic materials are those that have a *microstructure*, though the latter term can be understood in various ways.

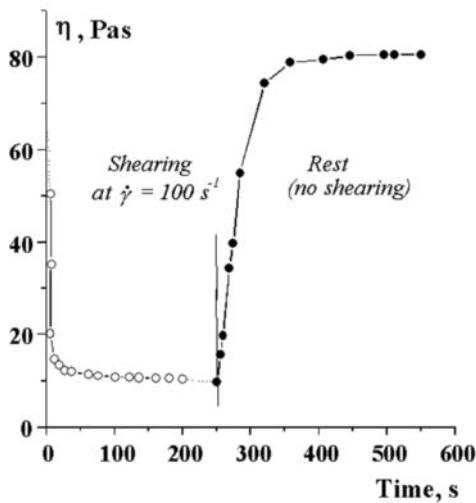


Figure 3.5.7. Thixotropic properties of a body lotion: decrease of viscosity in shearing and slow growth at rest. [Adapted, by permission, from G. Schramm, "A practical approach to rheology and rheometry", Haake, 1994].

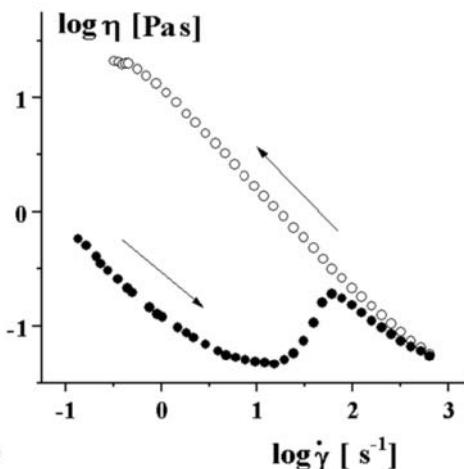


Figure 3.5.8. Apparent viscosity evolution in up-and-down changes of shear rate for a ternary system of alkali dimethyl oxide/alcohol/water. The period of shear rate scanning was 20 min. T = 25°C. [Adapted, by permission, from J. I. Escalante, H. Hoffman, *Rheol. Acta*, **39**, 209 (2000)].

degree of the viscosity decrease and the rate of its increase, though the quality of products in everyday observations are preferably judged as "good" or "bad".

The deformation process in some systems may lead, not to a decrease but to an increase in viscosity. This is called "*antithixotropy*" or "*rheopexy*". Sometimes, these effects are distinguished. Both terms are related to a continuous increase of viscosity with time at a constant shear rate, and/or thickening of material with increase in shear rate, and the difference between them lies in the time scale. Both effects are much more rare than thixotropy, but they occur in some materials, especially in systems containing active chemicals, e.g., ionic or polar groups. Deformation may enhance the intermolecular interaction, resulting in viscosity increase.

Thixotropic behavior of material is well demonstrated in cyclic experiments. The shear rate is continuously increased up to the upper level and then decreased to the initial value. The structure of the sample in such a deformation regime is first destroyed and then gradually rebuilt during the entire $\gamma(t)$ dependence. A thixotropic hysteresis loop is observed. The last point (at the lowest shear rate) may be different than the initial one if the characteristic time of scan is shorter than the time of structure formation, i.e., the time is not long enough for the initial structure to recover during the time of measurement.

Thixotropy, as well as rheopexy, is often observed for surfactant-water systems because intermolecular interactions in such systems are strongly pronounced. Shearing leads to structure transformation among colloid particles. Two examples from modern rheological literature illustrate the above-mentioned phenomena. First, the shear-rate dependence of the apparent viscosity measured in cyclic up-and-down deformation mode is shown in Fig. 3.5.8. Unusual effect of viscosity growth at about 10 s^{-1} is explained by transition of the bilayer structure to more viscous vesicle particles.⁷⁸ Then the positions of

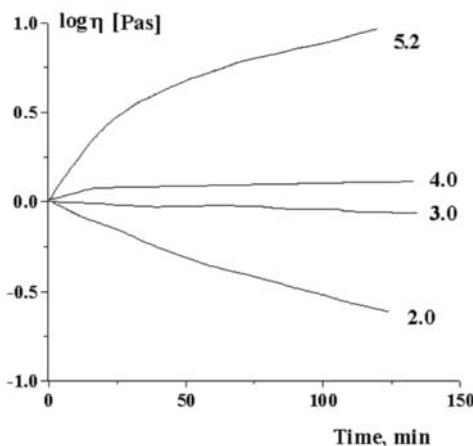


Figure 3.5.9. Steady-state viscosity evolution in time, measured at $\dot{\gamma} = 2.25 \text{ s}^{-1}$ for organogels containing 250 mg/mL lecithin. The ratio of water molecules to lecithin molecules is shown at the curves. [Adapted, by permission, from Yu.A. Shchipunov, H. Hoffman, *Rheol. Acta*, **39**, 542 (2000)].

ascending and descending branches of the flow curve are different because they represent different structures of the flowing colloid system.

The same material may exhibit either thixotropic or antithixotropic effect, and the observed rheological behavior sometimes depends on minor details of composition. Fig. 3.5.9 illustrates this phenomenon for lecithin solutions in water, forming polymer-like micelles.⁷⁹ By changing the molar ratio of water to lecithin it is possible to cause a transformation from shear thinning (thixotropic) to shear thickening (antithixotropic) rheological behavior in this colloid system. The effects observed are explained by the restructuring of the polymer-like micelles and their network. Kinetics of restructuring is slow in contrast to quick viscoelastic effects observed in colloid systems.

Quantitative description of thixotropic phenomena depends on the approach selected. Some authors consider it as a particular case of time-dependent effects in deformation of materials, analogous to viscoelastic effect. They prefer to treat it in terms of constitutive equations, i.e., in the framework of a mechanical approach only.⁸⁰ However, it seems that this approach is not adequate, especially in practical applications, because the evident changes in rheological properties (in particular, viscosity) are observed even when no stresses can be measured. The situation is the same as with phase transitions or chemical reactions, which are not mechanical phenomena. It is therefore more fruitful to apply a quasi-chemical approach to thixotropy-antithixotropy phenomena, introducing a kinetic equation for some parameter of a system (it can be a number of bonds, or concentration of structure aggregates, or some arbitrary not rigorously defined “structure” parameter, and so on) determining viscosity or other rheological properties of material.

Slow changes in rheological properties, definitely related to structural effects, are well demonstrated in examining the shear stress evolution measured at constant shear rates, $\dot{\gamma}=\text{const}$. The $\sigma(t)$ dependence has a maximum characterizing the “strength” of the structure destroyed by deformations. If one repeats this experiment just after cessation of the previous shearing, the maximum disappears and a monotonous shear stress growth is observed. However, if one lets the material rest, the maximum in the curve appears again and its height depends on the time of rest. This is shown in Fig. 3.5.10, where the subsequent curves correspond to successively longer times of rest. These observations can be easily explained by the structure rupture caused by deformations and slow structure restoration during rest.

It is worth mentioning that this phenomenon of structuring is not directly related to stress relaxation. Indeed, Fig. 3.5.11 clearly demonstrates that both are developing in

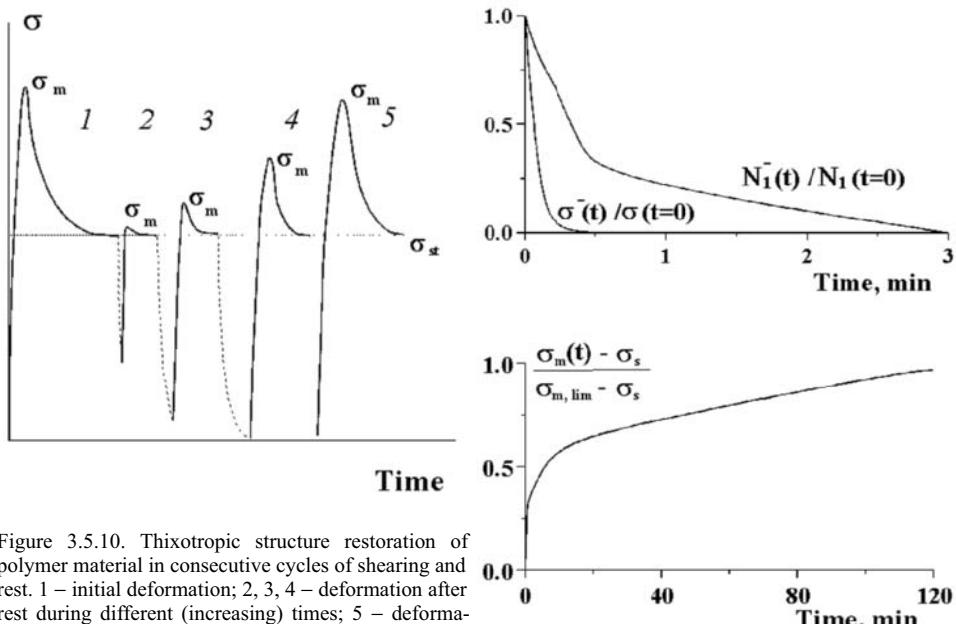


Figure 3.5.10. Thixotropic structure restoration of polymer material in consecutive cycles of shearing and rest. 1 – initial deformation; 2, 3, 4 – deformation after rest during different (increasing) times; 5 – deformation after very prolonged rest – complete restoration of the initial structure. Dotted lines – relaxation at rest.

absolutely different time scales: stresses completely disappear during several minutes while the approach to the initial value of the maximum, σ_m , on the $\sigma(t)$ dependence continues for several hours.

Examination of the transient behavior in shearing gives even more pronounced effects if one measures, instead of shear stresses, the first normal stress difference, $N_1^+(t)$.⁸¹ First of all, instead of a single maximum, two maxima are observed for normal stresses. Then, if the position of the first maximum is close (in time-scale) to the shear stress maximum, the second normal stress maximum appears after prolonged deformations reaching several hundred units. So, this effect must be related to a cooperative movement of macromolecules but not to relaxation of the individual chains. It is definitely a structure formation effect due to intermolecular interactions induced by shearing. Structures formed during prolonged shearing in some cases can be found by direct optical observations. These structures are thixotropic by their nature: they are destroyed and again restored at slow deformation and long rest time.

It is interesting to notice that in measuring transient $N_1^+(t)$ dependencies, oscillations of stress are observed. Possibly this effect is also related to formation and disintegration of larger structures in flow, which influence the rheological properties of the system as a whole.⁸²

Structure evolution in transient deformation regimes were well documented in the experiments performed with model immiscible polymer blends,⁸³ as well as with textured

Figure 3.5.11. Comparison of the relaxation rates of shear, $s(t)$, and normal, N_1^+ , stresses after sudden cessation of steady shear flow (upper figure) along with the kinetics of structure restoration at rest as observed by the relative increase of maximal stress in transient flow (lower figure). Polyisobutylene. $T = 20^\circ\text{C}$. [Adapted, by permission, from G.V. Vinogradov, A.Ya., Malkin, E.P. Plotnikova, V.A. Kargin, *Dokl. AN SSSR* (Reports of the Academy of Sciences of the USSR – in Russian), **154**, 1421 (1964)].

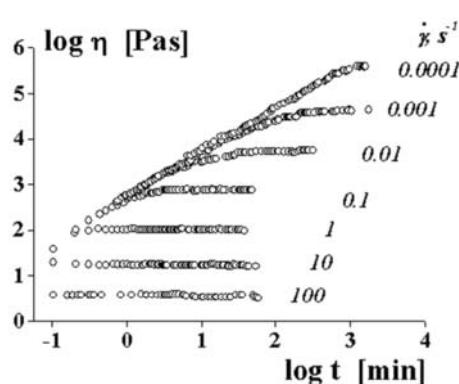


Figure 3.5.12. Evolution of viscosity at prolonged slow shearing of super-concentrated emulsion.

properties of multi-component or textured systems.

Thixotropy is usually attributed to the time-dependent shear-induced phenomenon. Peculiarities in rheological behavior can also be related to volume effects. Effects of this kind are called *dilatancy*.⁸⁵ This phenomenon was first described by Reynolds,⁸⁶ who noticed that traces of footsteps on wet sand stay when deformed. It means that volume changed under shear deformation. Dilatancy is important for humid soils, such as wet sands and clays: shearing leads to change in water content and in increase of viscosity. This phenomenon is called *shear thickening*.

Volume effects (dilatancy) caused by shear are also possible in elastic bodies, as well as in viscoelastic liquids. This phenomenon for solids was described by Kelvin,⁸⁷ who treated it as a second-order effect, i.e., volume changes are expected to be proportional to the square of shear deformations. In solids, it is known as the *Poynting effect* (see Chapter 4).

Many industrial materials are thixotropic. In technological practice, transportation of these materials through long pipes is an important and frequently complex problem. Therefore methods of designing pipelines for transportation of thixotropic inelastic liquids were developed.⁸⁸ The simulation procedures are based on formulation of the constitutive equation for time-dependent (and non-Newtonian) viscosity and solving the dynamic problems. However, the complexity of the governing equations always calls for extensive numerical methods for finding the final results.

The effect of *rheopexy* also belongs to the group of structure rearrangement induced by deformation. According to definition, rheopexy “is a solidification of a thixotropic system by gentle and regular movement”.⁸⁹ Fig. 3.5.12 demonstrates the effect of rheopexy for super-concentrated water-in-oil emulsion. It is seen that deformation at low shear rate is accompanied by slow growth of apparent viscosity covering several decades.

It is also important that rheoplectic effects can be observed at low shear rates only (i.e., at “gentle movement”). The experimental points in Fig. 3.5.13 were obtained at increasing and decreasing shear rate. The experimental points coincide in the high shear rate range, but the curves are different in the range of slow deformations and the difference increases with the shear rate decreasing. It is also worth mentioning that viscosity

polymeric liquid crystals.⁸⁴ In particular, it was demonstrated that the yield stress appears to be different depending on whether the shear rate increases or decreases in the cycle of measurement: if the shear rate is decreased and measurements are started when initial structure of material is destroyed, it is possible not to “notice” the higher yield stress value corresponding to σ_m .

The results of numerous observations confirm that the overshoot on the $\sigma^+(t)$ and $N_1^+(t)$ curves and evolution of rheological properties at rest are accompanied by large-scale structure effects related to thixotropic

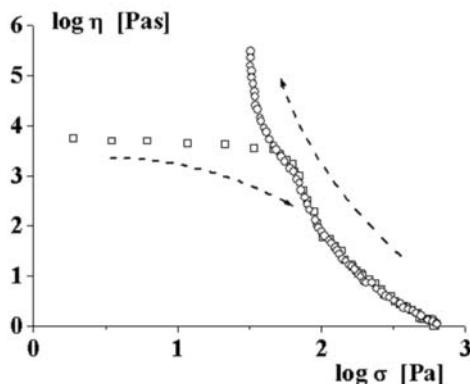


Figure 3.5.13. Flow curves of a water-in-oil super-concentrated emulsion measured at upward and downward changes of shear rate. [Adapted, by permission, from A.Ya. Malkin, I. Masalova, P. Slatter, K. Wilson, *Rheol. Acta*, **43** (2004)].

shearing can occur in self-oscillation (periodic) manner with corresponding periodic (in time) variation of apparent viscosity.⁹²

Structure formation leads to the anisotropy of rheological properties of a matter.

In discussing the rheology of fluids with their structure dependent on deformation, it is necessary to introduce additional structural (or internal) parameters that should be coupled with dynamic equations. As an example of such approach is the model incorporating the flow-induced anisotropic structural changes. The induced structure was described by the tensor, and its evolution was governed by a relaxation-type differential equation.⁹³

Finally, it is interesting to report that structure effects in shearing occur in a self-oscillation (periodic) manner with corresponding periodic (in time) variation of apparent viscosity.⁹⁴

3.5.3 SHEAR INDUCED PHASE TRANSITIONS

The interrelation between temperature of phase transition is well known in classical thermodynamics. The following dependence was established:

$$\frac{dT}{dp} = \frac{T\Delta V}{\Delta H} \quad [3.5.1]$$

where dT/dp is a change of the phase transition temperature due to changes in pressure, T is temperature, ΔV is a change of molar volume at the phase transition point, and ΔH is the molar heat of transition.

This equation, known as the *Clausius-Clapeyron equation*,⁹⁵ relates the shift in the equilibrium phase transition temperature to hydrostatic pressure, i.e., to the volume changes of material.

Rheology considers shift in phase transitions induced by shear deformation (proceeding mainly without volume changes).

The first observation related to the subject was the effect of extension-induced crystallization of rubbers.⁹⁶ The full theory of this effect as an analogue of the pressure-

drops from the upper to the lower curve almost immediately after cessation of shearing. Structure rearrangement at rest, after shearing proceeds very quickly, can be explained by elastic deformation of dispersed droplets that causes a rheoplectic effect.

Deformation can lead to self-organization in a flowing medium. Some examples of this effect have been already described in Sections 3.2.3 and 3.6.3. Self-organization and induced anisotropy can also be created in dense suspensions of rigid particles.⁹⁰ Here, it is reasonable to add that self-arrangement can also lead to the formation of anisotropic micellar structures in flow of block-copolymers.⁹¹ It is interesting to report that structure effects in

induced shift of the crystallization temperature is well known.⁹⁷ Later, it was shown that the shearing induces phase transitions in amorphous systems too.⁹⁸

It was stressed by many authors that shearing may result in two opposite effects: homogenizing of multi-component systems and flow-induced phase separation.⁹⁹ Shear deformation always favors homogenizing of a multi-component system due to pure geometrical reasons, and this is not necessarily related to the phase transition from a two to a one phase system. The shear-induced phase separation is caused by the same thermodynamic reasons as the phase transition due to static pressure. It is caused by changes in the free energy of a system due to its deformation.¹⁰⁰ It becomes possible in shear flow because the flow in some systems (primarily polymer solutions) is accompanied by the storage of rubbery deformations, i.e., elastic energy (see Section 3.4).¹⁰¹

There are three aspects of flow-induced phase transition.

- the *thermodynamic effect*: deformations can lead to a shift of the equilibrium phase transition temperatures
- the *kinetic effect*: deformations change the kinetics of a phase transition at the fixed temperature
- the *morphological effect*: deformation-induced phase transition leads to formation of different molecular and supermolecular structures, which determine the properties of the end product.

These three aspects are connected: a shift in the equilibrium phase transition temperature results in a shift of the distance from a given temperature to an equilibrium one, and this is the reason for changes in the process kinetics, and so on.

The general result of thermodynamic studies of deformation-induced phase transitions is a theory which is principally close to the Clausius-Clapeyron equation. This result can be represented by the equation:

$$\frac{1}{T_m^0} - \frac{1}{T_m} = \frac{R}{\Delta H} f(\epsilon) \quad [3.5.2]$$

T_m^0 is the equilibrium (in the absence of deformations) phase transition temperature, T_m is the phase transition temperature observed when deformation is superimposed, R is the universal gas constant, ΔH is the molar heat of transition (as in Eq. 3.5.1), and $f(\epsilon)$ is some function of deformation, ϵ . This function is written in various forms depending on the model used, though in all models $f(\epsilon)$ is an increasing function of ϵ , and therefore, $T_m^0 < T_m$, i.e., the phase transition temperature must increase with the growth of ϵ .

This rule was rigorously proven for uniaxial extension. It is also true for shearing (when flow is accompanied by the storage of elastic deformations): the increase in shear deformations leads to the growth of the equilibrium melting temperature of polymer liquids.

The influence of deformation on the transition temperature was observed for both amorphous phase separation and crystallization. Fig. 3.5.14 shows dependence of the shift in the equilibrium transition temperature, ΔT , as a function of shear rate for two polymer solutions of different concentrations. The dominating factor is the shear stress. Fig. 3.5.15 demonstrates that the dependence of ΔT on the shear stress is similar for solutions of different polymers. The influence of shear flow on the equilibrium transition temperature can be as high as 30-40K.

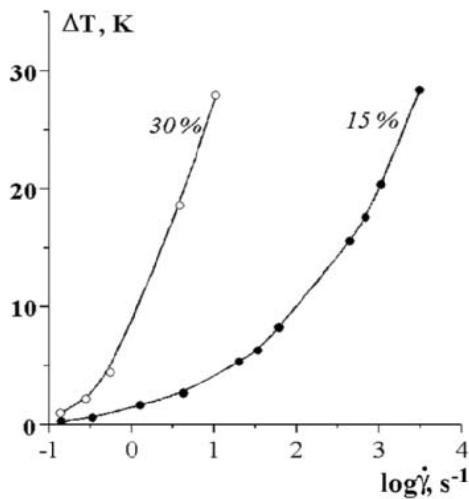


Figure 3.5.14. Shift in the phase separation temperature as a function of shear rate. Polyvinyl acetate solutions in ethanol. Concentrations are shown on the curves. $T = 25^\circ\text{C}$. [Adapted, by permission, from A.Ya. Malkin, S.G. Kulichikhin, G.K. Shambilova, *Vysokomol. Soedin.*, (Polymers – in Russian), **33B**, 228 (1991)].

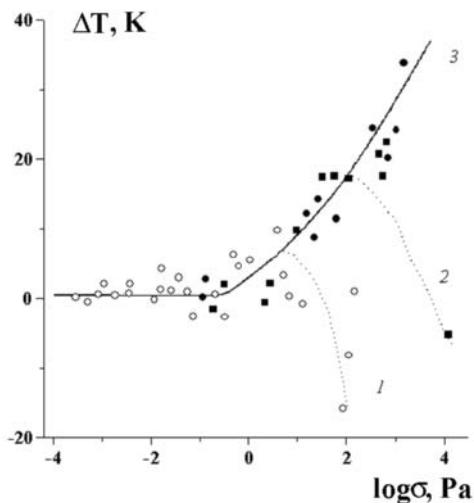


Figure 3.5.15. General dependence of the shift of separation temperature on shear stress for: 1 – polystyrenes of different molecular masses; 2 – polybutadiene solutions in toluene/ethanol mixture; 3 – polyvinyl acetate solutions in ethanol. [Adapted, by permission, from A.Ya. Malkin, S.G. Kulichikhin, V.A. Kozhina, *Vysokomol. Soedin.* (Polymers – in Russian), **38A**, 1403 (1996)].

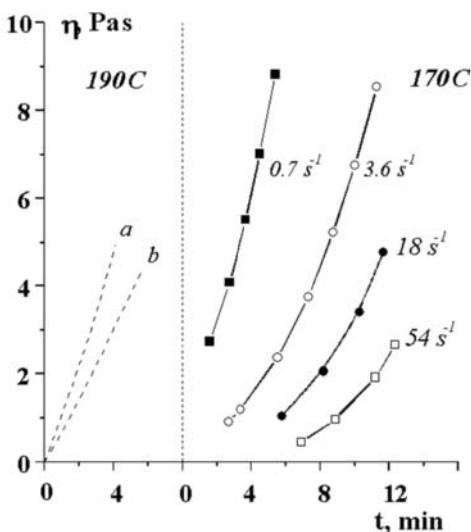


Figure 3.5.16. Viscosity evolution in polymerization of caprolactam at different temperatures and at different shear rates (shown on the curves). The field between the curves 0a and 0b covers points obtained in the shear rate domain from 0.1 to 100 s^{-1} . [Adapted, by permission, from A.Ya. Malkin, S.G. Kulichikhin, *Makromol. Chem., Macromol. Symposia.*, **68**, 301 (1993)].

Two dotted lines are drawn in Fig. 3.5.15. They show that the apparent transition temperature begins to decrease at very high shear rates. This observation is explained by the homogenizing effect at high shear rates.

The influence of shearing on the phase transition temperature is not only of pure academic interest. The following example illustrates its technological significance. Fig. 3.5.16 shows the increase of viscosity in a reacting medium during polymerization of caprolactam in bulk.^{102,103} The viscosity increase parallels an increase in concentration and/or molecular mass of polymer formed, i.e., the kinetics of polymerization. At high temperature, shearing does not influence the kinetics of polymerization. However, at lower temperatures, an increase in the shear rate decreases the rate of polymerization until almost complete cessation of the process. It is a peculiar

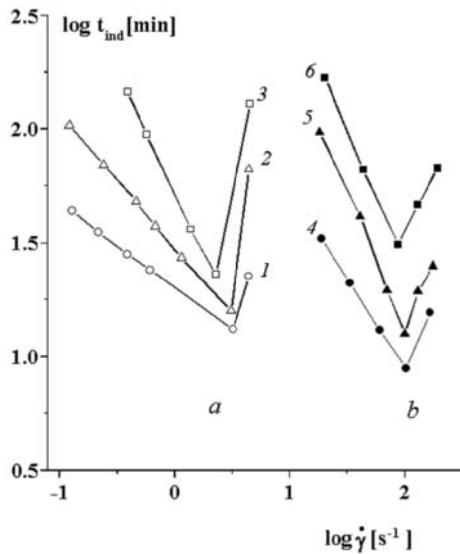


Figure 3.5.17. Influence of shearing at different shear rates on the induction period, t_{ind} , of crystallization for polyamide-6 melt (a) and 30% polyamide-6 solutions in caprolactam (b). Temperatures, °C: a: 1 – 230.0; 2 – 232.5; 3 – 235.0; b: 4 – 160.0; 5 – 162.5; 6 – 165.0. [Adapted, by permission, from A.Ya. Malkin, S.G. Kulichikhin, *Kolloid Zh.* (Colloid J. – in Russian), **41**, 141 (1979)].

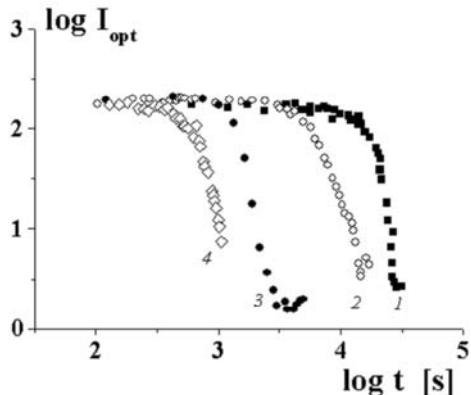


Figure 3.5.18. The intensity of the transmitted light as a function of time in crystallization of isotactic poly(1-butane) at 103°C under different shear rates, s^{-1} : 0 (1), 0.1 (2), 1 (3) and 10 (4). [Adapted, by permission from S. Acieno, B. Palomba, H.H. Winter, N. Grizzuti, *Rheol. Acta*, **42**, 243 (2003)].

behavior because it can be expected that an increase in the shear rate (increase in intensity of mixing) should accelerate the reaction. But the observed effect is the opposite, and this is because of phase separation of polymer from the reactive solution.

The flow-induced phase separation has some special features in non-homogeneous polydisperse systems. In these cases, two effects take place. The forces forming curvilinear shear fields are different, especially if one bears in mind that all real polymers undergo separation differently since they contain species of various molecular masses. Therefore, the separation by the chain length (*shear-induced fractionation*) can proceed due to a difference in the migration speed.¹⁰⁴ The effect is weak and it becomes important for very long chains, primarily for biopolymers.

The influence of shear flow on kinetics of crystallization is shown in Fig. 3.5.17 where the kinetics of crystallization is characterized by an induction period, t_{ind} . An increase in the shear rate shortens the induction period, i.e., accelerates the crystallization process. However, after passing through a minimum, the induction period begins to increase again. This can be explained by the destruction of crystallization nuclei at high stresses, which is the reason for slower crystallization.

In other experiments, the formation of crystalline phase was followed by monitoring the transparency of polymer melt by the intensity of light transmission, I_{opt} , through a sample as a measure of crystalline content.¹⁰⁵ Fig. 3.5.18 demonstrates strong influence of shearing on the kinetic of crystallization. Analogous effect is shown in Fig. 3.5.19 for isotactic polypropylene. Use of the Avrami kinetic equation shows that the rate of crystallization is enhanced as $\gamma^{1.22}$, i.e., the influence of shear rate is strong.

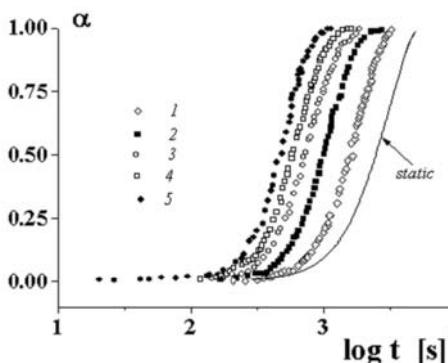


Figure 3.5.19. Kinetics of crystallization of isotactic polypropylene in static state and under shearing at different shear rates, s^{-1} : 0.15 (1); 0.3 (2); 0.5 (3); 1 (4) and 1.4 (5). $T = 136^\circ\text{C}$. [Adapted, by permission, from N. Devaus, B. Monasse, J.-P. Haudin, P. Moldenaers, J. Vermant, *Rheol. Acta*, **43**, 210 (2004)].

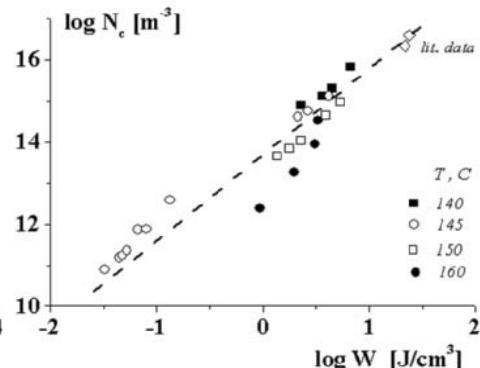


Figure 3.5.20. Density of nuclei formation as a function of work applied to polypropylene melt. Dashed “averaging” line is drawn by us. [Adapted, by permission, from H. Janeschitz-Kriegl, E. Ratajski, M. Stadbauer, *Rheol. Acta*, **42**, 355 (2003)].



Figure 3.5.21. Formation of ultra-fine fibers in the capillary flow of a two-component blend. Scanning electron microscope photograph of an extrude transversal section of the polyoxymethylene/copolyamide blend. [Adapted, by permission, from M.V. Tsebrenko, G.P. Danilova, A.Ya. Malkin, *J. Non-Newton. Fluid. Mech.*, **31**, 1 (1989)].

result in the appearance of various structures. One of the interesting examples is formation of a system of ultra-fine fibers of one polymer in the matrix of the other (Fig. 3.5.21).¹⁰⁸ It is possible that it is related to the viscosity ratio of both components. The criterion of phase inversion in shearing is the equality of viscosities of both components in a blend.¹⁰⁹ Generally speaking, the observed picture of structure formation is multi-faceted and depends on numerous rheological and technological factors.

The conformational transition gives us a possibility to obtain material with fully extended chains. It promises to produce material with outstanding mechanical properties. The theoretical possibility was proven experimentally.¹¹⁰ This approach was realized in

The mechanism of influence of deformation on the kinetics of crystallization of polymers is related to nucleation promoted by flow. The crystallization process relies on two components: nucleation and growth of crystals. Deformation influences the rate of the nucleation due to orientation of macromolecular chains. It was experimentally proven that the density of nuclei is directly related to the mechanical work applied to melt (Fig. 3.5.20).¹⁰⁶

The morphological aspects of the deformation-induced phase transition are worth mentioning. Shearing may lead to phase separation and to phase inversion in multi-component systems. The latter is especially frequent in blends of immiscible polymers. Direct microscopic observations confirm that morphological phase inversion is caused by shearing.¹⁰⁷ The phase separation of the components in polymer blends during shearing of a blend may

some technological processes, and polymeric materials were obtained with strength and Young's modulus approaching their theoretical (extremely high) limits.

The following consequences of shearing, related to the phase transitions, take place:

- increase in the equilibrium phase transition temperature
- decrease in the induction period of the isothermal crystallization
- increase in the degree of orientation of macromolecular chains
- decrease in the nuclei size of a new phase
- increase in the formation rate of the new phase nuclei
- phase separation and/or phase inversion in multi-component systems
- formation of oriented structures.

All these effects are more or less pronounced for different deformation modes (for example, for tension or shear), though they are always present. The scale of these effects may reach several decimal orders and deformations may induce the above-listed processes, which in turn may lead to their influence on the rheological properties of matter. It is also interesting to mention that shearing may result in a post-flow effect of crystallization. One reason for this effect is the acceleration of nucleation.¹¹¹

3.6 LIMITS OF SHEAR FLOW – INSTABILITIES

3.6.1 INERTIAL TURBULENCY

The term “*limits of shear flow*” in the title of this section should be understood as the limit of steady shearing before flow instability of any type appears. At higher velocities (or shear rates) shear flow continues but in an unstable mode.

Instability is the phenomenon of large and uncontrolled disturbances induced by a slight and accidental cause. The most general type of instability, common to all liquids, is known as the *Reynolds* or *inertial instability*. The origin of this phenomenon, first found by Reynolds,¹¹² is inability in suppressing occasional flow fluctuations by viscous dissipation. It means that at sufficiently high velocities inertial forces become large and exceed viscous forces. At low velocities, viscous forces damp any stream fluctuations, therefore streamlines are smooth and parallel layers of liquid slip over each other. This type of flow is called *laminar*. At higher velocity, fluctuations increase due to inertial forces and become more pronounced. Above some critical (threshold) velocity, the fluctuations cannot be damped by viscous resistance. As a result, streamlines become irregular and the pathway of any individual particle in the stream appears chaotic. Such type of flow is called *turbulent*, and the transition to turbulent flow results in much higher energy dissipation than in smooth laminar flow.

The criterion of appearance of inertial turbulence defines a threshold value of the dimensionless ratio of measures of inertial and viscous forces. The *Reynolds number*, Re , is such a criterion and it is expressed by:

$$Re = \frac{VD\rho}{\eta} \quad [3.6.1]$$

where V is the velocity, D is the characteristic geometrical size (e.g., diameter of a capillary as in Eq. 3.6.1; radius of a round tube or the distance between two parallel plates or

other geometrical factor can be used in the definition of the Reynolds number), ρ is density, and η is viscosity.

The critical value of the Reynolds number, corresponding to the transition from steady (*laminar*) to chaotic (*turbulent*) flow, is close to 2,300.

Inertial instability is very important for flows of numerous liquids, such as, water, low viscous oil products, and so on. Turbulent flow is a great field of studies, and a lot of original publications and monographs are devoted to this subject. However, inertial (or Reynolds) turbulence is not primarily a rheological phenomenon, though it can also be observed for non-Newtonian liquids. This phenomenon is important for weak (dilute) solutions and suspensions (for example, blood flow). In all these cases it is necessary to re-define the value of the Reynolds number, taking into account the shear rate dependence of the apparent viscosity entering the expression for Re.

3.6.2 THE TOMS EFFECT

For liquids of all types the dependence of flow resistance (or energy dissipation) on flow rate in a laminar flow is commonly expressed by the Hagen-Poiseuille law:¹¹³

$$Q = \frac{1}{\eta} \frac{\Delta p \pi R^4}{8L} \quad [3.6.2]$$

where Q is the flow rate, Δp is the pressure drop, η is viscosity, R and L are the radius and the length of a capillary, respectively.

In publications and applied work on fluid dynamics, some other form of the Hagen-Poiseuille law is preferred. It is based on the dimensional variables. The dependence of the coefficient of friction, λ_R , on the Reynolds number is defined as:

$$\lambda_R = \frac{\Delta p}{0.5 \rho V^2 L} \frac{R}{R} \quad [3.6.3]$$

Then, the Hagen-Poiseuille law is presented as

$$\lambda_R = \frac{16}{Re_R} \quad [3.6.4a]$$

where the characteristic geometrical size in the Reynolds number is R but not D , unlike in Eq. 3.6.1. The physical meaning of both dimensionless variables, Re_R and λ_R is not changed if the diameter of a tube, D , is used as a characteristic geometrical factor, but not the radius. However, the numerical coefficient in the dependence $\lambda(Re)$ appears different, and Eq. 3.6.4a is changed to the following formula (if D but not R is used as a geometrical factor for the coefficient of friction and the Reynolds number):

$$\lambda = \frac{64}{Re} \quad [3.6.4b]$$

The dependence $\lambda(Re)$, as expressed by Eq. 3.6.4b, is shown in Fig. 3.6.1 and marked by the letters H-P. The physical reality of this dependence was repeatedly confirmed by numerous experiments carried out for different liquids. It is illustrated by points that are related to both Newtonian (open circles) and non-Newtonian (solid circles) liquids. It is worth mentioning again that this dependence is the same for liquids of different

types. At the Reynolds numbers exceeding the critical threshold, $Re^* \approx 2,300$, the coefficient of friction begins to increase; this is transition zone (from laminar to turbulent regime). At the second decreasing branch of the $\lambda(Re)$ dependence, marked by the letter B, a well developed turbulent regime of flow exists. The $\lambda(Re)$ dependence in turbulent flow is described by very common equation, known as the *Blasius rule*:¹¹⁴

$$\lambda = \frac{0.3164}{Re^{0.25}} \quad [3.6.5]$$

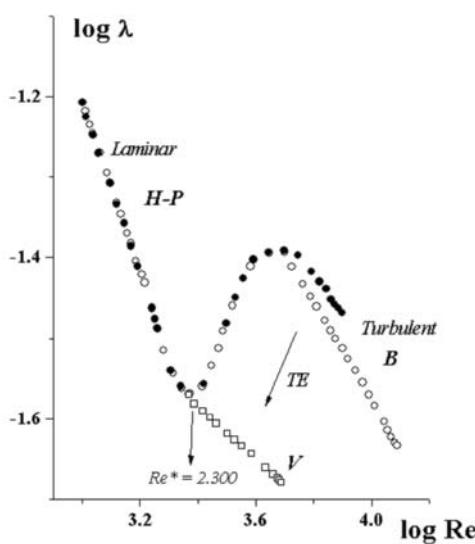


Figure 3.6.1. Dynamic resistance as a function of velocity (in dimensionless variables vs. Re) in flow through tubes. Open circles – Newtonian liquids; dark circles – non-Newtonian liquids; Squares – dynamic resistance due to the Toms effect. H-P – the Hagen-Poiseuille law; B – the Blasius rule; V – the Virk asymptote; TE – the Toms effect – decrease in dynamic resistance.

additives are polymers, and their amount does not exceed 100 ppm.¹¹⁷

There are two main classes of liquids to which the Toms effect applies: water (and therefore water-soluble polymers, such as polyoxymethylene, polyacrylamide, some natural polymeric substances are used) and oil products and some synthetic polyolefins.

The decrease extent of flow resistance depends on many factors, including concentration of additive, its chemical nature, temperature, and so on.¹¹⁸ However, there is a limit of drag reduction by the Toms effect. This limit is shown in Fig. 3.6.1 and marked by the symbol V. The Toms effect causes disappearance of the transition zone on λ vs. Re diagram and the shift of the $\lambda(Re)$ dependence in turbulent zone from B to V line in Fig. 3.6.1. This limiting curve corresponding to the maximum of drag reduction (line V) is called the *Virk asymptote* and it described by the equation:¹¹⁹

The Blasius rule is an empirical generalization of numerous experimental data obtained by different researchers for various liquids. It is an equivalent of the Hagen-Poiseuille law for a turbulent regime of flow. The coefficients of dynamic resistance in turbulent flow are much higher than in laminar flow. This is explained by more extensive dissipative losses in chaotic movement of liquid particles in comparison with regular displacement of layers in the laminar regime of flow.

Experimental data for non-Newtonian liquids in transient and turbulent regimes are very close to the generalized regularities found for Newtonian liquids if the convenient definitions for λ and Re are chosen.¹¹⁵

Toms¹¹⁶ showed that very small amounts of additives, dissolved in liquid, can suppress turbulent flow, or at least decrease turbulent losses to a great degree. This effect, known as the *Toms effect*, sometimes is called *drag reduction*. These

amounts of additives, dissolved in liquid, can suppress turbulent flow, or at least decrease turbulent losses to a great degree.

This effect, known as the *Toms effect*, sometimes is called *drag reduction*. These

$$\lambda = \frac{2.36}{Re^{0.58}} \quad [3.6.6]$$

The origin of the Toms effect is still the subject of intensive discussion. However, the common opinion is that the Toms effect is related to the elasticity of liquid caused by adding polymer to water (or an oil product) and, possibly, the crucial factor is the extensional (or elongational) viscosity of such solutions. It is thought that the turbulent losses are related to existence of multi-frequency oscillations superimposed on the main stream. Every mode gives its own input to dissipative losses. Then, it can be suggested that the decrease in turbulent losses due to the Toms effect can be explained by oscillations at some modes that do not dissipate but continue because these oscillations become elastic.

The Toms effect leads to a decrease in the flow resistance, which can be as high as 75%. This is a considerable change, and it was reasonable to search for its different applications. The most likely applications include increase in pumping rate of water and oil products in transportation through pipelines, or surface coating of sport boats and torpedoes by polymer additives in order to decrease resistance of their movement in water and consequently to increase their speed. The Toms effect favors the stability of liquid streams, and thus the presence of a small amount of polymer additive in water permits increase of the length of a jet from fire-pumps. The Toms effect was also applied to investigation of chemical reactions and physical transformations of dilute solutions.¹²⁰

3.6.3 INSTABILITIES IN FLOW OF ELASTIC LIQUIDS

3.6.3.1 Dynamic structure formation and secondary flows in inelastic fluids

Instability in flow of fluids does not necessarily lead to the formation of chaotic patterns. In many cases, self-organization, appearance of shear-induced structure and/or secondary flows can take place. The effect of the flow-induced crystallization (i.e., appearance of three-dimensional order) has been described in Section 3.5.3. Below, we will concentrate mainly on dynamic phenomenon not related to phase transitions, though there is no well defined boundary between different types of structurization in flow.¹²¹

The formation of the Taylor cells in flow between two rotating coaxial cylinders is a well known effect of dynamic shear-induced structure. One can expect that fluid elements placed between coaxial cylinders move along circumferences when cylinders rotate with different speeds. It is so called Couette flow. This suggestion is the base of rotational viscometry (see Section 5.3.2). Meanwhile at some relationship between speeds of rotation, streamlines form closed figures – cells, as shown in Fig. 3.6.2. These are so called *secondary flows*, which organize streamlines in the planes perpendicular to the direction of the main flow.

This phenomenon is due to the centrifugal (inertial) forces which push a liquid from the inner cylinder towards the outer. This type of flow pattern and its theory were proposed first by Taylor¹²² and then developed by other authors who discussed different kinds of rotational motions. When a stability threshold is overcome, inertial toroidal roll cells appear. Their height, h , is roughly equal to the gap clearance between the cylinders, i.e., the difference ($R_2 - R_1$). The term "instability" must be accepted here with certain accuracy; it only means that there are some secondary effects superimposed on the main stream. Meanwhile, these secondary streams can be quite stable in time and space.

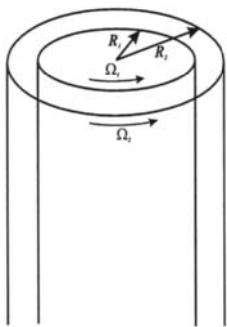


Figure 3.6.2. Taylor-Couette instability – formation of cells.

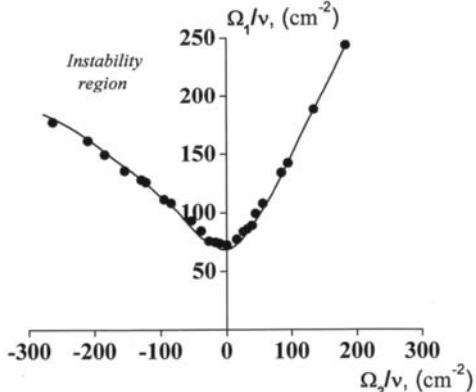


Figure 3.6.3. Limit of stability in formation of Taylor-Couette cells.

Since the Taylor-Couette instability is the consequence of inertial forces, it is determined by a definite relationship between centrifugal (as a measure of inertial effects) and viscous forces. This relationship is expressed by the dimensionless value called the Taylor Number, Ta , which is an analogue of the Reynolds Number by its physical meaning. The Taylor Number is expressed as

$$Ta = \frac{4\Omega^2 R^4}{v^2} \quad [3.6.7]$$

where Ω is the frequency of rotation, R is the average radius of coaxial cylinders, and v is the kinematic viscosity (Newtonian viscosity divided by density). The vortex structure (Taylor-Couette cells) becomes possible if the Taylor number exceeds some critical value Ta^* , which increases with the increase of the Ω_1/Ω_2 ratio,¹²³ while the minimum value of Ta^* is close to 1700.

The general "curve of stability" is shown in Fig. 3.6.3. This curve separates regions of stable and secondary flows. One can see that the experimental points perfectly correspond to the theoretical threshold curve.

The Taylor-Couette cells are also formed in a Bingham viscoplastic media¹²⁴ as well as in the flow of two immiscible viscous fluids.¹²⁵

It is interesting that cells are multiplied with the increase of the Reynolds Number and finally the laminar flow, though complicated with enhancing secondary flows, transforms to the turbulent regime of flow.

3.6.3.2 Secondary flows in the flow of elastic fluids

Cells of the Taylor-Couette type can appear in flow of elastic fluids. Systematic studies of the Couette flow of elastic liquids showed that cells are also formed in these liquids. It is possible to observe a continuous transition from the inertial to elastic instability by controlling rheological properties of a fluid.¹²⁶ Different types of coexisting cells of various sizes were observed in the flow of elastic liquids.¹²⁷

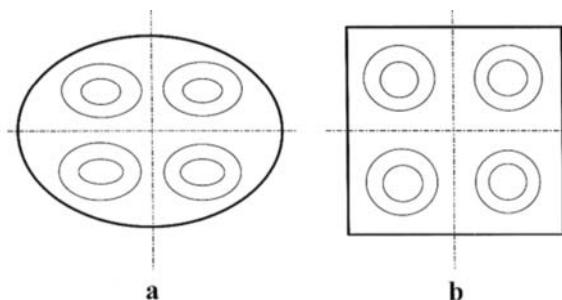


Figure 3.6.4. Secondary flows in channels of elliptical (a) and square (b) cross-sections. Main stream is directed perpendicularly to the plane of a drawing.



Figure 3.6.5. Secondary flows in sudden contraction – transition from a cylinder to a small diameter capillary.

conditions is defined by the Deborah number, De , which is the ratio of characteristic internal (relaxation) and external (rate of deformation) times. The Deborah number in rotational flows of an elastic fluid characterized by a single relaxation time is determined as

$$\text{De} = \frac{2\Omega_1 \lambda (1 + \varepsilon)^2}{(1 + \varepsilon)^2 - 1} \quad [3.6.8]$$

where Ω_1 is the frequency of rotation of the inner cylinder ($\Omega_2=0$) in the Couette flow, ε is the dimensionless gap defined as

Sometimes, the appearance of secondary streams in flow of an elastic liquid is considered as the consequence of the second normal stress difference. Though these stresses are not large, they are thought to be responsible for the development of elastic-type secondary flows during flow of a liquid through non-round channels.¹²⁸ Such secondary flows look as shown in Fig. 3.6.4 for a channel of an elliptical¹²⁹ (case – a) and square¹³⁰ (case – b) cross-sections.

Elastic instability can occur in different geometries of flow. So, effects of this type were investigated in the cross-channel flow,¹³¹ which can result in a steady asymmetric state even when flow takes place in perfectly symmetric geometry.¹³²

Secondary flows are also observed in flows through channels with a sudden contraction – for example in the transition region from a round cylinder to a small diameter capillary (Fig. 3.6.5). Also, it was proven (by both, numerical and experimental methods) that the second normal stress difference is the driving mechanism of secondary flows in tapered channels.¹³⁴ Besides, the second normal stress difference can be responsible for the edge fracture of viscoelastic liquids and suspensions (such as lubricating grease and toothpaste) in circular flow of a liquid between a cone and plate or two parallel plates.¹³⁵

It was shown that a regular dynamic structure can be observed in the flow of different elastic liquids. The quantitative measure of the critical conditions

$$\varepsilon = \frac{R_2 - R_1}{R_1} \quad [3.6.9]$$

Definition of R_1 and R_2 is shown in Fig. 3.6.2 and λ is the relaxation time.

The Reynolds number in all studies devoted to instability in elastic fluids was very low, less than 7×10^{-3} ; this is four orders of the magnitude less than the critical value corresponding to the onset of the centrifugal instability. So, the Taylor numbers in all cases were several orders less than the above-mentioned critical value of Ta^* . It means that this effect has nothing in common with the inertial mechanism, but is completely governed by the elasticity of a fluid.

It was found that there is a critical Deborah number De_{cr} (or, equivalently, the critical Weissenberg number, Wi_{cr}) equal to 35.5, which is responsible for the onset of instability. The critical Weissenberg number, Wi_{cr} depends on the gap clearance between coaxial cylinders, and according to Larson,¹³⁷

$$Wi_{cr} = 5.9 \varepsilon^{1/2} \quad [3.6.10]$$

Secondary flows of the elastic nature can be observed not only in polymeric systems but also in so called worm-like micellar colloids,¹¹⁹ though the term Taylor-Couette instability is frequently used for these structures. Mean-

while, the origin of these cells is definitely elasticity but not inertia of a medium and can be connected with the inhomogeneity of normal stresses along the direction of the velocity gradient in the Couette flow.¹³⁶

In concentrated solutions and polymer melts, other types of instabilities occur much before the onset of the inertial turbulence is reached. Indeed, their viscosity is very high and the denominator in the expression for the Reynolds Number is large. As a result, it is impossible to reach high values of Reynolds Number, close to the above-mentioned critical value, at any real velocity.

Hence, the appearance of unstable regimes of deformation for non-Newtonian polymer melts and concentrated solutions at high shear rates is not related to the inertial turbulence but has other physical reasons. In fact, different kinds of irregular flow, or instabilities, in the flow of polymer substances have been described, and generally speaking they are related to viscoelastic nature of deformation of these materials.¹³⁷

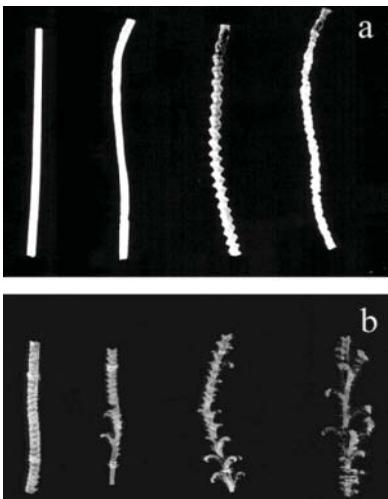


Figure 3.6.6. Typical polymer extrudates obtained at different shear rates (increasing from left to right) – transition from smooth stream to unsteady regimes of deformations. a: polyethylene; b: polyvinyl chloride. (Photographs were made in laboratory of Polymer Rheology, Institute of Petrochemical Synthesis of Academy of Sciences.)

Several examples of the ordinary sequence of irregularities developing with the increase of flow rate of industrial grade polydisperse polymers, pushed through a cylindrical channel (capillary, die) are shown in Fig. 3.6.6 (flow rate is increasing from left to right).

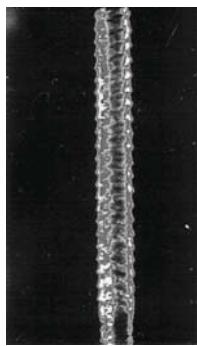


Figure 3.6.7. Small-scale screw-like surface defects – start of development of the unsteady flow of a polymer melt. Low density polyethylene.

Instabilities appear initially as the surface defects of an extrudate. The unsteady flow is noticed firstly in the form of small-scale surface defects and as a result, extrudate surface becomes matte. According to its look this effect sometimes is called "sharkskin". The most severe form of the sharkskin effect is the appearance of small-scale regular (periodical) thread-like or screw-type defects on the surface of a jet (Fig. 3.6.7).

In many cases instability of the sharkskin type in flow of polymer melts appears at stresses close to 0.1 MPa, though the exact limit and severity of the effect depend on the nature of a material and (to some degree) on the smoothness of a channel surface and the material which it is made from.¹³⁸

Appearance of these small-scale defects has negative consequences for the quality of industrial products such as films, which loose their gloss and brilliancy due to surface defects, wire insulation and others.

The sharkskin effect is believed to initiate at the die exit. The origin of sharkskin is definitely related to a special dynamic situation near the exit section of a channel. Indeed, the sharp edge of a channel near its exit is a singularity and transition from a parabolic velocity profile inside a channel to a flat profile, which occurs right after the exit from the channel. The rearrangement of the velocity profile near the exit is quite evident and was well documented by visualization of a stream. Optical observations confirmed that small pulsations are visible in the exit zone with the same frequency as surface defects of the extrudate,¹³⁹ whereas flow along the whole length of a capillary stays stable and is not influenced by small-scale instabilities of the sharkskin type.

Stability of a stream along the whole channel in spite of the appearance of sharkskin (related to the channel exit) allows one to measure the apparent viscosity in the range of stresses corresponding to this type of instability.

Sometimes the origin of periodic ("sharkskin-like") defects on the surface stream is related to cyclic generation of wall slip at the tube exit.¹⁴⁰ High-speed video microscopy technique demonstrates that cohesive failure downstream of the exit accompanies each sharkskin cycle while surface treatment can initiate strong slip and suppress sharkskin defects.¹⁴¹

The stress distribution near the exit section of a channel was examined by means of the technique of flow birefringence, and it was confirmed that not only shear but also tensile stresses appear close to the point of singularity.¹⁴² The following qualitative picture can clear up the origin of small-scale surface defects of an extrudate. When a melt is pushed out of a channel, the stream is hindered at the outlet section of the die. Meanwhile the central part of a stream continues to move forward and pulls the other outer layers of a liquid. When this pulling force becomes high enough the adhesive contact between a melt and a wall is broken, and the material is detached from the die. This process is repeated periodically and it leads to periodic pulsations or oscillations of the surface defects. The appearance of the small scale defects is definitely related to stress conditions at the exit edge of a die: some extra energy is necessary for tearing a flowing matter off a solid sur-

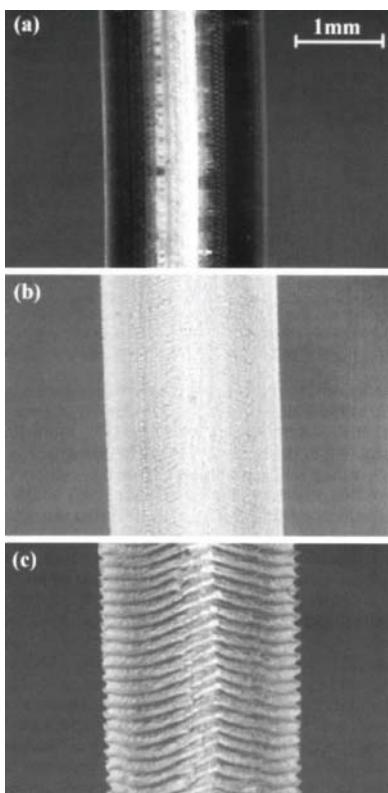


Figure 3.6.8 Developing of surface defects in extrusion. Velocity of flow increases from top to bottom. a - smooth surface; b - loss of gloss; c - sharkskin. [Adapted, by permission, from E. Miller, J.P. Rothstein, *Rheol. Acta*, **44**, 160 (2004)].

For linear polyethylene this stress is of the order 0.1 - 0.2 MPa.

A promising technological method of excluding sharkskin defects is related to adding some additives to polymer melt which create coating at the die wall and induce slip. This method was proposed, for example, for extrusion of low-density polyethylene. Fluoropolymer processing additives were effectively used to eliminate sharkskin surface defects. It was proven that these additives adsorb first in the entrance region of the die and then migrate towards the capillary exit where they suppress sharkskin defects.¹⁴⁶

It was noted that any tendency to slip at the die wall for the melt near the exit will reduce the acceleration of the surface layer and so reduce the stress level in that layer and so the severity of any rupture.¹⁴⁷

Bearing in mind the slip conception, the role of surface properties of the die becomes important. This is illustrated by Fig. 3.6.9, which clearly shows that the critical shear stress strongly depends on surface properties of a material used for preparing a die.¹⁴⁸

face, this energy is stored in the form of elastic deformations. After leaving a tube this energy is released and it results in the periodical swelling of a jet.

As a result of numerous visual observations and calculations, it was suggested that the mechanism of sharkskin is the *surface rupture under tensile stress* acting at the edge of a channel: periodic oscillations appear as the result of material rupture when this stress reaches some critical level.¹⁴³ Indeed, it was shown that small traction zones appear on the surface of an extrudate, and the dimensions of these zones is of the order of magnitude of sharkskin amplitude. So, we can think that the main reason for the sharkskin effect is rubber-like behavior of a melt near the die exit and cracks which appear perpendicular to the flow direction. They are due to elongational (normal) stresses created at the die exit and stored elastic energy is responsible for crack creation.

The appearance of the sharkskin effect is not a threshold effect but develops continuously. Fig. 3.6.8 illustrates the main stages of formation of regular surface defects.¹⁴⁴ It was noted that the waviness length and amplitude of teeth is a monotonous function of the shear stress,¹⁴⁵ though it is possible to estimate the critical stress corresponding to the appearance of slight visual effects. It is reasonable to think that the loss of gloss means that the order of magnitude of the defects becomes of the order of the wavelength of visible light, i.e. 0.4 - 0.8 μm .

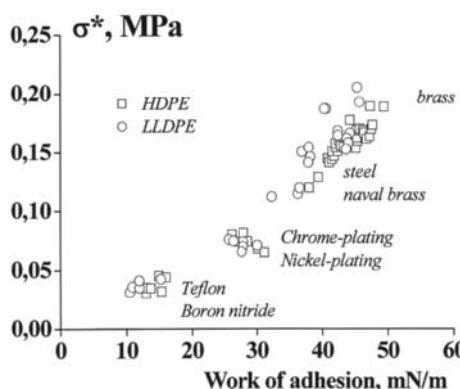


Figure 3.6.9. Influence of a surface properties on the critical shear stress corresponding to the sharkskin effect. [Adapted, by permission, from H.J. Larrazabal, A.N. Hrymak, J. Vlachopoulos, *Rheol. Acta*, **45**, 705 (2006)].

An increase in the flow velocity and corresponding stresses leads to the transition from sharkskin defects to large-scale periodicity of surface defects. They can have a very impressive effect (Fig. 3.6.10).

Different terms were used to describe this phenomenon: fluid wraps, fringes, rings, collars, surface cracks and so on. In all these cases, it is possible to point out to the exit section of a die as the origin of these defects.

An attempt to increase the speed of flow of monodisperse polymer melts leads to the transition from regular gross scale to irregular defects. They may have different appearances. The origin of these gross scale defects is attributed to peculiarities of deformations *inside a die* or even at the *inlet section* of the die.

When a monodisperse polymer melt is extruded through a die, the sliding of material along the solid wall of a channel begins at certain shear stress, σ_s . This effect was mentioned in Section 3.2.1 and it is known as *spurt*. The origin of spurt is attributed to *liquid-to-rubber transition* such as observed at high frequencies of oscillations (see Section 2.7.2), i.e., to the quasi-solidification (hardening) of a melt in a near-wall layer at high deformation rates.¹⁴⁹ It means that the lifetime of intermolecular contacts becomes longer than the characteristic deformation time (reciprocal shear rate) and the polymer melt behaves as a quasi-stable rubbery network. As a result, highly stressed boundary layers of material lose fluidity and adhesive contacts between polymer and wall is broken and the material begins to slide along the wall. Alternatively, cohesive breaks can happen because the strength of both is similar.

Existence of wall slip is accompanied by strong surface charge formation ("tribological effect") that is characteristic for friction of a dielectric material moving along metal; the electrical charge is a strong function of apparent shear stress.¹⁵⁰

It is interesting to note that critical shear stress, σ_s , corresponding to transition from flow to spurt does not practically depend on the molecular mass of the polymer (Fig. 3.6.11) and/or temperature, i.e., it does not depend on the viscosity of melt.

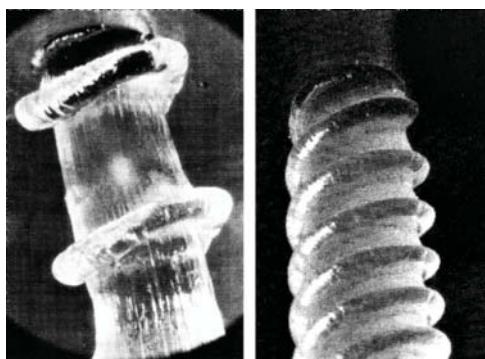


Figure 3.6.10. Large-scale periodic defects of the extrudate. [Adapted, by permission, from N. El Kissi, J.-M. Piau, T. Toussaint, *J. Non-Newton. Fluid. Mech.*, **68**, 271 (1997)].

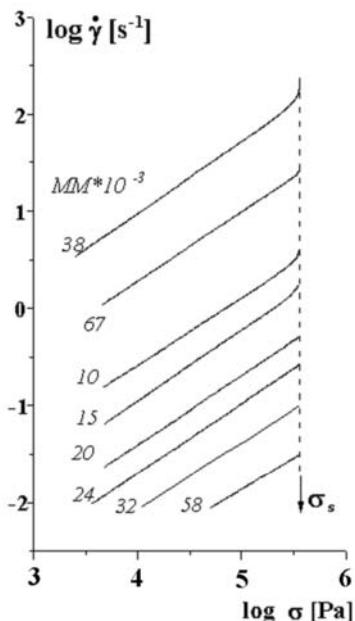


Figure 3.6.11. Flow curves and spurt stress for polybutadienes of different molecular mass (shown on the graph). [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, Yu. G. Yanovsky, E.K. Borisenkova, B.V. Yarlykov, G.V. Berezhnaya, V.P. Shatalov, V.G. Shalganova, V.P. Yudin, *Vysokomol. Soedin.* (Polymers in Russian), **14A**, 2425 (1972)].

sliding, known as the stick-slip phenomenon, leads to the appearance of periodical regular sequences of distorted and smooth parts on the surface of extrudate and it is accompanied by periodic fluctuations of velocity (Fig. 3.6.12) and instant output.

This effect is attributed to the behavior of flowing material on solid surfaces. Indeed, direct measurements of velocity profiles (made by the Doppler velocimetry method) confirmed that a classical velocity profile in the smooth part of the flow curve of high-density polyethylene is observed while strong macroscopic wall slip is documented for upper part of the flow curve.¹⁵² It is worth adding that the existence of the surface slip is now a well documented phenomenon.¹⁵³

Typical level of shear stresses responsible for appearance of stick-slip instabilities in capillary flow is the same as the spurt stress for flexible-chain polymer melts, i.e., it is about 0.3 MPa (compare with data in Fig. 3.6.9 where it is seen that sharkskin effect appears at lower stresses). Frequency of oscillations can be very different varying from 2-3 till 20-30 per second.

The stick-slip phenomenon is directly related to the existence of *multi-valued flow curves*, or hysteresis loops as shown in Fig. 3.6.13. This phenomenon was observed in various polymers, including high-density polyethylene, polybutadiene, polyisoprene, etc. The

Figure 3.6.12. Velocity fluctuation (at the axis of channel) during stick-slip regime of capillary flow. [Adapted, by permission, from L. Roberts, Y. Demay, B. Vergnes, *Rheol. Acta*, **43**, 89 (2004)].

For many flexible-chain polymers (such as polybutadiene or polyethylene) the spurt shear stress, σ_s , is close to 0.3 MPa. However σ_s is not the universal constant. More detailed analysis showed¹⁵¹ that there is a correlation between the rigidity of molecular chain and the σ_s values. It was found that for rigid-chain polyphosphazenes σ_s can be as low as 0.009 MPa.

Spurt is not typical of melts of industrial polydisperse polymers, though the phenomenon of transition from flow to sliding or periodic sliding is very general for all polydisperse polymers. This periodic

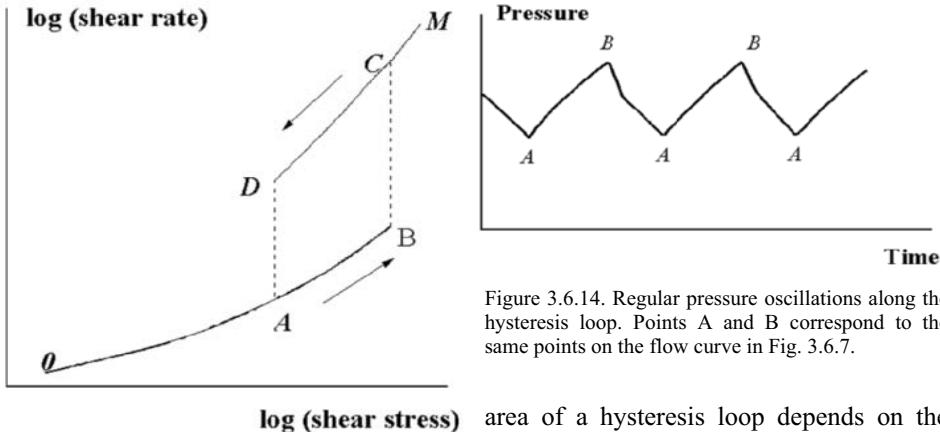


Figure 3.6.13. Hysteresis loop in measuring viscous properties of some polymer melts – multi-valued flow curve with spurt effect.

area of a hysteresis loop depends on the molecular mass and the polydispersity of the polymer. When apparent viscosity, or flow curve, is measured with a capillary viscometer, two principal modes of the experiment are possible. First, a pressure-controlled regime can be set. In this case, the pressure is constant and the flow output (or calculated shear rate) is measured. When pressure is increased, measured output follows curve branch 0AB. At the point B spurt happens, accompanied by jump to point C. Then, the points of the apparent flow curve lie on the CM branch. If the pressure is decreased beginning from the point M, the points on the apparent flow curve move along the upper branch MCD, and rapid change to the lower branch happens from the point D to point A, followed by a decrease of the shear rate along the curve branch A0.

Periodic oscillations of instant output also take place in a rate-controlled situation, i.e., when a total (averaged) flow rate is constant. For example, this occurs when a piston pushes material through a large radius cylinder and then through a die at the end of a cylinder. The velocity and output oscillates between upper and lower branches of a flow curve, as shown in Fig. 3.6.13. The oscillations of pressure in extrusion of monodisperse polymers may happen in regular intervals, as shown in Fig. 3.6.14. There is a correlation between the points along the hysteresis loop and the measured pressure values.

In some cases, periodic oscillations look rather whimsical. For example, pressure oscillations appear at different shear rate ranges in a capillary flow and look as double oscillations loops (see Fig. 3.6.15).

The hysteresis effect accompanied by regular periodic oscillations of the instant output rate is related primarily to melt compressibility of material in a large volume cylinder before entering into a capillary ("capacity model"): ¹⁵⁴ the elastic energy of volume deformations is stored in a large volume and periodically released. The second condition necessary for appearance of a hysteresis loop in an apparent flow curve is a possibility of the stick-slip phenomenon and/or spurt at a certain critical shear stress.

The position of points on a hysteresis loop is directly related to the types of extrudate distortions. The stream is smooth in the 0A zone, small periodic distortions (or a sharkskin effect) appear in the AB zone. Gross extrudate distortions are typical of higher pressures.

Figure 3.6.14. Regular pressure oscillations along the hysteresis loop. Points A and B correspond to the same points on the flow curve in Fig. 3.6.7.

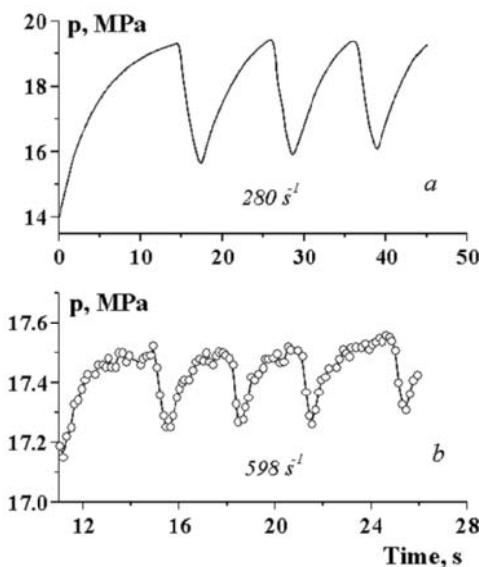


Figure 3.6.15. Double oscillation loops – pressure oscillations at two different shear rates in the capillary flow of linear polyethylene. a: main double-value zone on the flow curve (experimental points are omitted); b: secondary (high-shear rate) double value zone on the flow curve. [Adapted, by permission, from L. Robert, B. Vergnes, Y. Demay, *J. Rheol.*, **44**, 1183 (2000)].

As shown in Fig. 3.6.6 (the last samples on the right), the final stage of instability is the appearance of highly visible gross defects of different types. In the extreme cases a stream can even disintegrate into separate pieces. This stage of instability is called the *melt fracture*.

It can be thought that such gross effects are the consequence of rubbery deformations and elastic recovery after material leaves the channel and restrictions (applied by the solid walls of the channel) to the elastic recoil are removed. Ruptures of jet are caused by the large amount of elastic energy stored during deformations inside the channel.

At higher shear stresses or velocities, distortions become irregular and in limiting cases they result in the breakup of stream. Ruptures happen even inside a tube (channel) as was proven by direct observations.¹⁵⁶ In this experiment, black pieces were introduced into a white melt flowing through the capillary. Inner oscillations at low flow rates and discontinuous streamlines at high flow rates were clearly noticeable (Fig. 3.6.16).

It is interesting to mention that breaks occur along the channel axis, where shear stresses are absent. It suggests that these effects are caused by tensile stresses present at the die inlet. At high flow rates, deformation of material inside the channel becomes irregular. Possibly, the discontinuous flow lines first appear in the inlet sections of a channel at the corners near the entrance to the die, where the rearrangement of stream takes place and additional high shear and tensile stresses appear.

The transition from the steady flow regime to instability is clearly seen by direct optical observations and/or birefringence method (Fig. 3.6.17).



Figure 3.6.16. Deformations of stream inside a channel: oscillations of a stream correlated with periodical extrudate distortions; ruptures of a stream along the extrudate axis. [Adapted, by permission, from P.L. Clegg, in *Rheology of Elastomers*, Pergamon Press, 1958].

However, in some cases a smooth extrudate surface again appears at the upper branch of the "flow curve"; this is called *super-extrusion* and can be useful for increasing the output in processing of some polymers (for example, polytetrafluoroethylene).

Multi-valued flow curve can be also observed in a rather special case under a constant pressure condition if slip is built along half of the die wall. In this rather artificial situation, cyclic self-oscillations in capillary flow, accompanied with periodic changes in appearance of an extrudate, are observed.¹⁵⁵

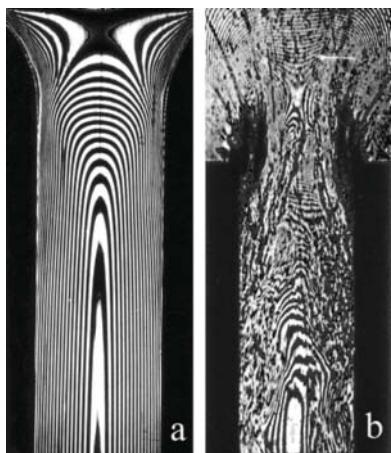


Figure 3.6.17. Birefringence pictures for steady (a) and chaotic (b) movement of polymer melt through a capillary. Polybutadiene. [Adapted, by permission, from G.V. Vinogradov, N.I. Insarova, V.V. Boiko, E.K. Borisenkova, *Polym. Eng. Sci.*, **12**, 323 (1972)].

The left picture demonstrates the regular stress distribution, whereas chaotic flow pattern with irregular variation of stresses is typical of instability regime (the right picture). Very strong stress concentration is evident in the inlet zone of channel (especially near the corners). The shear stress in inlet and outlet zones may achieve the critical value, whereas inside the die the shear stress at the wall may be substantially lower than its critical value. If the critical stress is reached at the sharp corners, the polymer passes into the rubbery state, its adhesion to the wall diminishes, and a local spurt occurs. As a result of the detachment of polymer from the walls, the acting stress decreases, the polymer relaxes, and then it begins to flow in the layer adjacent to the wall.

Then, in contrast to flow with the sharkskin effect, it is not useful to measure apparent viscosity or to apply the concept of steady flow (as well as to analyze dynamic problems of flow) in such situations, because in this case instability means that the real flow is absent.

It is possible to propose the following rough scheme of development of instabilities in the flow of viscoelastic polymer materials. First, *outlet instability* appears due to stress concentration at the outlet section of a die and its corners. It results in periodic small-scale defects. Then, with an increase in flow rate, oscillations spread inside a tube, leading to *surface (land) instability*, possibly in the form of spurt or stick-slip or other surface distortions. At last, *inlet instability* occurs at the entrance of the tube. Then it develops along the whole length of the die and demonstrates itself as the melt fracture.

As was discussed above, small scale disturbances (sharkskin) are dependent on the quality and material of the tube (or die), while the onset of gross defects is not influenced by the material of a die surface at all.¹⁵⁷

Obviously, instabilities of different types are related to the special surface effects and, at least in some cases, they are connected with wall slip of material. Three possible mechanisms of near-wall effects are discussed: an adhesive rupture inside a polymer melt, a cohesive failure and appearance of a lubricated layer at the wall.¹⁵⁸ It should be mentioned that adhesive and cohesive strength of polymeric materials are rather similar. Hence, whether it is an external or internal rupture it always depends on the nature of the surface material and the geometry of flow. Appearance of a lubricated layer is possible in flow of polymer solutions or polydisperse polymers: a low viscous solvent or low molecular mass fractions can migrate to the solid wall and stay there in the form of a very thin coating, sliding along this lubricated layer looks like wall slip.

It is also interesting to examine the flow regimes corresponding to a pressure gradient that is a little larger than the critical value. This is depicted in Fig. 3.6.18, where the die entrance is shown in the left part; and the die proper in the right part; the lower edge of the photograph corresponds to the middle part of the die along its length. With pressure gradi-

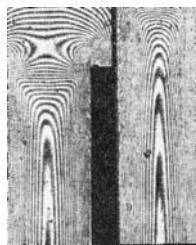


Figure 3.6.18. Optical fringe patterns during flow of polybutadiene in a rectangular duct under shear stress slightly above the spurt conditions. [Adapted, by permission, from G. V. Vinogradov, *Rheol. Acta*, **12**, 357 (1973)].

ents that create the flow pattern presented here, the ruptures in the flowing polymer extend over a limited zone adjoining the edges, and the random movement of the polymer takes place only in layers adjacent to the wall. As polymer lumps advance along the die walls, their internal stress is relaxed, and the distribution of interference bands of ever improving regularity appears near the walls.

The change in the slippage regime of the polymer – the movement of lumps of the polymer, which are randomly displaced relative to one another – explains the increase in the pressure gradient with increasing rate of flow under above-critical regimes of polymer movement in the die.

It should be emphasized that at sufficiently high pressure gradients and flow rates, a break in the continuity of the polymer occurs with a smooth entrance, as well. The sharp edges at the die entrance only facilitate this process but its origin is determined by polymer in the rubbery state undergoing a rupture when the deformation rates and stresses exceed certain critical values.

The transition from true flow to wall instability (regardless to its detailed mechanism) is evident from observation of capillary flow at high flow rates. However, there are two additional factors which prevent one from making definitive conclusions about wall slip: continuous input of the fresh material into a channel and the variation of stress conditions along the channel due to the hydrostatic pressure decrease from inlet to outlet.

It is possible to exclude both factors and to follow "pure" transition from flow to sliding. It is observed by imposing a continuous shear on a sample placed between a cone and a plate, where a homogeneous stress field exists (see Part 5, where the theory of viscometers of this type is considered). This instrumentation permits observation of slow dewetting from the solid surface. A sample does not slide along the solid surface at low shear stresses (or rates). An increase in the shear stress leads to separation of the sample from a solid wall, but it happens not just as the stress is applied but after some deformation or time of shear. This critical time, t^* , depends on the shear stress applied, as shown in Fig. 3.6.19. Hence, the *adhesive strength is time-dependent* and at stresses corresponding to melt fracture in capillary flow (marked by the horizontal bar in Figure 3.6.19) this critical time becomes instantaneous for an observer.

Regular surface defects or regular variations of the form of a stream formally do not correspond to the rigorous definition of instability as large and uncontrolled disturbances. However, physical reasons of both effects – superposition of elastic and plastic deformations at high stresses – are similar and there is a continuous development of increasing extrudate distortions. That is why all extrudate defects are considered together in this Chapter.

Indeed, all above discussed types of instabilities in flow of polymer solutions and melts are related to their viscoelasticity. Therefore, it is reasonable to introduce a dimensionless criterion, characterizing relationship between inherent relaxation properties of material and rate of deformation. This is the so-called the *Weissenberg number*, Wi^{159} determined as

$$Wi = \dot{\gamma}\theta \quad [3.6.11]$$

where $\dot{\gamma}$ is the rate of deformation, and θ is a characteristic relaxation time.

It can be suggested that the instability begins at some critical value of the Weissenberg number.¹⁶⁰ The exact numerical value of this threshold Weissenberg Number depends on the method of determination of the relaxation time.

The rubbery deformation, γ_r stored in flow is one of the possible alternatives of the Weissenberg number, Wi . If one defines $\dot{\gamma}$ as σ/η and θ as η/G , where G is elastic modulus, then the Weissenberg number can be presented by

$$Wi = \frac{\sigma}{G} \quad [3.6.12]$$

The ratio σ/G is elastic (rubbery) deformation. In this approximation the critical value Wi is equal to some critical value of rubbery (stored) deformation, γ_r , responsible

for the melt fracture effect. Different authors proposed that this critical value of γ_r lies between 3 and 7, and on average it is close to 5 units (500%). Possibly, this estimation is valid for polydisperse polymers and solutions, but γ_r (at the spurt stress) of monodisperse polymers is much less due to their high rigidity (high values of G), and for polymers of this type critical value of the Weissenberg number $Wi \approx 1$.

Using the Weissenberg number as the criterion of melt fracture reflects the general physical possibility of the event. However, the description of the real situation in treating the instability needs to apply a mathematical model of the rheological properties of material and to develop a rigorous analysis of the specific dynamic situation.

The theoretical analysis of the cell formation in elastic fluids is ordinary limited by low Weissenberg numbers. One can expect that cells can duplicate themselves with increase of Wi values, as occurs during transition to the Feigenbaum fractal chaotic structures. Indeed fractal approach was successfully applied to analyze the sharkskin effect.¹⁶¹ Such chaotic structures were observed in strong capillary flows, as shown, for example, in Fig. 3.6.17b.

3.6.3.3 Shear banding

Instability in rotational flows of some systems, primarily of worm-like micellar colloids, and also of polymer solutions, can express itself by *shear banding*, where the boundary of bands passes in the circumferential direction. It is shown in Fig. 3.6.20.

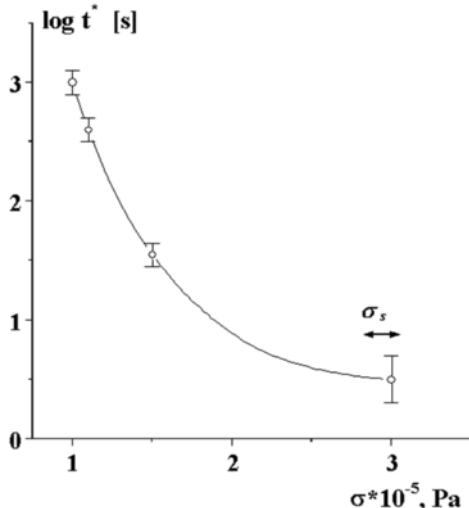


Figure 3.6.19. Stress dependence of time corresponding to the break of the adhesion contacts between the polymer melt and a solid wall. Polyisobutylene. MM=1*10⁵. T = 25°C. [Adapted, by permission, from A.Ya. Malkin, B.V. Yarlykov, *Mekh. Polym.* (Polymer Mech. – in Russian), #5, 930 (1978)].

During transition to the Feigenbaum fractal chaotic structures. Indeed fractal approach was successfully applied to analyze the sharkskin effect.¹⁶¹ Such chaotic structures were observed in strong capillary flows, as shown, for example, in Fig. 3.6.17b.

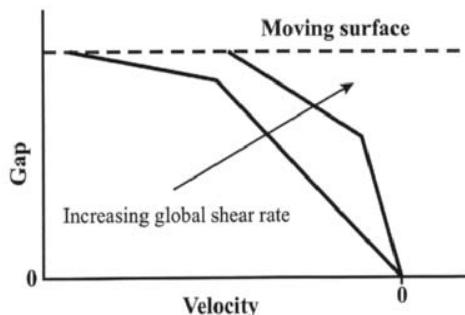


Figure 3.6.20. Velocity profile in flow of a fluid in the gap between stationary and moving surfaces after formation of shear bands.

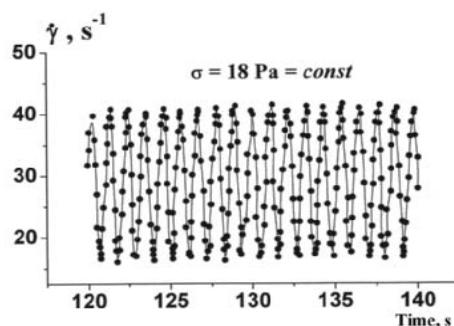


Figure 3.6.21. Self oscillations in shear banding formation (aqueous solution of cationic surfactant and Na-salicylate). According to Herle H., Fischer P., Windhab E.J., Langmuir, 21, 9051 (2005).

Physically, this effect is due to a separation of the initially homogeneous multi-component fluid into two parts with different rheological properties. The phenomenon of gradient banding is the most widely observed and studied for worm-like micellar (colloid) systems (see e.g., ref.¹⁶² discussing rheologically (and structurally) similar to polymer solutions). Moreover, micelles can be formed by polymeric substances, e.g., block copolymers.¹⁶³ The bands can contain different concentrations of a dispersed phase or can have different order of structure organization. Accordingly, they exhibit different flow properties leading to different velocity gradients, as shown in Fig. 3.6.20.

Usually, the phenomenon of shear banding is related to multi-valued flow curves of the type shown in Fig. 3.6.13. Then each band corresponds to lower or higher branches of a flow curve and consequently its properties are characterized by different viscosity. As a result the velocity distribution becomes as shown in Fig. 3.6.20.

Shear banding can be observed in a stationary mode and also can take place in an oscillatory mode, as shown in Fig. 3.6.21.¹⁶⁴ Similar periodic effects were observed by following the structure of shear bands along a hysteresis loop.¹⁶⁵ Periodic formation of shear banding can be related to an isotropic-nematic phase transition induced during shearing and after-shearing rest.¹⁶⁶

3.7 EXTENSIONAL FLOW

3.7.1 MODEL EXPERIMENTS – UNIAXIAL FLOW

Uniaxial extension is not easy to induce in some liquids. It is difficult to maintain the shape of a stream of low viscous liquid and stretch it while measuring its properties. Elongational flow can be observed for substances having high viscosity, such as honey or resin. Molten glass threads are convenient objects for creating elongational flow. However, the most popular and important materials for studying elongational flows are polymer melts or concentrated solutions. The ability to stretch and to form fine fibers or thin films is a very special rheological property of polymers, which is the basis of many technologies in the textile industry and in polymer processing. It is easy to imagine why polymeric substances can be stretched: uniaxial extension of polymeric substances leads to alignment of

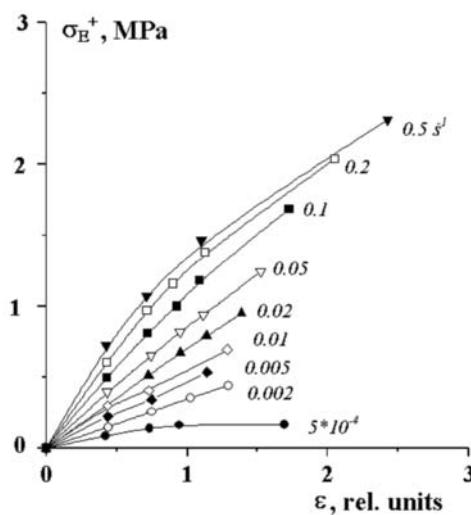


Figure 3.7.1. Stresses vs. deformations in uniaxial extension at different constant deformation rates. Polyisoprene. MM = 5.75×10^5 . 0°C. Deformation rates are shown on the curves. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, V.V. Volosevitch, V.P. Shatalov, V.P. Yudin, *J. Polym. Sci.: Polym. Phys. Ed.*, 13, 1721 (1975)].

deformations). The theory predicts (see Section 3.1.1) that the *Trouton law* (Eq. 3.1.6) is valid for such inelastic liquids.

In experiments carried out at constant deformation rates ($\dot{\epsilon} = \text{const}$) one could expect that the stress is also constant. However, the real case is quite different. Fig. 3.7.2 shows dependence of ratio $(\sigma_E/\dot{\epsilon})$ on time at different deformation rates. The values of the ratio $(\sigma_E/\dot{\epsilon})$ in Fig. 3.7.2 are normalized by their limiting value obtained at high deformations, and that is the elongational viscosity, η_E , at steady flow. The argument can be also treated as deformation, ϵ , because at $\dot{\epsilon}=\text{const}$, the deformation is proportional to time of elongation. The data presented in this figure were obtained at different temperatures and reduced to 25°C.¹⁶⁸

At first glance, the experimental results presented in Fig. 3.7.2 seem to contradict the Trouton equation because the ratio $(\sigma_E/\dot{\epsilon})$ is not constant but continuously increasing with the increase in deformation. However, one must be accurate in discussing this situation. Resistance to deformation increases, but it does not necessarily result in an increase of viscosity. Eq. 3.1.6 is related to a “pure” flow but the stretching of polymer melts consists of superposition of the elastic (recoverable or rubbery) deformations and flow (or plastic deformation). Then, the stress evolution with deformation of a polymer melt under extension must be treated as a behavior of viscoelastic body.

The theory of viscoelasticity is discussed in Chapter 2. The experimental results presented in Fig. 3.7.2 must be modeled to understand their significance.

For a linear viscoelastic material, the stress evolution in an uniaxial extension is expressed by

macromolecules and creates a dominating orientation of matter. It results in increasing resistance to further deformation of this stress-induced macromolecular structure.

All industrial polymers are polydisperse, but the rheological behavior of monodisperse polymers is easier to study.¹⁶⁷ This section is devoted to experimental results obtained in studies of uniaxial extension of monodisperse samples.

Stresses increase in uniaxial extension (see Fig. 3.7.1). Deformations in Fig. 3.7.1 are understood in the Hencky sense, i.e., $\epsilon=3$ corresponds to about 20-fold draw ratio.

The net tensile stress, σ_E , divided by the rate of deformation, $\dot{\epsilon}$, gives the ratio which is the *elongational viscosity*, η_E :

$$\eta_E = \frac{\sigma_E}{\dot{\epsilon}} \quad [3.7.1]$$

It is an elongational viscosity of “pure” liquids (which deform without storing rubbery

$$\sigma^+(t) = 3\dot{\varepsilon} \int_0^\infty \theta G(\theta)(1 + e^{-t/\theta}) d\theta \quad [3.7.2]$$

where $G(\theta)$ is the relaxation spectrum, measured, for example, at small-amplitude harmonic oscillation in a wide frequency range. This is the same relaxation spectrum used in treating experimental data in shear deformation. Similar to the rheological behavior in shear, extension is expressed by the same form of equation for stresses with change of a shear rate, $\dot{\gamma}$, to an elongational deformation rate, $\dot{\varepsilon}$, and the difference is in the coefficient 3, only. In particular, the limiting value of the expression for stress, σ , at $t \rightarrow \infty$ gives the Trouton viscosity, η_E , which equals 3η .

Dividing *tensile growth stress function*, $\sigma_E^+(t)$, by $\dot{\varepsilon}$, according to Eq. 3.7.2, one can expect the universal dependence of $\sigma_E^+(t)/\dot{\varepsilon} \eta_E$ vs. time. If this ratio is normalized with respect to its limiting value, which is the elongational viscosity, then the limit of the universal dependence of $\sigma_E^+(t)/\dot{\varepsilon} \eta_E$ and time should be equal 1. This is true for a model polymer liquid, as shown in Fig. 3.7.2. It means that this material can be treated as a linear viscoelastic liquid with a constant viscosity.

Fig. 3.7.3 presents results of direct measurements of the elongational viscosity at different deformation rates. It is seen that the elongational viscosity does not depend on the rate of deformation and it equals 3η .

The increase in the elongational viscosity at high deformation rates is sometimes considered as a necessary condition for stability of a stream being stretched. However, this is not so as seen from Fig. 3.7.3. High draw ratios can be reached without a noticeable increase in viscosity. A many-fold increase in the deformation rate does not lead to necessary growth of the apparent elongational viscosity.

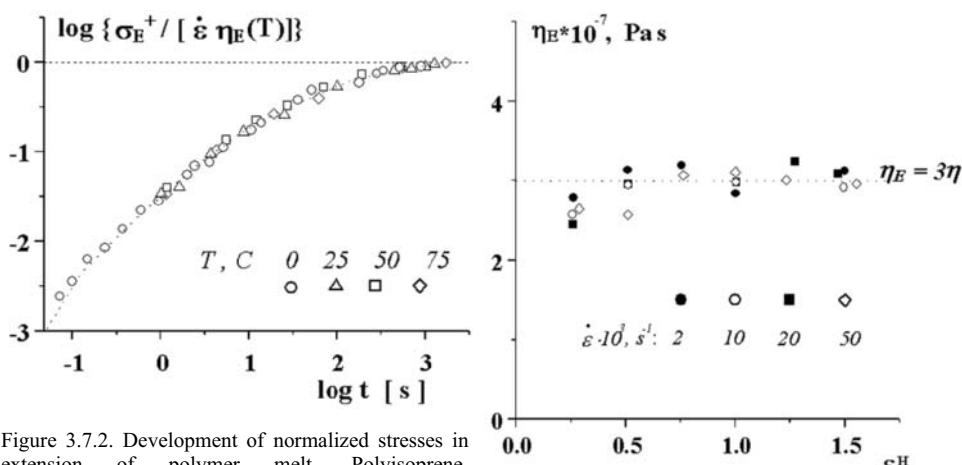


Figure 3.7.2. Development of normalized stresses in extension of polymer melt. Polyisoprene, $M=5.75 \times 10^5$. Initial experimental data obtained in the temperature range from 0 to 75°C are “reduced” to 25°C. The stress scale is normalized by the final value of steady-state viscosity. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, V.V. Volosevitch, V.P. Shatalov, V.P. Yudin, *J. Polym. Sci.: Polym. Phys. Ed.*, **13**, 1721 (1975)].

Figure 3.7.3. Measured elongational viscosity at steady-state flow at various deformation rates. Polyisoprene. $M=5.75 \times 10^5$. $T=25^\circ\text{C}$. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, V.V. Volosevitch, V.P. Shatalov, V.P. Yudin, *J. Polym. Sci.: Polym. Phys. Ed.*, **13**, 1721 (1975)].

The experimental results presented in Figs. 3.7.2 and 3.7.3 for monodisperse polymers as well as the constancy of their Newtonian viscosity in shear are not universal for real materials, such as commercial polydisperse polymer materials.

3.7.2 MODEL EXPERIMENTS – RUPTURE

Steady flow is possible up to some critical stress or shear rate level. What happens then on further extension? The material is ruptured above some critical stress or deformation rate level. This is predicted by a simple model of an *elastic liquid*.¹⁶⁹ If the rheological behavior of liquid is characterized not only by viscosity but also by a relaxation time, θ , then due to the effect of large deformations the elongational viscosity, η_E , as a function of deformation rate, $\dot{\varepsilon}$, is expressed as

$$\eta_E = \frac{\sigma_{11}}{\dot{\varepsilon}_{11}} = \frac{3\eta}{(1 + Wi)(1 - 2Wi)} \quad [3.7.3]$$

where

$$Wi = \theta \dot{\varepsilon} \quad [3.7.4]$$

is the Weissenberg number. It is the dimensionless ratio of the rate of deformation and rate of relaxation.¹⁷⁰

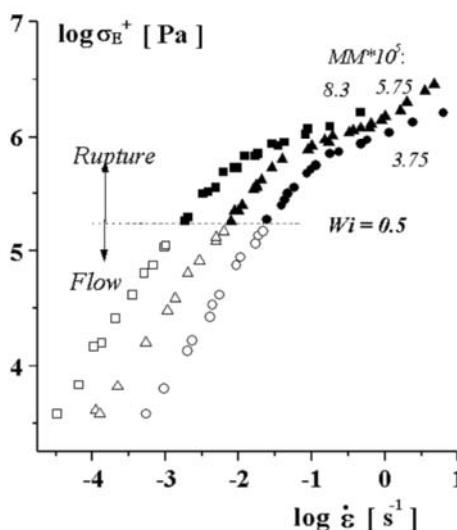


Figure 3.7.4. Limiting stresses (at steady flow – open symbols, or at rupture – solid symbols) as a function of deformation rate for polyisoprenes of different molecular mass (shown on the curves). Experimental points were obtained in the temperature range from -25 to 75°C. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, V.V. Volosevitch, V.P. Shatalov, V.P. Yudin, *J. Polym. Sci.: Polym. Phys. Ed.*, **13**, 1721 (1975)].

At large deformation rates, namely at $Wi \rightarrow 0.5$, the apparent elongational viscosity and consequently the normal stresses increase unlimitedly. This means that the rupture occurs before a steady state flow regime is reached. There is a critical value of the Weissenberg number separating domains of flow and stretching, which leads to rupture.

Fig. 3.7.4 shows dependencies of limiting stress values reached in elongation at different deformation rates. In the domain of low deformation rates, the limiting stresses are reached when the steady elongational flow regime is reached. These points correspond to constant values of elongational viscosity (that is why these limiting stresses are proportional to deformation rates). Regimes of steady flow are marked by open symbols in Fig. 3.7.4.

If the deformation rate is increased, the steady flow regime cannot be reached because the sample breaks before this state is attained. Then, the maximum (limiting) stress corresponds to the moment of rupture. The points corresponding to rupture are

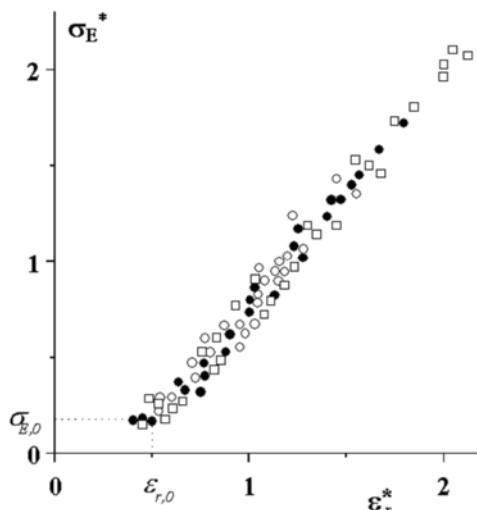


Figure 3.7.5. Relationship between stress and rubbery deformations at the moments of rupture reached at different rates of deformation. Solid circles – polybutadienes of different MM at different temperatures; Open circles – polyisoprenes of different MM at different temperatures; Squares – polybutadienes at 25°C in different liquid media (water and alcohols). [Adapted, by permission, from A.Ya. Malkin, C.J.S. Petrie, *J. Rheol.*, **41**, 1 (1997)].

unlimited stress growth in extension, indicating that steady flow is impossible. The experimental confirmation that the transition from open to solid symbols in Fig. 3.7.4 (the transition to unsteady extension and rupture) takes place at $Wi = 0.5$.

However, the extension cannot be carried any further. An increase in the deformation rate leads to growth of limiting (maximum attainable) stress, as shown in Fig. 3.7.4. There is universal dependence between this limiting (breaking) stress, σ_E^* , and the stored (elastic) deformation at the moment of break, ϵ_r^* . The latter, according to Eq. 3.7.5, is one of the possible interpretations of the Weissenberg number. This dependence is presented in Fig. 3.7.5 and it is expressed by the following linear relationship:

$$\sigma_E^* = \sigma_{E,0} + K(\epsilon_r^* - \epsilon_{r,0}) \quad \text{at} \quad \sigma_E^* > \sigma_{E,0}, \epsilon_r^* > \epsilon_{r,0} \quad [3.7.6]$$

where $K = 1.2$ MPa is an empirical constant; $\sigma_{E,0} = 0.18$ MPa and $\epsilon_{r,0} = 0.5$ are the parameters of the “transition point”, where flow becomes impossible and stretching causes breakup of a sample.

Fig. 3.7.2 demonstrates that the development of stresses in extension of polymer liquids is the consequence of their viscoelastic properties. Eqs. 3.7.3 to 3.7.6 confirm that elasticity plays the dominating role in extension of these liquids. The understanding of the rheological behavior of polymeric substances in uniaxial extension must be based on treatment of stress development as a result of their viscoelastic properties – superposition of elastic (rubbery) deformations and plastic flow.

solid symbols in Fig. 3.7.4. There is a point of transition from deformations regimes, at which stretching leads to a steady elongational flow, to regimes when stretching ends by rupture before steady flow occurs.

The location of transition from flow to rupture is important for understanding rheological behavior of viscoelastic polymer materials in a uniaxial extension.¹⁷¹ The most important experimental result concerning this transition is that it happens at a certain value of the Weissenberg number, Wi , as predicted by theory, Eq. 3.7.4.

This criterion can be presented in different forms. In particular, the following rearrangements are pertinent:

$$Wi = \frac{\sigma_E \eta_E}{\eta_E E} = \frac{\sigma_E}{E} = \epsilon_r \quad [3.7.5]$$

where ϵ_r is elastic (rubbery) deformation stored in extension, or tensile recoil.

According to the theory for linear elastic liquids, there is a critical value of the Weissenberg number corresponding to unlimited stress growth in extension, indicating that steady flow is impossible. The experimental confirmation that the transition from open to solid symbols in Fig. 3.7.4 (the transition to unsteady extension and rupture) takes place at $Wi = 0.5$.

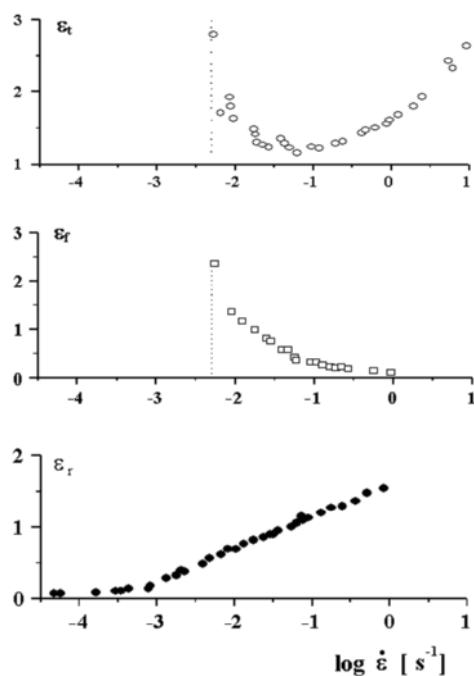


Figure 3.7.6. Separation of the total deformation into plastic and elastic parts: limiting total, ϵ_t , plastic, ϵ_f , and elastic, ϵ_r , deformations at the moment of rupture. Experimental points are “reduced” to 25°C. [Adapted, by permission, from G.V. Vinogradov, A.Ya. Malkin, V.V. Volosevitch, V.P. Shatalov, V.P. Yudin, *J. Polym. Sci.: Polym. Phys Ed.*, **13**, 1721 (1975)].

stretching ends with sample failure. Beyond this transition line, the flow becomes less and less noticeable but rubbery deformations (at the moment of rupture) continue to increase together with the growth of stress. Combination of the decreasing ϵ_f and increasing ϵ_r results in appearance of the minimum on the total $\epsilon_t(\dot{\epsilon})$ dependence. At a sufficiently high deformation rate, flow becomes negligible and the total deformation of stretching liquid appears to have a rubbery character.

The experimental data presented in Fig. 3.7.6 constitute only a part of the characteristics of the limiting deformation evolution as a function of the deformation rate, because they do not show what happens in the domain of very high deformation rates. The complete sequence of events taking place during extension as a function of increasing deformation rate is shown in Fig. 3.7.7. The domains I, II and the left part of the domain III are the same as in Fig. 3.7.6, but in comparison with Fig. 3.7.6 additional domains (part of III and IV) exist. In a single experiment, it is very difficult to move through the whole deformation range covering all domains, as in Fig. 3.7.7, because, in fact, the $\dot{\epsilon}$ scale spreads through 8-10 decimal orders. That is why the generalized picture, presented in Fig. 3.7.7 is obtained by “reducing” experimental data to one reference temperature (see Chapter 2).

The total deformation, ϵ_t , can be separated¹⁷² into a recoverable (elastic), ϵ_r , and flow (plastic), ϵ_f , part to follow the development of both components as a function of the deformation rate. The results of such separation in the linear region of the viscoelastic behavior are shown in Fig. 3.7.6, where limiting values of deformations which can be reached at different deformation rates are presented.

There are several regions in which the character of the deformation evolution is different. At low deformation rates, the total deformation may grow unlimitedly due to a steady flow (both upper parts of Fig. 3.7.6). Rubbery deformation, ϵ_r , increases with increase in deformation rate (and, accordingly, stress). The values of ϵ_r , presented as a function of $\dot{\epsilon}$, are the equilibrium values corresponding to the steady flow limit. The vertical dotted lines in Fig. 3.7.6 have the same meaning as the horizontal line in Fig. 3.7.4 – they correspond to $Wi = 0.5$ and divide the whole deformation rate scale into two domains – slow (left of the line), where the steady flow regime is acceptable, and fast (right of the line), where the steady flow is not possible and this transition line, the flow becomes less and less noticeable but rubbery deformations (at the moment of rupture) continue to increase together with the growth of stress. Combination of the decreasing ϵ_f and increasing ϵ_r results in appearance of the minimum on the total $\epsilon_t(\dot{\epsilon})$ dependence. At a sufficiently high deformation rate, flow becomes negligible and the total deformation of stretching liquid appears to have a rubbery character.

The solid line in Fig. 3.7.7 is for breaking (total) deformations and the dotted line, converging to the solid line at high deformation rates, is for elastic deformations. The physical meaning of the four domains in Fig. 3.7.7 is as follows:

- Domain I is a *flow* region, where extension causes a steady flow and the total deformation is unlimited. The boundary between domains I and II corresponds to $Wi = 0.5$
- Domain II is a *viscoelastic* region characterized by the superposition of elastic and plastic deformations, the latter equals the difference between the solid and dotted lines
- Domain III is a rubbery or pure *elastic* region, where flow is negligible and large deformations realized in extension are completely elastic (rubbery)
- Domain IV corresponds to a decrease in possible deformation due to high-deformation-rate-induced solidification of material and the end of this domain could be called a *glassy* region.

The transition through the domains $I \rightarrow II \rightarrow III \rightarrow IV$ corresponds in polymer physics to well-known transitions through different relaxation states of amorphous polymer induced by increasing deformation rates.¹⁷³

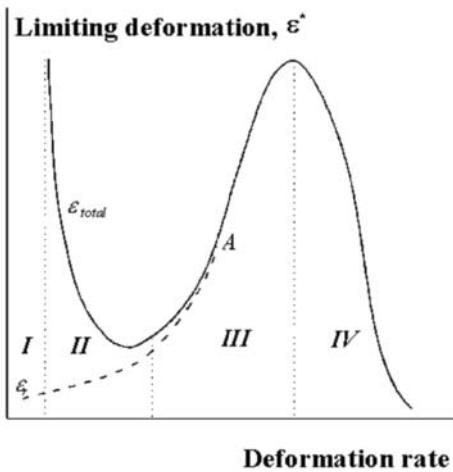


Figure 3.7.7. General picture illustrating deformation rate dependencies of limiting total (solid line) and elastic (dashed line) deformations. Roman numbers show principal regions of viscoelastic behavior observed as a function of deformation rate. Vertical dotted lines are approximate boundaries of these regions. [Adapted, by permission, from A.Ya. Malkin, G.V. Vinogradov, *Vysokomol. Soedin.* (Polymers – in Russian), **27**, 245 (1985)].

The real relationships observed for industrial polymers may be more complex and more difficult to understand. The common features of the superposition of flow and rubbery deformations, and the dependence of their relative values on the deformation rate and transitions through different relaxation states are the same for any polymeric

There is a special point in Fig. 3.7.7 – that is, a maximum located in the transition from the rubbery to elastic region. It was suggested¹⁷⁴ that the maximum value of the elastic deformation in extension of polymer melt is close to 2 (it corresponds to the draw ratio about 7.3). It seems that this value is in agreement with the experimental data in Fig 3.7.5. However, a more general idea was advanced:¹⁷⁵ it was proposed that the maximum elastic deformation (the maximum on the curve in Fig. 3.7.7) equals the maximum extensibility of a macromolecular chain, which forms a statistical coil in an undeformed state. Then this maximum ϵ_e value depends on the molecular mass of polymer.

Figs. 3.7.5 and 3.7.7 present results of model experiments carried out for mono-disperse polymers and related primarily to the linear regime of viscoelastic behavior of these materials. They represent a general tendency in deformation evolution during extension of polymer melts and solutions.

material. Analogous qualitative results confirming the applicability of the general concept of Fig. 3.7.7 were obtained for industrial grade polydisperse polyethylene and polyisobutylene.¹⁷⁶

Rupture of liquids described in this section is, by its physical mechanism, equivalent to the rupture of crosslinked rubbers. Temporary molecular junctions in melt, present due to macromolecular physical interactions (for example, chain entanglements), are analogous to chemical crosslinking in rubbers. The difference is in the lifetimes of these junctions. However, if the characteristic time of deformation is short (or deformation rate is high), physical junctions behave like permanent chemical junctions (at $Wi > 0.5$). Therefore, the mechanism of rupture during the extension at high deformation rates is similar to that of rupture of rubbers that can be treated as elastic.

3.7.3 EXTENSION OF INDUSTRIAL POLYMERS

Uniaxial extension of polymeric materials is considered as a model for different technological processes, primarily fiber formation and film orientation. This is also a physical method which can be useful for material structure characterization. These are the reasons why this method is widely used in investigations of real industrial polymers.¹⁷⁷ The experiments in uniaxial extension of industrial polymers were initially based on a technique that utilized measurements in the regime of the constant deformation rate.¹⁷⁸ Then many experimental investigations were made along the same lines. Their goal was to develop a variety of different polymers and to compare results of these experiments with the molecular structure of material (molecular mass distribution, branching of chain, chemical structure of polymer, or the content of blend).¹⁷⁹

The most obvious difference in the results of experimental investigations of many industrial polymers and the model data, as presented in Fig. 3.7.2, is the potential influence of *strain hardening*. It is often thought that the effect of strain hardening is of primary importance for polymer processing in fiber formation and in some other technologies. A comparison of the stress evolution in uniaxial extension of several polymers is shown in Fig. 3.7.8,¹⁸⁰ where both possibilities are presented: a smooth increase of the stress up to the regime of steady flow is reached at low deformation rates (a) and an increase of stresses – “*strain hardening*” observed as the unlimited growth of stresses until the break at a high deformation rate (b). The situation presented in Fig. 3.7.8a is quite equivalent to the model case shown in Fig. 3.7.2, whereas what is seen in Fig. 3.7.8b is different. The unlimited growth of stresses until breakup can be expected, as predicted by Eq. 3.7.4, and it happens earlier in time with increase in the deformation rate.

The increase in stress was discussed by the authors of original publications in terms of *strain hardening*, though the mechanism of this effect can be treated as the transition to domain III in Fig. 3.7.7, when elastic deformations become dominating and finally lead to rupture. Quantitative conditions of the breakup were not specified in the experiments under discussion, though it is possible to think that the final stress increase at higher deformation rates is similar to experimental results obtained for model systems, as shown in Fig. 3.7.5.

The difference in evolution of normal stresses in Fig. 3.7.8 is remarkable and this is definitely the reflection of differences in the molecular structure of materials under investigation. As the closest version, a smooth increase in stresses is expected from melts of linear polymers (PP-1 and PP-3), whereas the strain hardening effect reflects the existence of

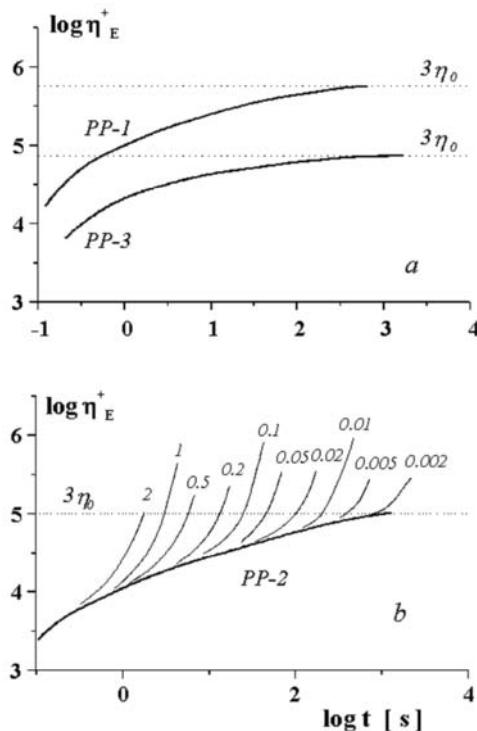


Figure 3.7.8. Stress growth in elongation of polypropylene samples. Experimental data points, presented by the authors, are omitted in reproducing this figure. PP 1, 2, and 3 are different PP samples. [Adapted, by permission, from S. Kurzbeck, F. Oster, H. Münstedt, T.Q. Nguyen, R. Gensler, *J. Rheol.*, **43**, 358 (1999)].

branching in the macromolecular structure (PP-2). The next reason for differences in rheological behavior can be connected with the molecular mass distribution of commercial polymers. Also, it can be suggested that, at least in some cases, an intensive stress growth in extension can be caused by the stress-induced phase transition, possibly, even crystallization of oriented chains.

Some cases are known when the steady state regime during extensional flow cannot be reached at all, even at very low deformation rates. This is typical, for example, for thermotropic liquid crystalline polymers (*Vectra A950*),¹⁸¹ for which the regime of constant elongational viscosity does not exist but only strain hardening is observed. Possibly it corresponds to the well-known fact of the absence of a Newtonian flow range for liquid crystals, because at low stresses a tendency of viscosity growth with decrease of stresses (apparent approach to the yield stress) is observed.

3.7.3.1 Multiaxial elongation

Multiaxial elongation is a special case of elongational flow. There are various possible combinations of deformation modes. The reasonable classification of these cases is based on the analysis of the deformation rate tensor written as¹⁸²

$$\dot{d}(t) = \dot{\varepsilon}_0 \begin{bmatrix} 1 & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & -(1+m) \end{bmatrix}$$

In the special case (discussed above) $m = -0.5$. This is *simple elongation*. The case of $m = 0$ is treated as *planar elongation* and the case of $m = 1$ is called *equibiaxial elongation*. An example of apparent elongational viscosity evolution as a function of strain is presented in Fig. 3.7.9.¹⁸³ Here elongational viscosity is normalized by the initial Trouton viscosity value (i.e., $\eta_E^0 = 3\eta_0$) in order to begin all curves from the same initial point. For equibiaxial elongation only one elongational viscosity, η_B^+ , (called the *biaxial stress growth coefficient*) exists, while in planar elongation two viscosity values can be measured along two directions of elongation. In this Figure, η_B^+ is the *biaxial stress growth coefficient*, which is defined as the ratio of normal stress to the deformation rate. This

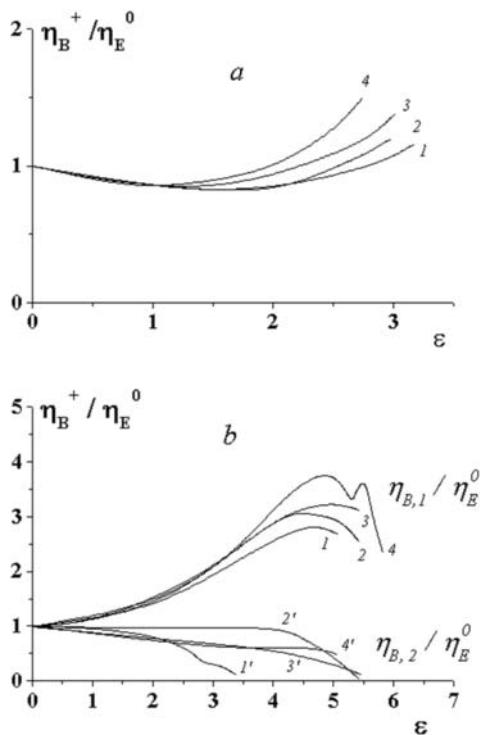


Figure 3.7.9. Elongational viscosity (normalized by the initial Trouton value) in equibiaxial (a) and planar (b) elongation of high density polyethylene as a function of strain (Hencky measure). 150°C. Deformation rates, s^{-1} , a: 0.003 (1); 0.010 (2); 0.030 (3); 0.099 (4); b: 0.003 (1, 1'); 0.009 (2, 2'); 0.028 (3, 3'); 0.093 (4', 4'). [Adapted, by permission, from: P. Hachmann, J. Meissner, *J. Rheol.*, **47**, 989 (2003)].

3.7.4 THE TUBELESS SIPHON EFFECT

Uniaxial extension of elastic (rubbery elastic) materials capable of storing very large deformations produces unusual effects. One of them is the so-called *tubeless siphon*.¹⁸⁴ This effect is observed during extension of dilute solutions of polymers (synthetic or biological) of ultra-high molecular mass. Such solutions are not very viscous but they are capable of storing large elastic deformations. In Fig. 3.7.7, the behavior of such solutions corresponds to the domain III.

The tubeless siphon effect is schematically presented in Fig. 3.7.10a. The fluid from a large free surface is drawn up through a nozzle by a vacuum. Then the nozzle is raised above the surface of the liquid. The liquid stream preserves its form and stability and it continues to flow upwards into the nozzle, even if a distance from the free surface to the die reaches several centimeters.

Another example of the siphon effect is shown in Fig. 3.7.10b: in this case, a stream taken from a free surface is winding on a rotation roll.

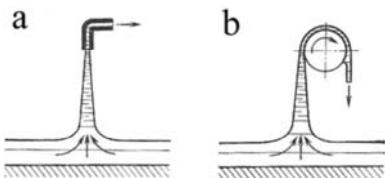


Figure 3.7.10. The tubeless siphon effect.

value coincides with elongational viscosity in the absence of elastic deformations only (see Eq. 3.7.1 and its discussion).

The elongational viscosity varies in a very different manner, depending on the mode of deformation. In equibiaxial stretching, apparent viscosity is almost constant, i.e., the behavior of melt is close to the linear viscoelastic, though a weak effect of strain softening also exists. In planar stretching, one apparent viscosity demonstrates the remarkable effect of strain hardening (like in simple elongation) and the second (normal to the first) viscosity value decreases at high strains. It is also worth mentioning that the type of elongational viscosity behavior depends on the nature of the material.

The driving force for this effect is undoubtedly the elasticity: initially created elastic deformations pull liquid upwards. In this regard, the behavior of liquid in a tubeless siphon is rubbery-like rather than fluid-like. It is interesting to note that it is impossible to create the siphon effect for Newtonian liquid even if its viscosity is high.¹⁸⁵

The siphon effect produces high deformation rates in extension of a low viscosity (but highly elastic) liquid. This can be the basis of the original experimental method for measuring rheological properties of such liquids,¹⁸⁶ based on a direct observation of the stream profile. However, the interpretation of the experimental results is not easy and it is intimately related to the rheological model used for treating the experimental data.

3.7.5 INSTABILITIES IN EXTENSION

3.7.5.1 Phase transitions in extension

The influence of deformation (either in extension or in shear, though much more pronounced in extension) on the phase transition is related to the partial or complete uncoiling of a polymer chain. This phenomenon can be directly observed, and it was demonstrated that the transition from a coil to an extended conformation of a polymer chain is a phase transition. It was proven by birefringence measurements in very dilute solutions, where individual macromolecules are deformed separately.¹⁸⁷ The ratio of current birefringence to its limiting value corresponding to a completely extended chain, $\Delta n / \Delta n_\infty$, is a measure of chain conformation, or extension of a polymer statistical coil. It is useful to apply the dimensionless deformation rate as a measure of the intensity of loading. This dimensionless value (which was named above as the Weissenberg number) in the publications related to the subject under discussion, is usually named the *Deborah number*, De , which is (similar to Eq. 3.7.4) defined as

$$De = \theta \dot{\varepsilon} \quad [3.7.7]$$

where θ is the characteristic relaxation time and $\dot{\varepsilon}$ is the deformation rate.¹⁸⁸ According to the molecular theory the θ value is determined as

$$\theta = \frac{aM[\eta]\eta_0}{RT} \quad [3.7.8]$$

where a is a constant of the order of one, M is the molecular mass of macromolecule, $[\eta]$ is the intrinsic viscosity, η_0 is the viscosity of solution, R is the universal gas constant, and T is the absolute temperature.

Numerous experiments showed¹⁸⁹ that the dependence of the degree of uncoiling on the deformation rate is similar to that shown in Fig. 3.7.11. It means that change in macromolecular conformation occurs in a rapid manner as a typical phase transition. It also happens at the critical Deborah number of the order of 1, i.e., this phenomenon is determined by the ratio of deformation and relaxation rate measures.

It is also well known that aligning macromolecules (and their forced ordering) favors crystallization. Therefore, this phenomenon must be taken into account in constructing models of technological processes (kinetics of stress-induced crystallization is a necessary part of simulating melt spinning process).¹⁹⁰

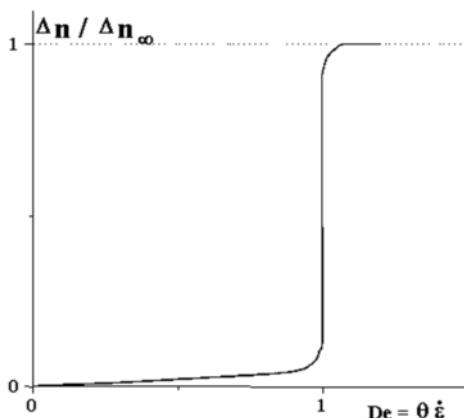


Figure 3.7.11. Increase in the degree of orientation (characterized by $(\Delta n)/(\Delta n_\infty)$) of individual macromolecules as a function of the dimensionless shear rate ($De = \theta \dot{\epsilon}$). Phase transition takes place at $De \rightarrow 1$.

drops is caused by the action of surface (capillary) forces. The thermodynamic cause of drop formation is a tendency for the minimization of the surface energy of fluid. Surface energy is not at minimum for a stream but the optimum shape is a spherical drop.

The surface of a stream is disturbed by occasional factors. These small disturbances create surface waves which intensify until they disrupt the stream. The final result of theoretical investigation is expression for length, L , of stream before disintegration:

$$L = 8.46 u_0 \left(\frac{\rho R^3}{\sigma} \right)^{1/2} \quad [3.7.9]$$

where u_0 is the stream speed, R is stream radius, ρ is density, and σ is the surface tension.

Viscosity does not enter this expression. However, detailed analysis¹⁹² showed that if the viscous forces are taken into consideration, another expression for the limiting length of a stream, L , is valid:

$$L = \frac{5 u_0 R \eta}{\sigma} \quad [3.7.10]$$

where η is viscosity. This equation is correct for fluid moving through a medium with much lower viscosity than that of a viscous liquid stream flowing in air.

Development of a theory of fluid stream disintegration leads to the field of spraying or atomization of streams leaving a nozzle with a very high speed. This problem is principal for the operation of a carburetor in car engines and many other engineering devices. However, an analysis of this problem goes beyond the field of rheology.

3.7.5.2 Rayleigh instability¹⁹¹

Experimental data presented in Figs 3.7.6 and 3.7.7 show that in domain I, the total deformation is unlimited. But the extensional deformation cannot be unlimited because unlimited jet thinning is not possible. In this sense, extension, in contrast to shear, cannot continue unlimitedly. A rupture of a stream in domain I occurs due to different causes than the elastic rupture in other domains in Fig. 3.7.7. The breakup of the stream in this case is the consequence of the *Rayleigh instability*.

It is well known and observed every day that when a liquid stream leaves a die (or a capillary) it disintegrates into separate drops. The mechanism of this phenomenon is as follows. If the speed of stream movement is not high, the breakup of liquid into

3.7.5.3 Instabilities in extension of a viscoelastic thread

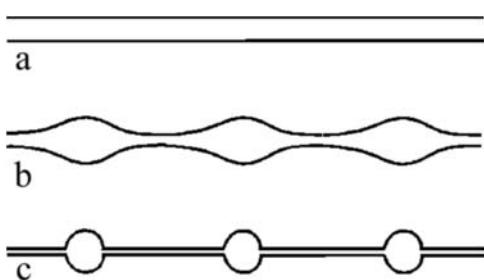


Figure 3.7.12. A view of viscoelastic jet leaving a nozzle: regular extrudate (a), draw resonance – periodic changes in thread diameter (b) and formation of a series of droplets joined by thin threads (c).

phenomenon is of special interest for the technology of fiber formation because periodic oscillations in thread diameter lead to a decrease in fiber quality.

A principal possibility of oscillations exists even for Newtonian liquid.¹⁹⁴ It was proven that the draw resonance appears at a high draw ratio,¹⁹⁵ and the critical value of the draw ratio, λ_{cr} , is close to 20.¹⁹⁶ The theoretical analysis of the stability problem in an extension of viscoelastic liquid showed¹⁹⁷ that the transition from stable to unstable zone is determined by the dimensionless Deborah number, De, which is similar to that in Eq. 3.7.7, and defined as

$$De = \frac{\theta V_0}{L}$$

where θ is the characteristic relaxation time, V_0 , is the extrusion velocity (at the outlet of a fiber forming nozzle) and L is the length of thread.

The theory predicts that elasticity stabilizes thread diameter. It was shown that for any Deborah number there are two limits of the stability zone:

- the lower limit, which is practically constant for any De and corresponds to the $\lambda_{cr} \approx 20$
- the upper limit, which appears due to elasticity and therefore the upper limit depends on De. The position of this upper limit of stability depends on the choice of model, which incorporates the elasticity into consideration.

The stability in relation to the draw resonance phenomenon depends on whether fluid has extension thinning or extension thickening properties; the latter stabilize the form of the thread. Thickening might also be understood as the transition from the flow regime of deformation to the regime dominated by elastic deformations in extension.

The draw resonance effect can be avoided by quick thread cooling,¹⁹⁸ which is an ordinary procedure in real technological processes.

In some cases, which are typical for low viscosity but highly elastic liquids, it was observed,¹⁹⁹ that instead of breakup of a stream into separate drops, a thread looks like that are shown in Fig. 3.7.12c, i.e., the stream rearranges into a series of small droplets joined by a thin thread. The elasticity of liquid stabilizes stream and prevents it from for-

If liquid is not purely viscous and elastic (rubbery) deformations superimpose on flow (some polymeric solutions, biological liquids, such as saliva), a stream's breakup mechanism is changed dramatically.

There are two main types of regular instabilities appearing in extension of a thread. This is a draw resonance and the formation of small droplets along the thread (Fig. 3.7.12).

The draw resonance is the effect of large-scale periodic smooth variation in thread diameter (Fig. 3.7.12b) when this thread is taken up at constant speed.¹⁹³ This

mation of separate drops.²⁰⁰ This effect can be explained by transition of viscoelastic fluid connecting threads to domain III type behavior (in Fig. 3.7.7), in which they deform like an extendable rubber cord. This effect can be treated as the “extension thickening” property of liquid, though it is related primarily not to viscosity growth but to the rubbery elasticity of the medium.

Theoretical and direct visual observations confirm the difference in the mechanisms of stream and drop breakup for viscous Newtonian and viscoelastic liquids.²⁰¹

3.8 CONCLUSIONS – REAL LIQUID IS A COMPLEX LIQUID

The concept of *liquid* seems commonly known. Nobody doubts that water and gasoline at room temperature are liquids. But toothpaste or adhesive are not commonly considered liquids. This shows that liquid is not necessarily material that flows. A more rigorous definition is needed to properly assign the behavior of real materials.

It may be suggested that liquid is material that undergoes *unrecoverable (irreversible) deformations*, i.e., the changes in shape remain after the action of external forces is removed. It should be noted, however, that this definition is too wide because it covers all real materials. For example, one would need to consider metals as liquids because during some technological operations, e.g., punching of golden articles, wire drawing of silver, or rolling steel ingots, unrecoverable deformations are undoubtedly created. These examples show that the above definition covers two different types of behavior: *viscous* and *plastic*. In the first case, unrecoverable deformations (or *flow*) can be detected at *any* stress, regardless of how small it may be. In the second case, unrecoverable deformations appear only when stress overcomes a certain level, which is called the *yield stress* or *yield point*. This means that a plastic medium can be called “liquid” only with some precautions. Nevertheless, treating deformations of plastic materials at stresses exceeding the yield stress as flow seems reasonable.

Liquids can also be defined as materials which can flow (or are able to accumulate unrecoverable deformations) under the action of an infinitesimal stress. The possibility to flow under infinitesimal stress means that liquid at rest cannot store any stress. Formally, this definition is acceptable. But two questions arise, as follows:

- if stress is decreased by one (two, three, etc.) orders-of-magnitude, is it possible to reach the yield point at which flow, at very low stress, does not occur? Or is it reasonable to think that yield stress exists in the case of any liquid but can be so small that it cannot be observed under ordinary experimental conditions but can be attained if conditions are changed? Indeed, it is never certain that the level of stress attained in an experiment is *sufficiently* low to assume that material is a liquid *from a rigorous point of view*.
- perhaps during the period of observation (or an experiment) unrecoverable deformations are so small that they cannot be detected by ordinary methods, even though they presumably exist. If an experiment is continued, should flow of material under investigation occur? It was demonstrated in Section 3.2 by several examples for viscoplastic materials, which can flow below the yield stress, as high viscosity materials, that a very long time is needed to detect flow.

Rheologists like to cite the famous exclamation from the Bible's Deborah: “*The mountains melted from before the Lord*”,²⁰² bearing in mind that in the scale of eternity,

the Lord can observe the flow of rocks (mountains). That is true, and the general answer to the problem raised by the theoretician lies in comparison of the inherent time scale of material, t_{inh} , and time of observation, t_{obs} . This characteristic inherent time, t_{inh} , can be treated as the time of relaxation, i.e., the time necessary for the recovery of a stable structure after the removal of external forces. Then it is reasonable to introduce the dimensionless criterion t_{obs}/t_{inh} , which is called the *Deborah number*, De. The general form of this number is:

$$De = t_{obs}/t_{inh}$$

If $De \gg 1$, material behaves like liquid. This happens when t_{inh} is small and relaxation occurs very quickly (in comparison with time of observation). On the opposite side of the time-scale (when $De \ll 1$), unrecoverable deformations cannot be detected, flow cannot be detected and material must not be treated as liquid.

Another citation also illustrates this idea: “*Measuring – measure time in thou thyself*”.²⁰³ Indeed, estimation has real meaning in the scale of human existence.

Finally, a very general definition of liquid might be constructed on the basis of an energy concept. Any action is connected with energy consumption. Then two types of the post-effects can be established:

- the energy can be stored in material and the stored energy returns after the removal of external forces. Storage of energy is characteristic of an elastic medium (elastic behavior in rheological media is discussed in Chapter 4.).
- the energy of deformations can be dissipated by its conversion into heat, and this type of behavior is characteristic of viscous liquids, because the viscous resistance to movement means heat dissipation of the work produced by the forces applied.

A viscous liquid, then, can be defined as a medium deformed in such a manner that the *energy needed for deforming completely dissipates* in the process of deformation. In essence, it means that no energy source for further deformation exists in the material after the action of external forces ceases and that is why deformation cannot be recovered (no driving force exists for the process).

Intermediate cases may exist when the energy of deformation is partly stored by material and only part of this energy can be dissipated. Such is the case of viscoelastic bodies, and in particular, of viscoelastic liquid.

The energy concept dividing materials according to their reaction to the work of deformation is the most general approach of characterization of the type of material behavior. Such concept is not related to any considerations of local values of stresses and deformations and does not need to be related to the observation of material behavior in the coordinate axis. In this sense, the energy approach is invariant with respect to coordinate transformations and satisfies the general requirements of rheological equations of state.

All real liquids are *complex liquids* and the following principal effects are more or less pronounced in their deformations:

- non-Newtonian viscosity in steady flow
- elasticity (rubbery deformations)
- time-dependent slow structure transformations to self-organization and/or phase transitions

- existence of limits of flow (instabilities of various types at high velocities or deformation rates).

The fundamental reasons of these phenomena are:

- superposition of large elastic deformations on viscous flow, this leads to numerous second-order effects
- changes in the intensity of energy dissipation depending on the deformation rate due to changes in streamline conditions at deformations or orientation of disperse phase particles in multi-component systems (stress-induced deformation of macromolecules in solutions, rotation of solid particles and formation of necklace structures in suspensions)
- increase in the share of solid-like modes in molecular movements and decrease of energy dissipation in flow of viscoelastic media (this is the most typical for concentrated polymer solutions and melts)
- destruction of molecular or supermolecular structure of matter, which exists due to physical interactions (polar forces or other secondary interactions) or mechanical contacts between particles in multi-component systems (this is typical for liquids loaded with an active solid filler, highly concentrated suspensions, polar macromolecules in solutions, liquid crystals).

The observed behavior of various media can be different and very strongly dependent on the peculiarities of conditions of deformation and observation. Sometimes, effects characteristic of complex liquids are evident in behavior of real liquids; in other cases, these effects appear under very special deformation conditions. This is the reason for a rheologist to say: do not ask what type of a material is, either liquid or solid, but try to understand how this material behaves – like a liquid or a solid.

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QUESTIONS FOR CHAPTER 3

QUESTION 3-1

Can viscosity be negative? Explain the answer.

QUESTION 3-2

In measuring viscous properties of polymer solution, it appeared that the experimental data within the experimental range of shear rates can be fitted with the power law equation (Eq. 3.3.4). Analyze the possibility of extrapolating this equation to the range of very high shear rates.

Additional question

Which kind of rheological behavior at high shear rates is expected in this case?

QUESTION 3-3

What is the difference in stress relaxation of viscous liquids and viscoplastic materials?

QUESTION 3-4

Can we expect that the values of the yield stress, σ_y , found by treating a set of experimental data by means of Eqs. 3.3.7 to 3.3.9, are the same?

QUESTION 3-5

Calculate shear stresses in flow of liquid through a straight tube if flow is created by the pressure gradient $\Delta p/L$ (L is the length of a tube).

Additional question

Are the results valid for Newtonian liquid only?

QUESTION 3-6

Calculate the radial distribution of shear rates and flow velocity of Newtonian liquid (having viscosity η) through a straight tube with radius R .

Additional question 1

Calculate the volume output, Q , for flow of Newtonian liquid.

Additional question 2

Express maximum shear rate, $\dot{\gamma}_R$, via volume output.

Additional question 3

Is the last expression valid for a liquid with arbitrary rheological properties?

QUESTION 3-7

Calculate the velocity profile in flow of a power-law type liquid through a straight tube with a round cross-section. The radius of a tube is R.

Additional question

Calculate the volume output, Q, as a function of Δp for a power-law type liquid.

QUESTION 3-8

An experimenter obtained two pairs of data: at $\dot{\gamma}_1 = 1 \cdot 10^{-3} \text{ s}^{-1}$ $\sigma_1 = 100 \text{ Pa}$ and at $\dot{\gamma}_2 = 1 \cdot 10^{-2} \text{ s}^{-1}$ $\sigma_2 = 600 \text{ Pa}$.

Assuming that the flow curve is described by a power-law type equation, find the constants of this equation for a liquid under study.

Additional question

How do you find the constants of the power-law type equation if an experimenter obtained three or four pairs of experimental points?

QUESTION 3-9

Analyze the flow of a viscoplastic ("Bingham-type") liquid through a straight tube of radius, R. Find radial stress and velocity distributions and calculate volume output as a function of pressure gradient.

QUESTION 3-10

A ball with a radius R is falling in a Newtonian liquid having viscosity η . After some transient period, the velocity of ball movement becomes constant. Find the velocity of steady movement, V_∞ .

QUESTION 3-11

An experimenter measured viscous properties of material at different shear rates and obtained a flow curve. What can he say concerning viscous properties of this material in uniaxial extension? Explain the answer.

QUESTION 3-12

Prove the validity of Eq. 3.1.7 – the dependence between normal stress and deformation rate for Newtonian liquid in two-dimensional (biaxial) extension.

QUESTION 3-13

Normal stresses in shear appear as a second-order effect. However, at high shear rates they exceed shear stresses. Estimate the condition under which it becomes possible.

QUESTION 3-14

Can normal stresses appear in shear flow of suspension of solid particles? Explain the answer.

Additional question

Estimate the characteristic time ("relaxation time"), θ , of this process.

QUESTION 3-15

An experiment was carried out in shear at the constant shear rate, $\dot{\gamma} = \text{const}$, and the curve similar to shown in Fig. 3.5.1 or Fig. 3.5.2 was obtained. Can the ratio $\sigma(t)/\dot{\gamma}$ be treated as the evolution of viscosity of liquid? Explain the answer.

QUESTION 3-16

A liquid layer is intensively sheared at shear rate $\dot{\gamma} = 1*10^2 \text{ s}^{-1}$. A liquid is Newtonian and its viscosity $\eta = 500 \text{ Pa*s}$. Shearing continued for 10 s. Temperature dependence of viscosity is neglected; density is assumed to be 1 g/cm^3 and heat capacity is 0.5 J/(g*K) .

What temperature rise is expected?

Additional question

If shearing proceeds for a longer time, what physical phenomena must be taken into consideration and what final thermal effect of shearing can be expected?

QUESTION 3-17

Analyze the Mooney equation (3.3.27) for concentration dependence of viscosity for the limiting case and, in particular, calculate the intrinsic viscosity of dilute suspensions.

QUESTION 3-18

Newtonian viscosity of polymer with molecular mass $M_1 = 3*10^5$ is $\eta_1 = 5*10^5 \text{ Pa*s}$. There is also another polymer of the same chemical structure with molecular mass $M_2=4*10^4$. How can one decrease the viscosity of the polymer by 10 times?

QUESTION 3-19

Experiments show that an electrical charge appears on the surface of polymer stream leaving a capillary in an unstable or spurt regime. Explain the origin of the charge.

Answers can be found in a special section entitled Answers.