

RHEOMETRY

EXPERIMENTAL METHODS

5.1 INTRODUCTION – CLASSIFICATION OF EXPERIMENTAL METHODS

This part of the book is devoted to selection and evaluation of modern experimental methods of rheology. The main attention is given to methods used in studies of rheological properties of liquids.

To measure rheological properties, the numerical values of constants that are included in rheological equations of state of various materials have to be found. Depending on the choice of equation, experiments are carried out in order to establish the influence of these constants on results. However, irrelevant of the choice of a model of rheological behavior, the measurement of two fundamental characteristic functions of material always plays a central role – viscosity as a function of a shear rate, and viscoelastic properties, such as dynamic moduli, as a function of frequency.

Experimental methods of measurement of rheological properties are defined by the general term *rheometry*, while, a more narrowly defined term, *viscometry*, is typically used in measurements of viscosity.

Two approaches are possible to determine rheological properties of materials – *absolute and relative* measurements. Both approaches are widely utilized in modern research and technological practice, with each playing its own role.

Absolute methods of viscosity measurement are based on direct utilization of the main equation, Eq. 3.1.1, that defines the concept of viscosity. In this case, the shear stress and shear rate are measured and viscosity is calculated as a ratio of these quantities. Both values are termed as *local* values, i.e., they are referred to as some point in space occupied by liquid. Thus, in determining the shear stress and shear rate, the solutions of the problem of hydrodynamics are utilized to provide relationship between measured macroparameters and dynamic (stress) and kinematic (shear rate) characteristics of stream at a point. In the experiment, force, pressure, torque, etc., may serve as values determining the dynamic macroparameters. A linear or angular velocity plays a role of kinematic macroparameters. Thus, the main goal of absolute methods of viscosity measurement is to establish a relationship between pairs of values dependent on flow geometry defined by a design of a measuring device:

- *force (torque) – stress*
- *flow velocity – strain rate.*

Relative methods of viscosity measurement are based on comparison of properties of fluid under investigation with a model fluid of known properties. Sometimes it is sufficient to find some characteristics of one fluid in comparison with another that is considered to be standard even if its absolute viscosity values are unknown. Relative characteristics of viscosity can be assumed, such as the time required for fluid to empty a vessel through a nozzle (similar to hourglass). In this experiment, the main focus is on keeping the same flow conditions and vessel dimensions. In this case, the term *calibrated* (strictly reproducible) dimensions are used. In contrast to the absolute method of viscosity measurement, relative viscosity characteristics are determined, for example, flow time.

Classification of methods of viscosity measurement, absolute as well as relative, is based on the *geometry of flow*.

Three main cases of flow are possible:

- flow of fluid between solid surfaces or through a hole in a solid body
- flow of fluid around a solid body
- free stream flow, relevant only to extension of a fluid stream.

Fluid flow between two solid surfaces can be realized in the following geometries:

- fluid flow through a capillary with cross-section of capillary being usually, but not necessary, circular
- rotational flow in which fluid is subjected to a circular motion in a gap between rotating cylinders, in a gap created by cone and plate or two conical surfaces, in a gap between two spherical surfaces, or other combinations of circular bodies
- shear flow of fluid between two parallel plates
- squeezing flow of fluid layer between two parallel plates approaching each other
- indentation of a solid body into material.

Viscosity measurement in fluid flowing around solid bodies is usually carried out according to the following schemes:

- flow around a spherical or other surface moving in fluid with its resistance to flow depending on fluid viscosity. The space occupied by fluid may be restricted by solid walls or be infinite
- indentation of a solid body (*indenter*) into the fluid layer with shapes of the indenter being different – conical, spherical, cylindrical, etc.

Experimental methods also differ because of kinematics or dynamics of deformation, namely: force or velocity may be maintained constant or varied according to a given protocol; in modern instruments variations and/or combinations thereof are frequently used.

Properties of final product may be defined and the technological process may be controlled either by removing samples from a process and studying them in the laboratory, or by using in-line measurement techniques during processing. The design and construction of the utilized instruments may vary accordingly, but principles of measurements remain similar.

As mentioned in Chapter 3, shear flow of many liquid media is accompanied by storage of elastic (recoverable) deformations and development of normal stresses. Measurement of the normal stresses at various shear rates is a separate problem of rheometry that is important for selection and evaluation of adequacy of rheological models.

Measurement of viscoelastic characteristics of materials represents observation involving transient regimes of deformation (see Chapter 2). When one of its characteris-

tics (kinematic or dynamic) is kept constant, the time dependence of other characteristics can be measured.

Thus measurement of viscoelastic characteristics is usually carried out in the following regimes:

- a constant stress is imposed and variations of strain with time are measured, i.e., *creep* is studied at various stresses
- a constant strain is imposed and variations of stress with time are measured, i.e., a *relaxation* of stress at various deformations is studied.

A special place among the rheological measurements is occupied by periodic deformations, when frequency of oscillations of strain (or stress) is given and changes in stress (or strain) response are measured. This most important method in rheology is called the *dynamic or vibrational* method and is widely utilized for the study of viscoelastic properties of materials as well as viscosity.

Similar to viscosity, the measurement of viscoelastic characteristics of materials can be performed according to different geometrical schemes. Thus, it is not necessary to include separate classification of methods of measurement of viscoelastic characteristics according to their geometrical schemes of deformation. In addition, many modern instruments permit a combination of viscometric measurements determining the relationship between the shear stress and the shear rate, as well as dynamic testing and/or creep and relaxation of stresses.

Rheological measurements can be combined with various physical methods that are especially important for the study of structural transformations caused by deformation. Here it is important to utilize optical methods in various ranges of frequency. These methods permit direct observation of characteristics of fluid flow by tracing particles in a stream to measure velocity fields. Of particular interest is a measurement of *double refraction* or *birefringence* during flow, since dynamic anisotropy of optical properties is directly related to the material stress state. The use of other physical methods such as, for example, X-ray analysis, neutron scattering, calorimetry, and others along with rheometry is also of special interest.

5.2 CAPILLARY VISCOMETRY

5.2.1 BASIC THEORY

Capillary viscometry is the oldest and most widely used method of qualitative estimation and viscosity measurement. Its ubiquity is due to obviousness of experiment, simplicity of experimental units, relative inexpensive, and its easy to standardize test procedure.

The essence of method consists in measuring the resistance to flow of liquid through a calibrated channel. The central task of capillary viscometry is establishing the correspondence between volumetric flux (output), Q , and pressure drop in capillary, Δp , which induces flow. Pressure at the entrance is usually much higher than at the exit. Therefore, it is possible to replace the pressure drop, Δp , by the pressure at the capillary entrance, P .

The term “capillary” usually means any tube (channel) with arbitrary length and cross-section, though, as a general rule, cylindrical tubes (capillaries) with large length-to-radius, L/R , (or diameter, D) ratio are used.

The basic theory of capillary viscometry uses the following assumptions:

- the Newton-Stokes law (proportionality of stresses and shear stresses) is valid at any point of a stream
- velocity is not very high and flow is laminar
- flow along the main part of a capillary is steady and rearranging the velocity profile along the length does not take place; this assumption is not valid near the ends of a capillary: at the entrance and near the exit, the radial component of velocity appears due to velocity rearrangements
- circular and radial fluxes are absent; it might be not true if channels with non-round cross-section are used; in the latter case, circular flux appears
- flow is isothermal in the whole volume of liquid¹
- a capillary radius is constant along the full length and in all cases $L/R \gg 1$; if so the flux can be considered as steady along the dominating part of the length
- velocity at wall equals zero ("*hypothesis of stick*"); this is the reason for velocity

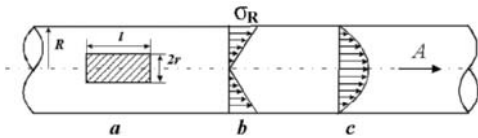


Figure 5.2.1. Basic scheme for viscosity calculation during liquid flow through capillary. Direction of flow is shown by arrow A. a: liquid element separated in stream; b: radial profile of shear stresses with σ_R being the shear stress at wall; c: radial velocity profile.

distribution along the radius of a channel; this assumption may not be valid in some cases, and, if so, the case requires special treatment.

Quantitative analysis of flow through a channel is based on formulation of equilibrium conditions for an axisymmetric, cylindrical element shown in Fig. 5.2.1a.

The following forces act on this element: pressure drop, dp , along the length, dl , shear stresses, σ , applied on the surface $2\pi r dl$. The balance of forces for a stationary flow (i.e., in absence of acceleration) is written as

$$dp(\pi r^2) = 2\pi\sigma dl \quad [5.2.1]$$

Then, the following expression for distribution of shear stresses along the radius is obtained:

$$\sigma(r) = \frac{1}{2} \frac{dp}{dl} r \quad [5.2.2]$$

In the stationary flow, dp/dl does not depend on the longitudinal coordinate. Therefore,

$$\frac{dp}{dl} = \frac{\Delta p}{L} = \frac{P}{L}$$

and, finally, the expression for radial distribution of shear stress takes a form:

$$\sigma(r) = \frac{Pr}{2L} \quad [5.2.3]$$

This expression is conveniently represented by shear stress, σ_R , which acts on a capillary wall, and it is calculated from Eq. 5.2.3:

$$\sigma_R = \sigma(R) = \frac{PR}{2L} \quad [5.2.4]$$

Then the final formula for $\sigma(r)$ takes the following form:

$$\sigma(r) = \sigma_R \frac{r}{R} = \frac{PR}{2L} \frac{r}{R} \quad [5.2.5]$$

Thus, the radial distribution of shear stress during flow in capillary of a circular cross-section is always linear. This distribution is shown in Fig. 5.2.1b. It is significant that this result is not connected with the Newton-Stokes hypothesis, but directly ensues from the common formulation of equilibrium condition, i.e., Eq. 5.2.5 is valid for any liquid with arbitrary rheological properties, including Newtonian liquids.

Shear stresses are applied in direction opposite to the flow direction, i.e., to arrow A in Fig. 5.2.1. Therefore (if the longitudinal axis is oriented along the arrow A), the stresses should be assigned a negative sign.

It is now necessary to examine the kinematics of flow, i.e., to determine the distribution of velocities along a radius of capillary, $u(r)$, and to calculate shear rate:

$$\dot{\gamma} = \frac{\partial u}{\partial r} = \frac{du}{dr}$$

For Newtonian liquid, the calculation of velocity distribution is based on the Newton-Stokes equation, which is written as:

$$\dot{\gamma} = \frac{du}{dr} = \frac{1}{\eta} \sigma$$

Hence, the radial distribution of shear rate is easily found:

$$\dot{\gamma} = \frac{du}{dr} = \frac{1}{\eta} \frac{PR}{2L} \frac{r}{R} \quad [5.2.6]$$

The distribution of deformation rates along radius, as well as stresses, are linear.

Hence, taking into account boundary conditions ($u = 0$ at $r = R$), the following expression for distribution of velocity along the capillary radius is obtained:

$$u(r) = \frac{1}{\eta} \frac{PR^2}{4L} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad [5.2.7]$$

Thus, the radial distribution of velocity during flow of Newtonian liquid through a channel of a circular cross-section is expressed by a parabolic function (equation of the second order).

Velocity is at maximum on the axis of channel, i.e., at $r = 0$. This maximum velocity, V_{\max} , is expressed as

$$V_{\max} = u(R) = \frac{PR^2}{4\eta L} \quad [5.2.8]$$

Then the radial distribution of velocities can be expressed through V_{\max} in the following manner:

$$\frac{u(r)}{V_{\max}} = 1 - \left(\frac{r}{R}\right)^2 \quad [5.2.9]$$

The obtained radial distribution of axial velocity is shown on Fig. 5.2.1c. The formulas, obtained for the radial distribution of velocity, permit calculation of the volumetric flow rate. For Newtonian fluid, it is expressed as follows:

$$Q = \int_0^R 2\pi r u(r) dr = \frac{\pi P R^4}{8\eta L} \quad [5.2.10]$$

Sometimes, instead of Q , it is convenient to use the average velocity, \bar{V} , which is expressed as

$$\bar{V} = \frac{Q}{\pi R^2}$$

i.e., the average velocity is the volumetric flow rate divided by the cross-sectional surface area of a channel.

Eq. 5.2.10 and following from it, proportionality of the volumetric flow rate to the fourth power of radius, is known as the *Hagen-Poiseuille law*.²

Thus, for Newtonian liquid the volumetric flow rate is directly proportional to a pressure applied (the proportionality factor depends on the geometric dimensions of a channel) and inversely proportional to viscosity.

The method of determining viscosity of a Newtonian liquid is based directly on Eq. 5.2.10. If the volumetric flow rate at the assigned pressure is measured, then the viscosity is calculated as

$$\eta = \frac{\pi P R^4}{8QL} \quad [5.2.11]$$

Although Eq. 5.2.11 gives a completely obvious and single-valued method for enumerating the viscosity, it is an integral value, i.e., it does not directly use the basic determination of viscosity such as Eq. 3.1.1. This is not essential for Newtonian liquids, since the stresses and the shear rates at any point of flow are pre-determined, but it is important for liquids with arbitrary and *a priori* not specified rheological properties.

The convenient expression for $\dot{\gamma}_R$ is found directly from Eq. 5.2.10, which, after simple transformation, leads to the following formula:

$$\dot{\gamma}_R = \frac{4Q}{\pi R^3} = \frac{4\bar{V}}{R} \quad [5.2.12]$$

This formula for shear rate at a wall of channel is valid only for Newtonian liquid, since it is derived from the Hagen-Poiseuille law also valid for Newtonian liquid. The integral definition of viscosity, i.e., Eq. 5.2.11, can be represented in a somewhat different form, namely:

$$\eta = K \frac{P}{Q} \quad [5.2.13]$$

where $K = \pi R^4/8L$ is the shape factor (or form-factor), determined from known dimensions of the measuring device (capillary).

The last formula is easily generalized for capillaries of any cross-section. The exact analytical solutions are known for channels with simple geometrical forms. The values of shape factor for channels of an arbitrary cross-section can be calculated using modern computer technology with any desirable accuracy. An approximate method for calculating flow of fluids in channels of noncircular cross-section, based on dimensional analysis, is also proposed.³

Another empirical method for determining the shape factor for channel with an arbitrary cross-section is based on experiment: Q and P are measured for liquid of known viscosity. Then, from Eq. 5.2.13, the geometric constant is calculated in an obvious manner.

The theory of measurements of apparent viscosity of non-Newtonian liquids is based on the same prerequisites, which were formulated for Newtonian liquids. Here one fundamental exception is made that at any point of flow field, the Newton-Stokes law is not satisfied, i.e., the assumption about the proportionality of shear stress to the shear rate does not hold.

If the experimentally observed dependence $Q(P)$ is nonlinear, then liquid is non-Newtonian, and determination of apparent viscosity must be based on a general definition of the apparent viscosity, according to Eq. 3.1.1.

Eqs. 5.2.3-5.2.5 for shear stresses remain valid for liquids with any rheological properties. But the expressions for shear rates obtained above are not applicable to non-Newtonian liquids, since the linear relationship between shear rate and shear stress is not fulfilled.

The general solution of calculation of apparent viscosity of non-Newtonian liquid according to a method of capillary viscometry is based on enumeration of shear rate at one specific point, namely at a wall of channel. The shear rate is a certain, *a priori* unknown, function of shear stress:

$$\dot{\gamma} = f(\sigma)$$

Volumetric flow rate for liquid of any type is calculated as

$$Q = \int_0^R 2\pi r u(r) dr \quad [5.2.14]$$

the integration of this expression leads to the following formula:

$$Q = \pi \int_0^R r^2 \left| \frac{du}{dr} \right| dr$$

In the last expression, the variable of integration, r , is substituted with Eq. 5.2.5 for σ . After performing corresponding operations, the following formula is obtained:

$$\dot{\gamma} = \sigma_R^{-3} \int_0^{\sigma_R} \sigma^2 f(\sigma) d\sigma \quad [5.2.15]$$

where $\dot{\gamma} = Q/(\pi R^3)$ is the average shear rate.

The last expression is differentiated with respect to σ_R resulting in

$$\frac{d\dot{\gamma}_0}{d\sigma_R} = -\frac{3}{\sigma_R^4} \int_0^{\sigma_R} \sigma^2 f(\sigma) d\sigma + \frac{1}{\sigma_R^3} [\sigma_R^2 f(\sigma_R)] \quad [5.2.16]$$

The function $f(\sigma_R)$ is shear rate at wall of channel, i.e. $\dot{\gamma}_R$. Then, the comparison of Eqs. 5.2.15 and 5.2.16 makes it possible to obtain the following relationship:

$$\dot{\gamma}_R = 3\dot{\gamma}_0 + \sigma_R \frac{d\dot{\gamma}_0}{d\sigma_R} \quad [5.2.17]$$

or equivalent to the latter, but sometimes the following expression is more convenient in applications

$$\dot{\gamma}_R = \dot{\gamma}_0 \left[3 + \frac{d \log \dot{\gamma}_0}{d \log \sigma_R} \right] \quad [5.2.18]$$

Eqs. 5.2.17 and 5.2.18 are known as the *Rabinovitsch-Weissenberg equation*.⁴ These formulas solve the stated problem, since they allow one to calculate shear rate at a wall of channel, $\dot{\gamma}_R$.

Instead of the average shear rate, $\dot{\gamma}_0 = Q/\pi R^3$, sometimes a quasi-Newtonian shear rate, $\dot{\gamma}_N = 4\dot{\gamma}_0$, i. e., $\dot{\gamma}_N = (4Q)/(\pi R^3)$ is used. However, in the general case, $\dot{\gamma}_N$ is not equal to the shear rate at wall $\dot{\gamma}_R$; $\dot{\gamma}_N = \dot{\gamma}_R$ only for Newtonian liquids.

The present method of calculation of flow curves applies to measurements using circular capillary. In practice of capillary viscometry, the slit capillaries, having thickness $H = 2h$ and width $B \gg h$, are also used.

The shear stress at wall of the slit capillary, σ_H , and the corresponding shear rate, $\dot{\gamma}_H$, are calculated as:

$$\sigma_H = \frac{PH}{2L} \quad [5.2.19]$$

and

$$\dot{\gamma}_H = 4\dot{\gamma}_0^H + 2\sigma_H \frac{d\dot{\gamma}_0^H}{d\sigma_H} = \dot{\gamma}_0^H \left(4 + 2 \frac{d \log \dot{\gamma}_0^H}{d \log \sigma_H} \right) \quad [5.2.20]$$

where the average shear rate $\dot{\gamma}_0^H$ during the flow in the slit capillary is calculated as $\dot{\gamma}_0^H = q/(BH^2)$, where B is the width of a slit channel.

If results of measurement are processed correctly, the dependence $\sigma(\dot{\gamma})$ that characterizes viscous properties of liquid being investigated must be independent of dimensions and geometric form of the capillary.

Thus, the dependence $\dot{\gamma}_N(\sigma_R)$ is the initial result obtained from experimental data. A further treatment of experimental data depends on selection of a rheological model, i.e., function $\dot{\gamma}(\sigma)$. If the model is unknown *a priori*, then it is necessary to use Eq. 5.2.18. If the model is known, then the task is reduced to determination of a limited number of con-

stants, entering the appropriate equation. This can be done by a computer program suitable for determination of constants of function by minimization of error – deviation of the calculated function from experimental data.

Such computation method of determining a flow curve is sometimes examined within the framework of a general approach to the solution of incorrectly posed inverse problems. The special feature of such tasks is that an unknown function is under the integral, while the measured function is related to it by means of integral equation. It is significant that even a small (inevitable) measurement error can bring a large error in calculation of the unknown function. In connection with capillary viscometry, the analysis of this task is based on somewhat modified Eq. 5.2.15, which is written in the following form:

$$Q = \frac{\pi \sigma_R}{R} \int_0^R \frac{r^3}{\eta(\dot{\gamma})} dr \quad [5.2.21]$$

Here the function $Q(\sigma_R)$ is measured, and the function $\eta(\dot{\gamma})$ is to be determined. For this purpose, the function $\eta(\dot{\gamma})$ is represented by a certain analytical expression with a small number of constants to be determined. Minimizing the mean value of deviation of the calculated dependence from experimental data, the constants are determined and also the flow curve of material under study is known.⁵⁻⁷

5.2.2 CORRECTIONS

In reality, the measurements of viscosity require a number of corrections, which are intended to account for deviations of specific conditions of experiment from idealized requirements, which were formulated in the beginning of Section 5.2.1. Even in measurements of viscosity of Newtonian liquid, deviations from linearity of dependence of volumetric flow rate on imposed pressure can be observed. These deviations are caused by factors, which lead to the introduction of *corrections*. Corrections are of general importance in the practice of capillary viscometry.

5.2.2.1 Kinetic correction

Liquid being investigated typically enters a capillary from a large reservoir. Then, the flow velocity of the stream substantially accelerates as a result of change in cross-section, i.e., kinetic energy of flow increases. This change requires additional expenditure of energy, which looks like a growth of viscosity, since viscosity is a measure of expenditure of energy required to create flow.

If the total measured pressure drop is P , then the part of this pressure, P_k , is spent on an increase of the kinetic energy of the stream, and only the remaining part, P_v , is responsible for overcoming resistance of flow through a capillary, i.e., for the measured viscosity.

Thus

$$P_v = P - P_k \quad [5.2.22]$$

where the value of P_k is responsible for the *kinetic correction*.

The value of P_k can be calculated as follows:

$$p_k = \frac{\rho \bar{V}^2}{\alpha} = \frac{\rho Q^2}{\alpha \pi^2 R^4} \quad [5.2.23]$$

where, as earlier, \bar{V} is the mean (output based) velocity, ρ is density, and α is the coefficient reflecting the influence of the velocity distributions on the value of kinetic correction. For Newtonian liquid with the parabolic velocity profile in capillary, it is considered that $\alpha = 1$, although different theoretical estimates give the value of α in the range from 0.74 to 2.0.

The correction taking into account a change in the kinetic energy leads to the following expression for Newtonian viscosity

$$\eta = \frac{\pi P R^4}{8 Q L} - \frac{\rho Q}{8 \pi L \alpha} \quad [5.2.24]$$

which is a modification of Eq. 5.2.11.

If we accept the standard value, $\alpha = 1$, then the introduction of kinetic correction leads to the measurement error, which can reach even 10%. For non-Newtonian liquids, it is difficult to determine the value of α *a priori*, but it is also of the order of 1.

The calculation of kinetic correction is important during measurements of viscosity of low-viscosity liquids, for example, dilute polymer solutions, where a high accuracy of measurements is required.

5.2.2.2 Entrance correction

An important role in the theory of capillary viscometry is played by the so-called *entrance corrections*, which combine different dynamic phenomena at the entrance to a capillary as a result of rearrangement of the inlet velocity profiles.

If we neglect the entrance corrections of different origin, then the results of measurements become dependent on the length of the capillary, due to the fact that the relative contribution of transient phenomena becomes greater when a shorter capillary is utilized for measurements. This effect can be seen in Fig. 5.2.2, where the results of measurements of dependencies of $\dot{\gamma}_N = (4Q)/(\pi R^3)$ on the shear stress at the wall of capillary are shown. Even for sufficiently long capillaries with $L/D = 61$, the results of measurements are not invariant relative to the capillary length.

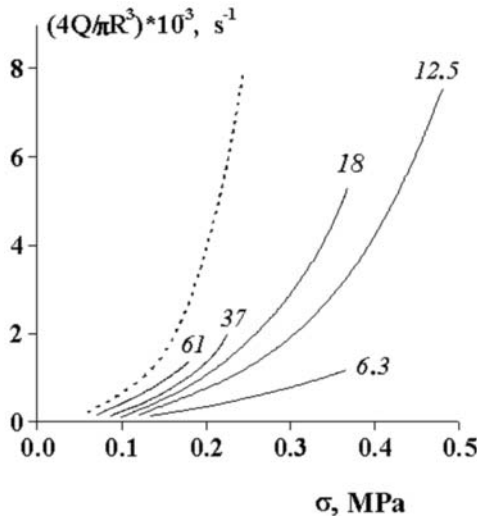


Figure 5.2.2. Dependence of quasi-Newtonian shear rate at a wall, $4Q/\pi R^3$, on the shear stress at a wall – role of L/D ratio. The values of L/D are shown on curves. Dashed line is a dependence of $4Q/\pi R^3$ on shear stress extrapolated to a capillary of infinite length. 60% solution of high molecular weight polyisobutylene in toluene. [Adapted, by permission, from E. Brenschade, J. Klein, *Rheol. Acta*, 9, 130 (1970)]

The same figure shows dependence on shear stress determined by extrapolation for an infinitely long capillary (dashed curve). Only in this case is the desired result achieved

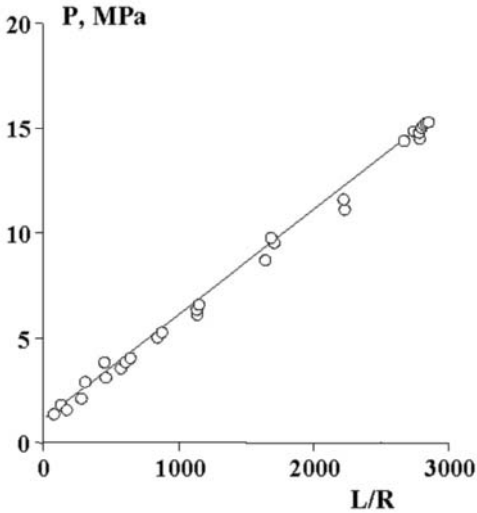


Figure 5.2.3. Dependence of pressure required to impose flow through capillary of different lengths at a constant value of quasi-Newtonian shear rate $\dot{\gamma}_N = 7 \times 10^4 \text{ s}^{-1}$. Experimental data for 60% solution of high molecular weight polyisobutylene in toluene. [Adapted, by permission, from E. Brenschade, J. Klein, *Rheol. Acta*, **9**, 130 (1970)].

– the obtained dependence precisely reflects the viscous properties of liquid.

For low-viscosity, inelastic liquids the so-called *Couette correction* plays the dominant role in the transient phenomena. It reflects effects which do not yield to direct evaluation, such as additional expenditures of energy for rearrangement of the velocity profile, the formation of the entry cone by liquid in a reservoir prior to capillary entrance, maintenance of vortices/eddies (secondary flows) around the entry cone, etc.

The influence of entrance effects becomes noticeable with the values of the Reynolds number, at least, the order of several tens, i.e., the corresponding effects become relatively significant for low-viscosity liquids.

In practice, a general method is developed for introduction of entrance correction as a measure of the effective length of a capillary.⁸ Let all additional losses of

energy (with respect to losses caused by flow of liquid through capillary) be determined by a certain fictitious additional pressure drop, P_k . Then, it is possible to imagine a certain fictitious capillary with the same radius, as utilized for measuring viscosity, but having larger length. This additional length is selected in such a way that at this length the pressure drop, P_k , would occur exactly. This additional length of capillary is expressed through a radius, R , as $m_k R$, where m_k is called the *entrance correction factor*.

Fig. 5.2.3 shows the experimental example of dependence of pressure at the entrance into capillary, on its relative length, L/R . According to the basic theory of capillary viscometry (see Eq. 5.2.4), the dependence of pressure, P , on L/R at any constant stress, σ_R , must be linear and start from the origin of coordinates, i.e., for a capillary of zero length, pressure is zero. This does not happen and even at the zero length of a capillary the pressure is non-zero, however, as a result of entrance correction.

Data of such type, as shown in Fig. 5.2.3, can be represented in the form:

$$P - P_k = \frac{2\sigma_R L}{R} \quad [5.2.25]$$

where P_k is the pressure loss that is responsible for the entrance correction (i.e., the value of the intercept of the straight line along the Y-axis in Fig. 5.2.3).

Introducing m_k , the calculation of the shear stress at the wall of a capillary is performed as follows:

$$\sigma_R = \frac{PR}{2(L + m_k R)} \quad [5.2.26]$$

with m_k varying with the flow rate or pressure.

For Newtonian liquids $m_k \approx 1$. The value can be much greater. In the practice of capillary viscometry a general, so-called differential, method is used for correction of m_k .

The essence of this method is seen in Fig. 5.2.3: measurements on capillaries of different lengths are made and the results of measurements are extrapolated to the zero length of the capillary, to determine P_k and thus m_k .

The use of a differential method and elimination of entrance corrections is required in the capillary viscometry of polymeric materials.

5.2.2.3 Pressure losses in a reservoir of viscometer

Capillary viscometer is a combination of two cylindrical channels – a reservoir of a large radius, whence the material being investigated enters the measuring part of a capillary having a small radius. If the ratio of radii is very large, then losses of pressure during flow through the reservoir can be disregarded. However, this is not always correct, since if a constant pressure, P , is imposed in a reservoir, the pressure at the entrance of capillary, P_0 , that is required for calculation of viscosity, increases as the reservoir is being emptied. This results in growth of volumetric flow rate with time during the duration of the experiment.

If a constant volumetric flow rate is imposed in an experiment, instead of a constant pressure, then the pressure at the entrance into the measuring capillary decreases with time. This reduces pressure loss in the reservoir.

The above indicated phenomena caused by flow in a reservoir prior to the entrance into the measuring capillary, indicate that a change in the apparent viscosity with time occurs. The reasons for these time-dependent effects, as explained above, are different.

It is possible to consider the pressure losses during the flow in the reservoir quantitatively, if the rheological properties of liquid being investigated are known. Then flow in the pair of cylinder-capillary channels is considered as flow in two sequential channels, and pressure losses as functions of shear rates are calculated for each of them.

5.2.2.4 Temperature correction

In the basic theory of viscometry, a flow is assumed to be isothermal, although it is well known that the viscous flow is accompanied by a dissipation of energy leading to temperature increase. The rate of heat generation depends on shear rate, and as such it is non-uniform along a radius. Furthermore, a part of heat is transferred to the environment as a result of heat transfer. Therefore, temperature varies along both radius and length of channel, which leads to appropriate changes in viscosity.

The temperature rise, ΔT , during the adiabatic flow of a Newtonian liquid with flow time, \dot{t} , is expressed as

$$\Delta T = \frac{\eta \dot{\gamma}^2 \dot{t}}{c\rho} \quad [5.2.27]$$

where c is the heat capacity of liquid and ρ is its density. A convenient expression for calculating viscosity change caused by heat dissipation is obtained from the following form:⁹

$$\eta_0 = \frac{\pi R^4 P}{8QL} \left(1 + \frac{kQP}{16\pi\lambda L} \right) \quad [5.2.28]$$

where λ is the heat transfer coefficient, and k is a coefficient of temperature dependence of viscosity, which is expressed as

$$\eta = \eta_0 e^{k(T - T_0)} \quad [5.2.29]$$

In this case, η_0 is viscosity at temperature, T_0 , imposed during experiment, which in the course of experiment rises to temperature, T , causing viscosity reduction to a value of η .

The true value of viscosity at temperature, T_0 , can be found using Eq. 5.2.28. For this purpose, the measurements should be conducted at several values of factor QP/L , entering this formula. Then, data are extrapolated to zero value of QP/L that corresponds to absence of dissipative contribution. The values of viscosity, η_0 , and the value of coefficient, k , can be found.

5.2.2.5 Pressure correction

Viscosity measurement during flow of liquid through a capillary may be affected by pressure. The higher the shear rate at which it is desirable to measure the apparent viscosity, the higher the imposed pressure. The pressure increase by itself may lead to viscosity increase, which sometimes leads to a very unique phenomenon. If a pressure necessary for viscosity measurement at high shear rate rises, it is expected that viscosity should decrease for shear-thinning liquids. Contrary to expectations, the measured viscosity increases. This occurs as a result of increase in pressure, which prevails over viscosity decrease because shear rate also increases.

The dependence of viscosity on pressure is usually expressed by exponential function:

$$\eta = \eta^0 e^{bP} \quad [5.2.30]$$

where η^0 is viscosity value $P = 0$, b is the baric (piezo) coefficient of viscosity.

The theoretical analysis, based on solution of dynamic equation of flow of Newtonian liquid, for which Eq. 5.2.30 is satisfied, gives the following expression for the volumetric flow rate:

$$Q = \frac{\pi R^4}{8L\eta^0 b} (1 - e^{-bP}) \quad [5.2.31]$$

where P is the pressure at the entrance into a capillary.

At low pressures (where $bP \ll 1$), this formula degenerates into the standard Hagen-Poiseuille equation. However, at large pressures, due to the influence of this factor, the effect cannot be disregarded.

Influence of pressure on rheological properties is substantial for compressible (foamed) materials. However, no reliable methods of rheological studies of such materials have been developed.

5.2.2.6 Correction for slip at a wall

The hypothesis that velocity of liquid at a wall equals zero (*no slip hypothesis*) is assumed in the analysis of liquid flow. There are situations when this hypothesis is not satisfied and slip occurs near a capillary wall. Usually, it is not essential whether slip of liquid along the solid wall actually takes place or the liquid ruptures near a wall or a very thin layer of liquid appears on a wall, along which the remaining liquid slides.

Slip may not necessary occur continuously, it may alternate with adhesion. This phenomenon, which is characteristic of flow of melts and concentrated solutions at high shear stresses, is called the stick-slip phenomenon. In this case, the corresponding mechanism of motion in channel proves to be unstable (see Section 3.6).

The slip effect at a wall in viscometric measurements can be found by observing dependence of results of viscosity measurements on capillary diameter. The procedure for calculation of slip velocity, V_s , and therefore viscosity in the shear flow based on these experimental results is called the *Mooney method*.¹⁰

Let the velocity of liquid at $r = R$ be equal to V_s . Then the velocity profile is expressed as

$$u(r) = V_s + \int_0^r \dot{\gamma}(r) dr = V_s + \int_0^r f(\sigma) dr \quad [5.2.32]$$

where, as for any liquid subjected to flow, $\dot{\gamma} = f(\sigma)$ is the flow curve.

It is possible, as usual in the theory of capillary viscometry, to introduce the value of an average shear rate $\dot{\gamma}_0^* = Q/(\pi R^3)$. However, in the case of flow with slip at a wall, the value of $\dot{\gamma}_0^*$ consists of two terms. The first term is the previously introduced value for flow without slip, $\dot{\gamma}_0$, and the second term is a contribution of slip at a wall and equal to V_s/R . Thus:

$$\dot{\gamma}_0^* = \dot{\gamma}_0 + \frac{V_s}{R} \quad [5.2.33]$$

where the slip velocity at a wall, similar to the shear rate, can be a function of shear stress.

The true shear rate at a wall, $\dot{\gamma}_R$, (assuming that the thickness of the wall boundary layer, if this layer does exist, is very small) equals $\dot{\gamma}_0$. It is computed from the Rabinovitsch-Weissenberg formula, but not from $\dot{\gamma}_0$.

The method of determining shear rate, $\dot{\gamma}_0$, and slip velocity directly follows from equation (5.2.33): the dependence of $\dot{\gamma}_0$ on R^{-1} should be plotted, and extrapolated to $R^{-1} = 0$. An example of this plot is shown in Fig. 5.2.4.

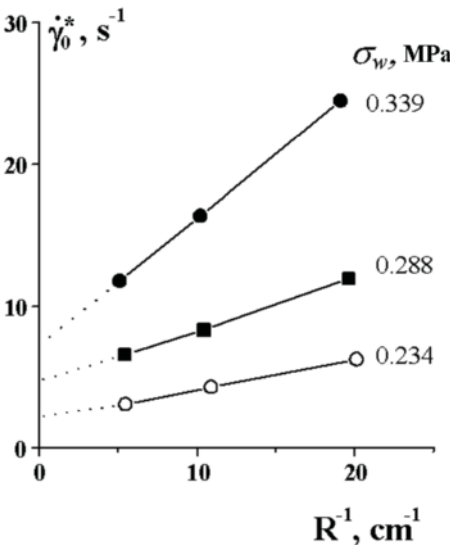


Figure 5.2.4. Determination of slip velocity according to the Mooney method of extrapolation to $R^{-1} = 0$. The example is given for butadiene rubber at 120°C.

The procedure assumes that the greater the radius of a capillary, the lesser the contribution of the slip effects such that it can be completely disregarded at $R^{-1} = 0$.

The phenomenon analogous to a slip at a wall can be observed during flow of multi-component materials. The diffusion of low-viscosity component to a wall of a capillary may affect shearing to be preferentially accomplished with this low-viscosity wall boundary layer and change velocity gradient. The measured apparent viscosity is less than mean viscosity in the volume of a multi-component material. A similar phenomenon can be observed during flow of polydisperse polymers. As a result of diffusion of low-viscosity fractions to a channel surface, the enrichment of wall boundary layer by low-viscosity fractions occurs leading to decrease of apparent viscosity.

5.2.2.7 Adsorption on a channel surface

In the study of viscous properties of dilute polymer solutions, the effect of adsorption of macromolecules on the surface of a capillary was noted¹¹ that is a reverse phenomenon to slippage at a wall. This phenomenon is especially noticeable during use of capillaries of a very small radius. It leads to decrease in surface area of effective flow, and, correspondingly, to increase in apparent viscosity. Adsorption is strongly enhanced in studies of polymer solutions capable of interactions with capillary surface.

Adsorption phenomena must be considered with capillaries having diameter of up to several tens of microns (e.g., filtration through porous media or capillary flow of biological substances).

The effect of adsorption is usually expressed by a certain effective thickness of the adsorption layer on the surface of a capillary and is computed using volumetric flow rates, measured on capillaries of different radii.

5.2.3 FLOW IN INCOMPLETELY FILLED CAPILLARY

Observation of the boundary shift of a sample, which partially fills a capillary, is a unique version of the capillary method of viscosity measurement. Such experiments are carried out at low external pressures, or, more generally, in the absence of external pressure. The driving force in such an experiment may be the gravitational forces or the surface tension forces.

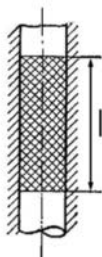


Figure 5.2.5. Partially filled capillary.

5.2.3.1 Motion under action of gravitation forces

Let us consider that liquid is filled into a capillary up to a certain height and it is moving in the absence of external pressure under its own gravitational force, as shown in Fig. 5.2.5. The height of the sample, l , the density of liquid, ρ , and viscosity, η , of liquid do not depend on shear rate. Then, the distribution of velocity along the radius is described by a parabolic law:

$$u(r) = \frac{\rho g R^2}{4\eta} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad [5.2.34]$$

where g is the gravitational acceleration, and product ρg determines the stresses arising under the action of weight of column of liquid.

If we now measure velocity of meniscus movement, U_0 , (on the axis of channel at $r = 0$), then viscosity is calculated from the formula:

$$\eta = \frac{\rho g R^2}{4U_0} \quad [5.2.35]$$

Velocity measurement of meniscus curving of an initially strictly cylindrical sample is a special case of the method under discussion. Viscosity is calculated from Eq. 5.2.35.

This procedure is especially convenient for viscosity measurements of high-viscosity materials at low shear rates and stresses. The range of shear rates in these measurements is 10^{-4} to 10^{-2} s^{-1} , and shear stresses are of an order of 10^2 Pa .

5.2.3.2 Motion caused by surface tension forces

Let liquid in a capillary, placed at angle ϕ to the horizontal surface, rise under action of surface tension. Then, from the condition of force equilibrium, the following formula is obtained for calculating the length of capillary, l_0 , filled with liquid:

$$l_0 = \frac{2\sigma \cos \beta}{\rho g R \sin \phi} \quad [5.2.36]$$

where σ is the coefficient of surface tension, β is the angle of contact formed by meniscus and surface of capillary, ρ is the liquid density.

The measurement of l_0 under equilibrium conditions makes it possible to determine $\sigma \cos \beta$, which defines velocity of liquid in a capillary. The shear stress at a capillary wall is calculated as

$$\sigma_R = \frac{\sigma \cos \beta}{1} - \frac{R \rho g \sin \phi}{2} \quad [5.2.37]$$

where l is variable length of a capillary filled with liquid under study.

Hence, viscosity is calculated from the formula:

$$\eta = \frac{R(2\sigma \cos \beta - R l \rho g \sin \phi)}{8l(dl/dt)} \quad [5.2.38]$$

This procedure can be used for measurements of viscosity of Newtonian liquids and yield stress of viscoplastic media.

5.2.4 LIMITS OF CAPILLARY VISCOMETRY

The capability of capillary viscometry is determined by fulfilling certain requirements that were formulated in Section 2.1.1. Therefore, the limitations of capillary viscometry are determined by the following effects:

- transition from laminar to turbulent flow conditions
- instability of flow as a result of fluid elasticity
- mechanical and thermal degradation of test specimen
- strong thermal effects at the high deformation rates.

The upper boundary of shear rates in capillary viscometry is $\sim 10^6 \text{ s}^{-1}$. In usual instruments, this limit is up to 10^4 s^{-1} . The upper range of 10^4 – 10^6 s^{-1} is only possible with special experimental techniques.

Lower boundary of shear rates is determined, to a considerable extent, by the patience of experimenter, because flow is very slow, and by some other considerations. First, the measurement of small movements of a fraction of a millimeter over a long time

requires use of a high-precision measurement technique, because of potential systematic instrument errors, caused by prolonged measurements. Second, the permissible duration of measurement is limited by both chemical and structural stability of the investigated material under the imposed experimental conditions. Therefore, as a general rule, during measurements by capillary viscometry, it is very difficult to go below shear rates of $\sim 10^{-2} \text{ s}^{-1}$.

The upper limit of shear stress is determined by the appearance of instability, excessive thermal effects, and by mechanical and thermal degradation. The upper limit in any case does not exceed the value of 1 MPa.

The lower limit of shear stress is determined by the influence of parasitic resistance, which appears practically in any design of capillary viscometers and contributes to error that is difficult to account for during measurements. In capillary viscometers it is practically impossible to go below the shear stress of $\sim 10^2 \text{ Pa}$.

The comparison of the above-indicated limitations on shear rates and shear stresses shows that capillary viscometers can measure viscosity in the range of 10^{-3} to $10^7 \text{ Pa}\cdot\text{s}$. Different measurement techniques are used for different ranges of viscosity.

5.2.5 NON-VISCOMETRIC MEASUREMENTS USING CAPILLARY VISCOMETERS

In addition to viscosity, numerous attempts are made to use capillary instruments for evaluating other rheological properties of materials. These evaluations are based on general principles of rheology. In these cases, the estimates of various properties are obtained but not their absolute values.

The most obvious is the use of a shape of flow curve as characteristics related to the structural features or elastic properties of polymeric materials.

The elasticity of melts and solutions of polymers are evaluated according to two parameters – the capillary entrance correction and the extrudate swell at the exit from the capillary.

The problems concerning determination of the entrance correction were previously discussed.

As far as the extrudate swell is concerned, evaluation of elasticity is based on the experimental fact that the diameter of extrudate at the capillary exit is larger than the diameter of the capillary. This effect is related to elasticity of flowing material. The extrudate swell (coefficient of swelling), α , defined as the ratio of diameters of extrudate and capillary, serves as a measure of the elastic properties of material.

The basic methodological difficulty in measuring the extrudate swell, α , is related to the fact that the measurements must be carried out under isothermal conditions on extrudate leaving a capillary, since α depends on temperature. The relationship between α and other rheological properties, or characteristics of molecular structure of polymer, is established on the basis of corresponding rheological theories and concepts.

5.2.6 CAPILLARY VISCOMETERS

5.2.6.1 Classification of the basic types of instruments

From the general theory of capillary viscometry, it follows that for determining the viscosity, two parameters, pressure and volumetric flow rate, have to be measured. Typically,

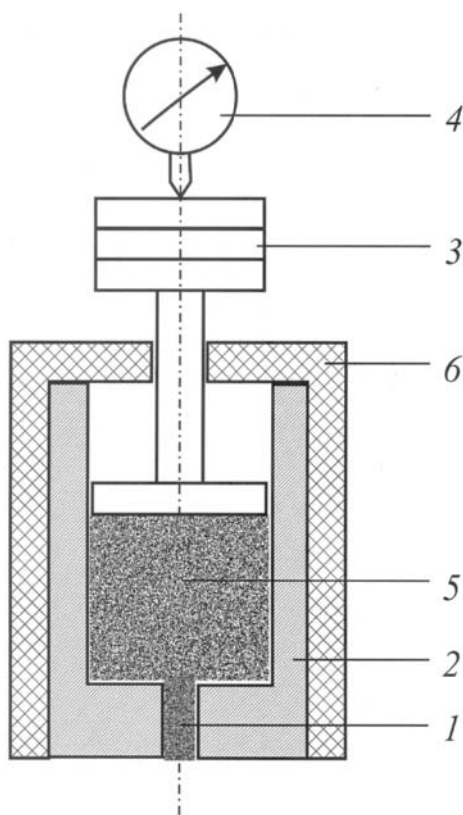


Figure 5.2.6. Typical scheme of a load capillary viscometer. Instrument for measurement of melt flow index. 1 – measuring calibrated capillary; 2 – reservoir; 3 – load; 4 – displacement indicator; 5 – polymer melt; 6 – heating element and heating chamber.

type are equipped with a high-precision drive with adjustable speed of motion over a wide range.

Modern instruments usually contain measuring devices (sensors) with output of the measured parameters acquired by a data acquisition system connected to a computer for automatic processing of measurement results using computer programs, supplied by the instrument manufacturer.

Below, the basic standard solutions will be examined, which have found wide applications in contemporary research practice.

5.2.6.2 Viscometers with the assigned load

5.2.6.2.1 Load viscometers

The most popular instrument of such type, utilized in many laboratories, is a *Melt Indexer*. This instrument measures the *melt flow index*, MFI, or the *melt flow rate*, MFR, of polymers. The MFI is the value of the volumetric flow during 10 min, measured under strictly standardized conditions at a specified temperature and load on instrument with the spe-

one of these parameters is *assigned*, and another is *measured*.

Pressure in the capillary tube viscometers is *imposed* by one of the following methods:

- by the load of a specific weight (in the load viscometers)
- by a pressure of compressed gas (in the gas viscometers)
- by a precompressed spring
- by a power drive, in which force with aid of the feedback control is maintained or is regulated according to a required program
- by the weight of liquid being investigated.

Imposition and regulation of velocity of piston stroke (or volumetric flow rate) is achieved with aid of a mechanical or hydraulic drive by a method of varying velocity.

The viscometers of the first group are usually simpler by construction and more frequently used for standardized measurements.

The viscometers of the second group are usually constructed on the basis of standard testing machines (used for measurements of mechanical characteristics of solids), since modern machines of such

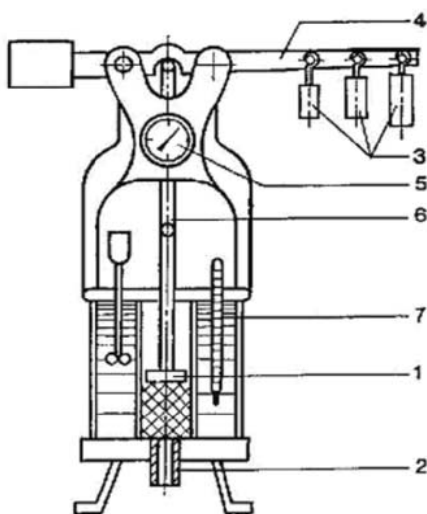


Figure 5.2.7. Load capillary viscometer with lever loading system. 1 – plunger transferring pressure to sample placed under it; 2 – measuring calibrated capillary; 3 – imposed load; 4 – lever; 5 – displacement indicator; 6 – intermediate rod transferring load; 7 – liquid thermostat.

method of measurement of volumetric flow rate by measuring the speed of a lowering piston with the aid of a dial indicator and stopwatch. However, in the majority of modern instruments, the automated method of measurement of the piston speed with an aid of various electromagnetic sensors is used. The standardized instruments for measurement of melt flow index are manufactured by a number of companies.

The pressure can simply be generated with the aid of a load as shown in Fig. 5.2.6, or using a lever system (Fig. 5.2.7). Here, pressure is varied not only by change of the load weight, but also by varying the length of an arm of the lever, through which the load is transferred to the test specimen. This way, it is possible to somewhat widen the range of the imposed loads.

5.2.6.2.2 Gas viscometers

A tendency to increase a range of imposed loads, and, correspondingly, the shear stresses, led to an idea of using pressure of compressed gas. This method may easily reach pressures of an order of 20 MPa (200 bar), and using multiplier it is possible to increase this pressure to 60 MPa (600 bar). With such loads, maximum shear stresses suitable for conducting rheological measurements can be reached.

The system for generating and controlling pressure in a typical gas viscometer is shown in Fig. 5.2.8. A standard pressurized tank of nitrogen gas is the primary source of pressure generation. Initial pressure is reduced and it is maintained at the required level using an intermediate tank of a large volume so that the gas flow during sample extrusion from the viscometer would not cause a noticeable pressure drop. Error of pressure mea-

cific dimensions of capillary and reservoir. According to definition, MFI is expressed in g/10min.

The schematic diagram of such an instrument is shown in Fig. 5.2.6. This instrument basically consists of a calibrated capillary with the following standardized dimensions: length, $L = 8.000 \pm 0.002$ mm; diameter, $D = 2.098 \pm 0.005$ mm.

According to ASTM D 1238, the length of the capillary must be 9.550 ± 0.007 mm.

The weight of the load, which creates pressure, is also fixed by appropriate standards. Basic weight is $2,160 \pm 10$ g. It is also permissible to use loads with weights of $5,000 \pm 10$ g, $10,000 \pm 15$ g, and $21,600 \pm 20$ g.

According to ASTM, different loads can be utilized, such that different combinations of temperature and load weight are possible, which determine measurement procedures.

Fig. 5.2.6 shows the simplest manual

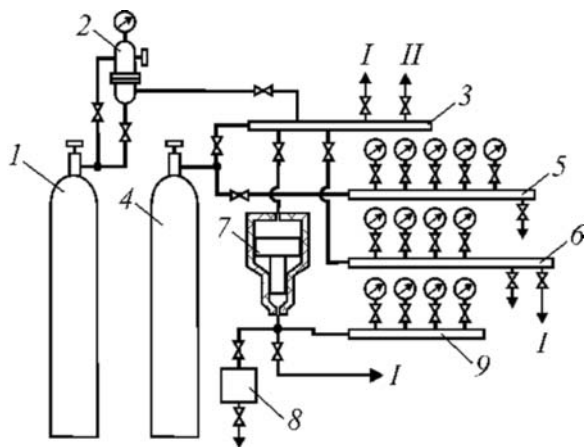


Figure 5.2.8. Scheme for imposing pressure in gas capillary viscometer. 1 – replaceable high pressure tank; 2 – pressure regulator; 3 – distributing manifold; 4 – intermediate tank maintaining imposed pressure; 5, 6, 9 – pressure gauge display including gauges of various ranges of pressure; 7 – hydraulic multiplier; 8 – liquid pump. I – line of pressure supply to reservoir of viscometer. II – line connected to vacuum system.

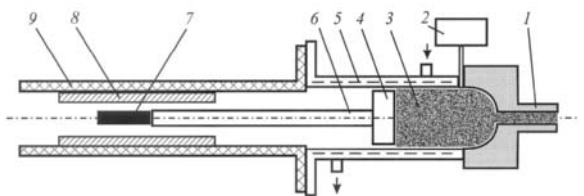


Figure 5.2.9. Scheme of gas capillary viscometer with automatic remote measurement of volumetric flow rate using a linear voltage differential transformer (LVDT). 1 – measuring calibrated capillary; 2 – pressure transducer; 3 – sample; 4 – plunger; 5 – thermostat; 6 – rod made of glass fiber filled plastics; 7 – LVDT rod; 8 – LVDT coil; 9 – main body of instrument. [Adapted, by permission, from J. E. Bujake Jr., *Rev. Sci. Instr.*, **36**, 1368 (1965)].

surement does not exceed 1%. The pressure ranges from 0.01 to 60 MPa (from 0.1 to 600 bar).

Gas viscometers are instruments typically used for research purposes. For realization of their great possibilities such viscometers are equipped with a series of capillaries of different lengths and diameters, made from various materials and supplied with inserts in order to vary the entrance geometry. These instruments are also used as components of different *rheo-optical* devices, in which the direct measurements of viscosity are supplemented by observation of the optical monitoring of flow.

Discharge velocity is usually measured by determining the weight of extrudate cut off at assigned time intervals.

Gas viscometers measure in the range of shear rates from about 10^{-3} to 10^4 s $^{-1}$ and shear stresses from about 10^2 to 10^6 Pa. Instruments are supplied with temperature controllers permitting measurements in the range of temperatures from -40 to 250°C using liquid for cooling/heating and electrical heating up to 400°C .

The method of measurement of volumetric flow rate is an essential drawback of an instrument of this type. In this instrument the weight of extrudate (not its volume) is measured. Density of melt at temperature of experiment has to be measured in a separate experiment.

A possible scheme of non-contact (remote) automatic measurement of volumetric flow rate is realized in the instrument shown in Fig. 5.2.9. In essence, this is a typical gas viscometer. However, this instrument is equipped with a closed system of the automatic measurement of speed, and also with a pressure sensor, mounted directly before the entrance into the capillary. Experimental data are processed by computer.

A modern industrial version of a gas capillary tube viscometer (in accordance with the requirements of various standards, ISO 11443, ASTM D 3836 and DIN 54811) is man-

ufactured by Goettfert (Germany) under the name *Rheograph 200*. In this instrument, measurements are accomplished using two cylindrical reservoirs installed in parallel (a version of this instrument with one cylinder is also possible). The instrument applies pressure in a broad range, from 0.1 to 210 bar. The heating chamber helps to obtain 400°C with deviations from the assigned temperature of not more than 0.1°C. The instrument can be used with change of cylinders and capillaries.

5.2.6.2.3 Viscometers with varying load

Two types of capillary tube viscometers with varying load are available. In the first case, the load is varied with the aid of various design solutions. This is based on a feedback control in which load changes according to a predetermined program, controlled by pressure sensor. Another version is based on automatic load change.

Instruments with the spring load were very popular in the 1960-1970's, but at present these instruments should be considered as antiquated, since the varying load (if necessary) is simpler to achieve using an automatic system for feedback control.

Instruments with the automatic load control are traditional according to their design features. The control system in these instruments is their main attribute, although it is also solved by conventional methods of control.

Instruments are loaded by weight of the column of liquid whose height changes during experiment. Instruments of this type are used for relative measurement of viscosity. The viscosity measurements are carried out by using some measures (for example, by measuring duration of discharge of a calibrated volume of liquid), or by comparison with the standard liquids.

These instruments include viscometers of free discharge, which can be called “cup” and “glass” viscometers.

5.2.6.3 Cup viscometers

A characteristic example of a cup viscometer is shown in Fig. 5.2.10.¹² The liquid being investigated is filled into container of a specific size, at the end of which the calibrated capillary is installed. Usually the time of discharge of a specified (standardized) volume of liquid through a capillary is measured. After removal of the plug from the instrument shown in Fig. 5.2.10, liquid flows to a measuring flask having a volume of 60 cm³. The time required to fill this volume is used as a measure of viscosity. The reliability and reproducibility of results are characterized by variation of the time of discharge of a standard sample. If measured values of the standard sample are not within 1%, the viscometer is rejected as a measuring device.

There is a wide group of instruments and methods similar to the instrument in Fig. 5.2.10. The *Engler* and the *Redwood viscometers* are utilized in European countries. These instruments were initially intended for measuring viscosity of petroleum products and lubricating oils, but they are now used for other liquids.

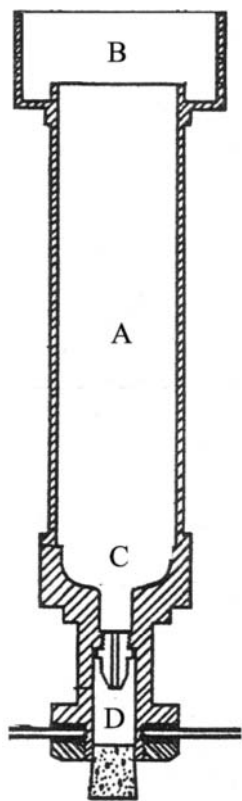


Figure 5.2.10. Measuring part of the Saybolt viscometer. A – internal reservoir; B – die of large diameter; C – lower die; D – calibrated capillary; E – cork.

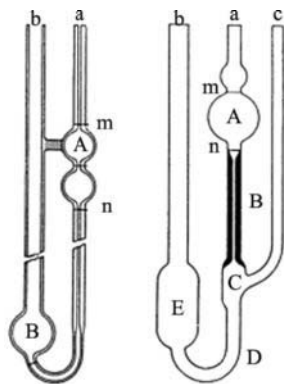


Figure 5.2.11. The Ostwald-Fenske (left) and the Ubbelohde (right) capillary viscometers. In Ostwald-Fenske viscometer: A and B bulbs; a and b – arms; capillary inserted in arm a; m and n – marks. In Ubbelohde viscometer: A – bulb with marks m and n; B – capillary; C – bulb; D – transition tube; E – reservoir bulb; a, b and c – arms.

Results of measurements are in relative units. Conversion tables of these values to the absolute viscosity are available.

These instruments seem primitive and obsolete, but they play an important role in standardization of methods of measurements and they are successfully used in industry.

5.2.6.4 Glass viscometers

Glass viscometers are included in a special group because they are made out of glass and utilized at comparatively small pressures, which cause flow. Pressure in such instruments is created by the weight of a column of liquid being investigated, although the application of additional pressure is not excluded. Instruments of such type are widely used in laboratories and industrial practice for evaluating viscosity of dilute polymer solutions, which, in turn, is used as a measure of molecular weight of polymer. Although many original constructions of capillary tube viscometers are known, two basic versions of glass viscometers used in practice are shown in Fig. 5.2.11.

The *Ostwald-Fenske viscometer* is filled through the arm b with investigated liquid, which is then sucked above marker m. Liquid is allowed to flow and time of flow from marker m to marker n is measured. This time serves as a measure of viscosity. If dimensions of a capillary are known, then the absolute value of kinematic viscosity can be calculated by comparison of time for unknown sample with time of discharge of a standard liquid of known viscosity. In reality, this instrument measures relative values of kinematic viscosity.

The *Ubbelohde viscometer* is an improved version of the Ostwald-Fenske viscometer. An important advantage of this instrument, which caused its wide acceptance, is automatic maintenance of an identical level of liquid that is independent of their individual properties. This method provides high accuracy and excellent reproducibility of measurements. To achieve reliable results of measurements, the viscometer is placed in the thermostating bath, which ensures the maintenance of the assigned temperature with high accuracy.

Glass viscometers can be used for measurement of viscosity from fractions of cSt to a few hundred St. Shear stress from 1 to about 100 Pa, and shear rates from 10^{-2} to 10^4 s $^{-1}$ can be measured.

Pressure changes in the process of measurement. It is not always clear at what shear stress viscosity is measured. A certain smoothing of influence of pressure change in the process of measurement is achieved by using a monostat, that is, a device for maintaining constant pressure, in essence similar to that discussed with gas viscometers. The discharge of liquid through a capillary occurs under external pressure acting in addition to the weight of a column of liquid. Then, flow is accomplished in the opposite direction. The effect of pressure of the column of liquid is excluded from the external pressure.

Glass viscometers are used for relative measurements. The calibration of the viscometer is performed on liquids of known viscosity. This permits measurement of absolute

values of kinematic viscosity using a ratio of discharge times. The main characteristic of the viscometer is the discharge time, t_0 , for a standard liquid. The discharge time depends on geometric dimensions, especially the diameter of the capillary. It is desirable that the discharge time satisfies this condition: $t_0 > 100$ s. If so, it is possible to disregard corrections for kinetic energy. Instruments have acquired primary acceptance in determination of *intrinsic viscosity* of highly dilute polymer solutions. Intrinsic viscosity is extrapolated from results of relative viscosity of polymer solutions at different concentrations to zero concentration of polymer.

Glass viscometers are manufactured with different sizes of measuring reservoirs and capillaries. This permits variation of mean pressure in sequential measurements. It also possible to monitor if there is a dependence of viscosity and shear stress. The automation of measurement procedure is the basic tendency with capillary tube viscometers. Higher accuracy and reproducibility of automated equipment reduces the measurement error of time to 0.001 s.

In the most improved version of this instrument, all basic elements of instrument operation are automated, such as the measurement of discharge time using photoelectric transducers, the stepwise dilution of solution (for example, by 1.5, 2, 3 and 6 times), which is necessary for obtaining the series of points for extrapolation to zero concentration, and calculation of intrinsic viscosity according to one of the known procedures. In commercially manufactured glass viscometers, a measurement error is $\sim 1\%$, in the most precise viscometers, it can be lowered to $\sim 0.01\%$.

For viscosity measurements at low shear rates (less than 1 s^{-1}), the capillary is made in the form of a long spiral. In this case the curvature of the channel can be disregarded because of low flow rate. Several designs of glass viscometers were also proposed for chemically active, unstable or highly volatile liquids.¹³

The number of versions of glass viscometers includes the combination of viscometer with a system of fractionation of polymers (achieved by a method of gel permeation chromatography). This makes it possible to fully automate the process of determining the molecular-mass distribution of polymers and/or evaluation of their degree of branching.¹⁴

5.2.7 VISCOMETERS WITH CONTROLLED FLOW RATE

Various methods are known for imposition of constant or controlled flow rate of liquid through a capillary varying according to a predetermined program. In this case, the measured parameter is the pressure at the entrance into the capillary or the force necessary for maintaining a given rate.

The following methods of regulating the rate of flow are available: mechanical power drive, which creates the motion of plunger, hydraulic drive, and extrusion of material through a capillary, installed in a discharge head.

5.2.7.1 Instruments with a power drive

These instruments are most frequently used for imposition of a constant volumetric flow rate. Adjustable drive creates a constant velocity of displacement of the plunger, extruding material from the reservoir of the viscometer through a capillary. The popularity of such instruments is caused by wide acceptance in research practice of mechanical testing machines for solid materials in extension or compression. These machines, produced by a number of companies, are well developed, reliable devices, supplied with heavy-duty

drives. The entire construction of the machine is sufficiently rigid to ensure a strict maintenance of the assigned conditions of deformation. Contemporary testing machines of such type are supplied with reliable force transducers capable of measuring pressure over a wide range and with a good accuracy.

All this makes such testing machines an excellent base for manufacturing viscometers of constant flow rates. For this purpose the upper clamp, rigidly attached to the adjustable drive, is connected to a plunger of the viscometer. The viscometer itself is installed on the lower fixed base plate of the testing machine.

Viscometers of such type, built on the base of the *Instron* testing machine, were manufactured under the name of *Rheometer 3210* or *Rheometer 3211*. These instruments measure viscosity of plastics in the range of shear rates from 10^{-2} to 10^5 s^{-1} and at practically unlimitedly high shear stresses. The lower range of reliably measured shear stresses is usually close to 100 Pa.

Control features of Instron viscometers permit conducting measurements not only at a constant speed, but also at a variable plunger speed according to a predetermined program.

Another instrument, similar to Instron, is the *Monsanto Processibility Tester*, MPT, originally manufactured by *Monsanto Instrument Company* (now *Flexsys*) for measurement of viscosity of elastomers under conditions of imposing flow rate. This instrument operates in the range of shear rates from 1 to several thousand s^{-1} . The pressure transducer in the MPT is placed in a reservoir just before the capillary entrance. It is also supplied with a laser source to measure the extrudate swell. The instrument is supplied with capillaries of various lengths and diameters if the need arises to measure the slip effect during flow of rubbers. A thermostat chamber is supplied to carry out measurements at different temperatures. This instrument is widely used in the rubber industry for evaluation of processibility of rubber compounds.

An instrument with all the basic capabilities of viscometers of this type is manufactured by *Rheometrics Scientific* (now *TA Instruments*, USA) under the name *Advanced Capillary Extrusion Rheometer* (ACER 2000). In this instrument, the drive makes it possible to regulate speed of the plunger at a ratio of 1:200,000, providing the possibility to vary shear rates from 0.02 to about $2 \times 10^5 \text{ s}^{-1}$. The replaceable force sensors make it possible to measure the maximal pressures up to 210 MPa, that, with the utilized sizes of operating units, ensures the possibility of reliable measurement of shear stresses on a wall of a capillary from 6×10^{-3} to 10 MPa. The temperature chamber is designed for studies in the temperature range from room to 400°C .

The instrument is supplied with an extensive library of application programs for the processing of experimental data. At the customer's will, the instrument can be fitted with additional devices, for example, for measuring extrudate swell after exit from a capillary.

Instruments of this type have a very high metrological characteristics: the stability of the assigned parameters, the high accuracy of measurement of force, the maintenance of baseline during a prolonged experiment, the compensation for parasitic loads, etc. All this makes these viscometers very valuable laboratory instruments for multi-purpose testing of different liquids.

5.2.7.2 Instruments with hydraulic drive

In such instruments the constant velocity of the plunger is imposed and maintained using a hydraulic system, controlled by an adjustable hydraulic pump. This method was realized, for example, in instruments manufactured in the USA by Standard Oil.¹⁵

This instrument makes it possible to conduct viscosity measurements in the range from 2.5 to 10^4 Pa*s with shear stresses below 6.5×10^4 Pa. Since the output of the hydraulic pump is constant, shear rate can be varied, only by a change of capillaries.

There is also a modification of this instrument, in which a continuous change of output of the hydraulic pump is realized and, accordingly, shear rate can be changed during measurements.

5.2.7.3 Extrusion rheometers

An extruder is a technological equipment, which creates a continuous flow of polymer melt. It suffices to install at the exit from the extruder a shaping die in a capillary form and to accurately measure pressure and temperature at the capillary inlet. Using these modifications a capillary tube viscometer of a constant flow rate is obtained. Viscosity of polymer melts can be estimated using a set of capillaries of different lengths.

This method of viscosity measurement is realized in some commercially produced instruments. The operating principle of these instruments differs by the construction of the pressure sensor. The uncertainty of sample prehistory, which may influence measurement results, is not considered in such instruments. With respect to their accuracy, extrusion viscometers are inferior to specially designed capillary tube viscometers.

5.2.7.4 Technological capillary tube viscometers

Capillary flow can be used as a method to control viscosity directly under production conditions. A device which has a measuring capillary is installed in such a way that there is a possibility of sampling from this installation. This can be a reactor, pipeline, etc. In essence, the viscometer itself, utilized for the purpose of continuous technological control, differs little from any other capillary tube viscometers; it is only essential that it is possible to install this instrument on the production line.

Some companies manufacture viscometers specially intended for use in the technological conditions of production. A characteristic example is a viscometer named the *Process Control Rheometer PCR-20*, manufactured by Rheometrics Scientific (TA Instruments, USA). In this instrument, sampling with a strictly controlled volumetric flow rate is achieved from a production line using a dosing pump. A sample being investigated is pushed through a slit capillary, at the ends of which pressure sensors are installed. This instrument is supplied with a set of capillaries of different sizes. Moreover, dosing pumps of different outputs can be used.

5.3 ROTATIONAL RHEOMETRY

5.3.1 TASKS AND CAPABILITIES OF THE METHOD

5.3.1.1 Viscometric and non-viscometric measurements

The use of rotational instruments makes it possible to measure various parameters characterizing rheological properties of materials. Therefore, in discussion of rotational viscometers, it is more appropriate to use a general term of *rheometry*.

Special features of application of rotational instruments for investigation of rheological properties of liquids are as follows. The use of rotational instruments makes it possible, firstly, to create within the sample the homogeneous regime of deformation with strictly controlled kinematic and dynamic characteristics, and, secondly, to maintain the assigned regime of flow for unlimited period of time.

During material testing by rotational rheometry, different regimes of deformation are possible. The most important among them is imposition of a constant rotational speed $\Omega = \text{const}$, or a constant torque, $T = \text{const}$. However, in many modern instruments the method of scanning (or sweep) – imposition of the controlled change of rotational speed or torque with time is realized.

Furthermore, in many rotational rheometers the capabilities of imposing harmonic oscillations for measuring the viscoelastic properties of materials have been created.

In all cases of application of rotational rheometry, a strictly one-dimensional circumferential flow is assumed with secondary flows being absent.

5.3.1.2 The method of a constant frequency of rotation

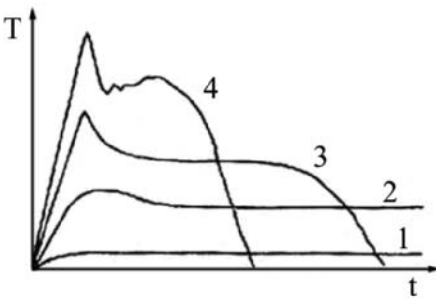


Figure 5.3.1. Typical relationships of torque, T , on time, t , at various rotational speeds. Rotational speed increases from curve 1 to 4.

The typical experimental results, obtained from tests by this method, are shown in Fig. 5.3.1 in the form of the time-dependent torque, T , which is related to the shear stress. In all cases, deformation at first leads to the appearance of a more or less extensive transient response. At the lowest speed (curve 1), the monotonic dependence of $T(t)$ is observed until a steady-state flow process is reached. With an increase of speed (curve 2) during the transient stage, the shear stress maximum (stress overshoot) appears. With a further increase of speed (curve 3), the stress overshoot becomes more pronounced, and

the region of steady flow, although it is observed, is followed by a drop in torque, which indicates that an unstable regime of deformation is approached. Finally, at very high speeds (curve 4) steady flow is generally impossible. As a general rule, a drop in torque is an indication of the appearance of ruptures in a sample or its detachment from the solid rotating or stationary surface (cohesive or adhesive rupture).

Sometimes, a periodic stick-slip behavior occurs which is evident because of periodic oscillations of torque. Significant influence on this phenomenon renders the rigidity (deformability) of the torsional shaft-force transducer assembly, since its deformation leads to deviation from the assigned regime of $\Omega = \text{const}$, which contributes to the onset of oscillations.

During imposition of regime of deformation with $\Omega = \text{const}$ and use of a rigid force transducer, a change in measured torque with time is equivalent to shear stress, moreover shear strains are easily calculated as

$$\gamma = \dot{\gamma}t$$

[5.3.1]

such that at $\Omega = \text{const}$ or $\dot{\gamma} = \text{const}$, the dependence of $\sigma(t)$ is equivalent to the dependence of $\sigma(\gamma)$.

From dependence of $\sigma(\gamma)$, it is possible to determine a number of characteristic (non-viscometric) properties of material being investigated.

The modulus of elasticity, G , in shear can be evaluated by different methods. The dependence of $\sigma(\gamma)$ at $t \rightarrow 0$ can be treated as a reflection of elastic deformations, because, at the initial stages of deformation, flow is absent. Then

$$G = \sigma/\gamma \quad [5.3.2]$$

The initial section of the deformation curve is always measured with a significant error because of the inertia effects and deformation of a transducer itself. In some rotational instruments a possibility of direct measurements of the accumulated elastic deformations, γ_r , is provided. Then, the modulus of elasticity can be evaluated as

$$G = \sigma/\gamma_r \quad [5.3.3]$$

where σ is shear stress.

Rubbery deformation, γ_r , can be measured in different stages of shear, in particular in a transient stage. Then it is possible to trace the evolution of elastic deformations, in particular, to find the maximum value of γ_r which is attained in the transient stage of shear. This value of $\gamma_{r,\text{max}}$ may be related to the maximum deformability of individual macromolecules or their segments before structural network is destroyed by deformation.

The limit of shear strength, σ_{max} , corresponding to its deformation, γ_m , at a given shear rate (i.e., the point of maximum on a shear stress-deformation curve) is frequently treated as a condition corresponding to destruction of the structural physical network, which impedes a development of flow. Both values, σ_{max} and γ_m , depend on the deformation rate.

5.3.1.3 The method of a constant torque

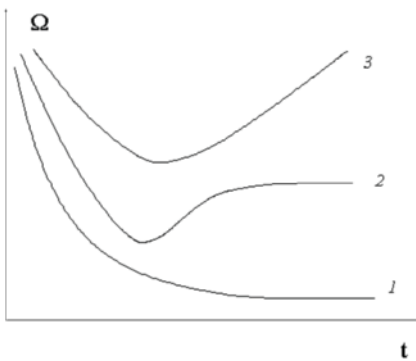


Figure 5.3.2. Typical dependencies of angular velocity on time at different levels of imposed constant torque: 1 – low torque (monotonic change of velocity before achieving steady state); 2 – medium torque (steady state flow is achieved after passing through a minimum of velocity); 3 – high torque (steady state flow is absent).

Typical character of an observed evolution with time of the rotation speed of measuring surface at different imposed constant values of torque is shown in Fig. 5.3.2. In all cases, in the region of small times, it is difficult to perform reliable measurements because of high initial velocity. Stress cannot be imposed instantly and, therefore, the initial section of curve remains undetermined. This uncertainty is further aggravated by the presence of inertia effects.

At low torque values (and, respectively, shear stresses) slow monotonic transition to the steady viscous flow is observed (curve 1). At higher stresses, speed passes through a minimum and only then the regime of steady-state flow is reached (curve 2). At very high shear

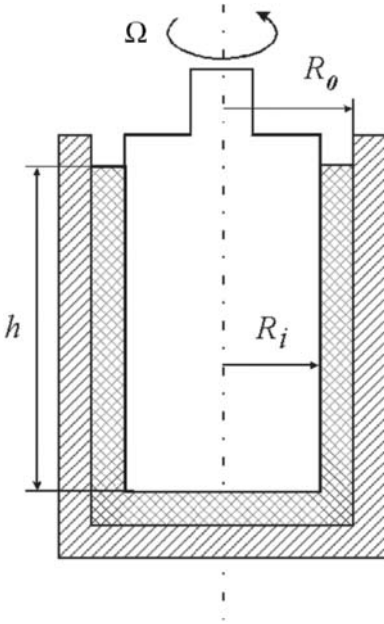


Figure 5.3.3. Schematic representation of viscometer with working cell consisting of two coaxial cylinders.

stresses, after achieving the minimum of speed, a steady-state flow is generally impossible due to a gradual adhesive detachment of sample from the measuring surface or a cohesive rupture of sample.

In practice of rotational rheometry, the application of a method of $T = \text{const}$ is limited. However, this method can be useful, at least, in the following cases:

- measurements of creep, which is one of the basic methods of determining the viscoelastic properties of material
- scanning regimes of tests, when torque changes according to a predetermined program
- evaluation of lifetime of adhesive or cohesive joints
- evaluation of elastic deformations at different stresses.

5.3.2 BASIC THEORY OF ROTATIONAL INSTRUMENTS

5.3.2.1 Instruments with coaxial cylinders¹⁶

A schematic diagram of a rotational viscometer of the cylinder-cylinder type is shown in Fig. 5.3.3.

Here R_o and R_i are the outer and inner radii of cylinders, respectively. Both cylinders have a common axis (i.e., they are coaxial). The ratio of radii R_o/R_i will subsequently be designated as ϵ . The height of liquid in the clearance between the cylinders is h , and Ω is the rotational speed of the inner cylinder. It is assumed that the outer cylinder is fixed, although only the speed of rotation of cylinders relative to each other is important.

The liquid being investigated is also filled at the bottom of cylinder end. Torque, T , for a layer of liquid, which is located at a distance r from the axis of cylinders is expressed as

$$T = 2\pi r^2 h \sigma \quad [5.3.4]$$

where σ is a shear stress, which acts over the area $2\pi r h$ at a distance r from the axis of the cylinders. At equilibrium condition, torque does not depend on radius. Therefore, the following expressions, which relate the shear stresses σ_o and σ_i acting on surfaces of the outer and inner cylinders, respectively, are valid:

$$T = 2\pi R_o^2 h \sigma_o = 2\pi R_i^2 h \sigma_i = \text{const} \quad [5.3.5]$$

Hence, it follows that the ratio between the stresses acting on the surfaces of cylinders is expressed as

$$\frac{\sigma_i}{\sigma_o} = \left(\frac{R_o}{R_i}\right)^2 = \epsilon^2 \quad [5.3.6]$$

It follows from the given formulas that the distribution of shear stresses along a radius is expressed as:

$$\frac{\sigma(r)}{\sigma_o} = \left(\frac{R_o}{r}\right)^2 \quad [5.3.7]$$

or

$$\frac{\sigma(r)}{\sigma_i} = \left(\frac{R_i}{r}\right)^2 \quad [5.3.8]$$

Thus, the degree of heterogeneity of stresses in liquid is determined by a value of ϵ , i.e., by the ratio of the radii of the cylinders. If ϵ is close to unity (which is typical of many rotational rheometers), then a practically uniform field of stresses in a clearance between the coaxial cylinders occurs. Specifically, the possibility of conducting an experiment in a practically uniform stress field is the major advantage of rotational viscometers.

Liquid resistance is determined by shear rate

$$\dot{\gamma} = r \frac{\partial \omega}{\partial r} \quad [5.3.9]$$

where ω is the angular velocity, which depends on a radial coordinate.

For Newtonian liquid a basic relation, Eq. 3.1.1, is fulfilled. Then, in a general case, obvious calculations give the following expression for velocity distribution, $u(r)$, in the gap between cylinders when the outer cylinder revolves with a frequency, Ω_o , and the inner cylinder with a frequency, Ω_i :

$$u(r) = \frac{(\Omega_o R_o^2 - \Omega_i R_i^2) r^2 - (\Omega_o - \Omega_i) R_i^2 R_o^2}{(R_o^2 - R_i^2) r} \quad [5.3.10]$$

This formula contains, as special cases, two situations when the inner cylinder rotates and the outer cylinder is fixed ($\Omega_i \neq 0$ and $\Omega_o = 0$), and *vice versa*, when the inner cylinder is fixed and the outer cylinder rotates ($\Omega_i = 0$ and $\Omega_o \neq 0$).

According to the diagram in Fig. 5.3.3:

$$u(r) = \frac{\Omega R_i^2 (R_o^2 - r^2)}{(R_o^2 - R_i^2) r} \quad [5.3.11]$$

In this case, the final expression for viscosity takes the form:

$$\eta = \frac{T}{\Omega} \frac{R_o^2 - R_i^2}{4\pi R_o^2 R_i^2 h} \quad [5.3.12]$$

where h is the height of liquid sample between cylinders.

This formula is called the *Margules equation*, which can be rewritten in the form:¹⁷

$$\eta = K \frac{T}{\Omega} \quad [5.3.13]$$

It means that the viscosity can be expressed through the ratio of T/Ω , and the geometry factor or *form-factor*, K :

$$K = \frac{R_o^2 - R_i^2}{4\pi R_o^2 R_i^2 h} \quad [5.3.14]$$

Eq. 5.3.13, according to its structure and physical meaning, is identical to Eq. 5.2.13 in the theory of capillary viscometry.

Let us write down an expression for distribution of shear rate along a radius:

$$\dot{\gamma} = r \frac{d\omega}{dr} = 2\Omega \frac{R_i^2 R_o^2}{R_o^2 - R_i^2} \frac{1}{r^2} \quad [5.3.15]$$

i.e., the distribution of shear rates with an accuracy of a constant factor is equivalent to the distribution of shear stresses (see Eq. 5.3.8).

It is significant that for liquid of a constant viscosity, the torque is proportional to the frequency of rotation. If the ratio of T/Ω is constant, then this is a direct proof that the medium being investigated exhibits properties of a Newtonian liquid.

The method of rotation of a cylinder in the infinite medium is frequently used for measurement of Newtonian liquids, i.e., conditions: $R \rightarrow \infty$ and $\Omega_o = 0$ are satisfied. The viscosity can be expressed as

$$\eta = \frac{T}{4\pi\Omega R_i^2 h} \quad [5.3.16]$$

i.e., again the viscosity is proportional to the ratio of T/Ω with the multiplication factor being the form-factor, K .

For calculating apparent viscosity of non-Newtonian liquids from a measured torque and frequency of rotation in the rotational instrument, the shear rate has to be estimated and correlated with the value of shear stress.

If the clearance between the cylinders, Δ , is small in comparison with the radii of cylinders, i.e.

$$\frac{\Delta}{R_i} = \frac{R_o - R_i}{R_i} \ll 1 \quad [5.3.17]$$

the problem is solved simply.

Then, it is possible to determine the average shear stress, $\bar{\sigma}$, as

$$\bar{\sigma} = \frac{\sigma_o - \sigma_i}{2} \quad [5.3.18]$$

The value of average shear rate is found from Eq. 5.3.15. It is equal to:

$$\dot{\gamma} = \Omega \frac{R_i + R_o}{2(R_o - R_i)} \equiv \frac{\Omega R}{\Delta} \quad [5.3.19]$$

In this case, it is practically not important what value should be used for R in the last formula, the value of R_o or R_i .

However, the situation is more complicated if it is not possible to consider that the clearance is small, or if the dependence of $\sigma(\dot{\gamma})$ is very strong, such that even insignificant changes in the shear rate in the narrow clearance would bring substantial changes in the shear stress.

Then, in a general case, it is possible to write that

$$\dot{\gamma} = r \frac{d\omega}{dr} = f(\sigma) \quad [5.3.20]$$

and since $T/2\pi h = \text{const}$, then $dr/r = d\sigma/2\sigma$ and $d\omega = f(\sigma)d\sigma/2\sigma$.

If the inner cylinder rotates, and the outer cylinder is fixed (i.e. $\omega = 0$ at $r = R_o$ and $\omega = \Omega$ at $r = R_i$), then:

$$\Omega = \frac{1}{2} \int_0^{\sigma_o} \frac{f(\sigma)}{\sigma} d\sigma \quad [5.3.21]$$

When the outer cylinder rotates and the inner cylinder is fixed, Eq. 5.3.21 is also valid but the sign should be changed.

Two cases are possible: the cylinder rotates in an infinite medium (i.e., the clearance between cylinders is infinitely large) or inequality (5.3.17) is not fulfilled.

If $R_o \rightarrow \infty$, then Eq. 5.3.21 takes the form:

$$\Omega = \frac{1}{2} \int_{\sigma_i}^0 \frac{f(\sigma)}{\sigma} d\sigma \quad [5.3.22]$$

The last equation can be differentiated with respect to σ_i to get

$$\dot{\gamma} = f(\sigma) = -2 \frac{d\Omega}{d \ln \sigma_i} \quad [5.3.23]$$

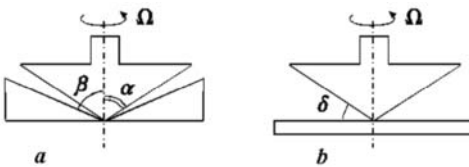


Figure 5.3.4. Schematic representations of rotational viscometers containing conical surfaces: a – cone-cone type viscometer; b – cone-plate type viscometer.

Hence, the dependence of $\dot{\gamma}(\sigma)$ can be determined as follows. The dependence of Ω on σ_i is obtained and then the derivative of this dependence gives the function of $\dot{\gamma} = f(\sigma)$.

The most general (although inconvenient from the experimental point of view) situation arises, when the clearance between cylinders is arbitrary. This case is methodically undesirable. In the practice of rotational rheometry, such a situation is avoided. If this cannot be avoided, then the unknown function of $f(\sigma)$ can be found by analytical methods of regularization, using known algorithms for finding unknown functions on the array of experimental data, if the relation between them is established by integral equation.

5.3.2.2 Instruments with conical surfaces

Instruments with conical surfaces are important in rheometry. They are especially valuable for the analysis of high viscosity fluids.

In this case, two versions of a device are possible, as shown in Fig. 5.3.4. A sample is placed into a clearance between two coaxial cones with a joint apex or into a clearance between the conical surface and the plate with the axis of the cone being normal to the flat surface. It is important that the angle between cones or the cone and the plate is small.

The theory of viscometers with conical surfaces is based on the analysis of flow of liquid in spherical coordinates such that the angle, α , is counted from the vertical axis.

Torque with respect to the vertical axis generates shear stresses, σ . From the equilibrium condition for the volume element of a sample placed into a clearance, it follows that the dependence of $\sigma(\alpha)$ can be expressed as follows:

$$\sigma = \frac{C}{\sin^2 \alpha} \quad [5.3.24]$$

where C is the constant of integration, determined through torque, T , acting on the cone surface.

Thus, if the height of the outer cone in Fig. 5.3.4a equals T , the stress on its surface is σ_α , then the torque is expressed as:

$$T = 2\pi \int_0^H \sigma_\alpha h^3 \frac{\sin^2 \alpha}{\cos^3 \alpha} dh = \frac{2\pi H^3}{3} \frac{\sin^2 \alpha}{\cos^3 \alpha} \sigma_\alpha \quad [5.3.25]$$

Hence, the shear stresses, σ_α , can be calculated from the measured torque values as:

$$\sigma_\alpha = \frac{3T}{2\pi H^3} \frac{\cos^3 \alpha}{\sin^2 \alpha} \quad [5.3.26]$$

The angular distribution of shear stresses in a sample, located in a clearance between cones, is described by the following formula:

$$\sigma(\theta) = \sigma_\alpha \frac{\sin^2 \alpha}{\sin^2 \beta} \quad [5.3.27]$$

The last formula estimates the degree of homogeneity of the stress state in a sample. It is expressed by the ratio $\sin^2 \alpha / \sin^2 \beta$. It also permits calculation of shear stresses at any point of a sample being investigated at any measured (or assigned) torque.

For instruments of the *cone-plate* type, which are most frequently used in practice, the angle δ between the conical surface and the plate is typically made very small ($\delta < 5^\circ$). Then, the degree of homogeneity of the stress state in a sample, that equals $\cos^2 \delta$, is not less than 99%. Therefore, it is possible to consider that $\sigma = \text{const}$ in the entire volume of a sample.

Then the formula for calculating the shear stress in the cone-plate viscometer takes the following form:

$$\sigma = \frac{3T}{2\pi R^3} \quad [5.3.28]$$

In the spherical coordinates a value of shear rate, which is a function of shear stress, is defined as

$$\dot{\gamma} = f(\sigma) = \sin\beta \frac{d\omega}{d\beta} \quad [5.3.29]$$

where ω is the angular velocity, which depends on the angle β .

The instruments with small angles δ are of basic practical interest. The shear rate field, as well as the shear stress field, is practically uniform, and the shear rate with a sufficiently high accuracy is calculated from the simplest formula:

$$\dot{\gamma} = \frac{\Omega}{\delta} \quad [5.3.30]$$

Thus, the apparent viscosity is calculated as

$$\eta = \frac{T}{\Omega} \frac{3\delta}{2\pi R^3} \quad [5.3.31]$$

where, as in the foregoing cases (see Eq. 5.3.13), viscosity is expressed as the ratio of T/Ω with multiplication factor being an instrument constant or form-factor K .

5.3.2.3 Bi-conical viscometers

The combination of cylindrical and conical measuring surfaces serves as a convenient method for elimination of the edge effect. The diagram of the rotational viscometer, called bi-conical, is shown in Fig. 5.3.5.

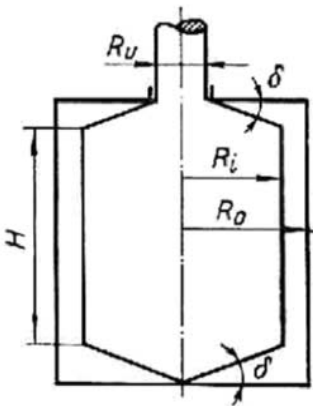


Figure 5.3.5. Schematic representation of rotational viscometer containing cylindrical and conical surfaces – bi-conical viscometer.

The use of a bi-conical viscometer makes it possible to maximally fill a liquid into a clearance between the rotating and the fixed surfaces of a working cell. This prevents viscoelastic material from escaping from a clearance during action of normal stresses (the Weissenberg effect) and, therefore, makes it easier to conduct tests.

It is usually considered that the influence of coupling cylindrical and conical surfaces on the results of measurements is insignificant and the distribution of stresses and shear rates can be calculated separately for the cylindrical and conical parts of the working cell.

The optimum condition of operation of viscometer of such type is realized when the equality of stresses and shear rates on both parts of the instrument is maintained. Then, disregarding possible local effects at the position of coupling of surfaces

of different geometries, it is possible to formulate the following requirement for the geometrical dimensions of bi-conical viscometers:

$$\delta = \frac{R_o - R_i}{R_o} \quad [5.3.32]$$

The relationship between shear stress and torque for the bi-conical viscometer is expressed by the following formula (notations according to Fig. 5.3.5):

$$\sigma = \frac{3T}{2\pi R_i^3} \left[2 + \frac{H}{R_i} - \left(\frac{R_o}{R_i} \right)^3 \right] \quad [5.3.33]$$

5.3.2.4 Disk viscometers

A disk viscometer can be presented as a viscometer in which both conical surfaces degenerate into the parallel plates (disk-disk) separated by a clearance of a height, h . In this case, the liquid being investigated is placed into a clearance between the disks, and one of the disks revolves relative to another around the common axis. This instrument is called the *disk viscometer*.

Torque arises as a result of action of shear stresses, distributed over the surface of disk. This torque is expressed as

$$T = 2\pi \int_0^R r \sigma(r) dr \quad [5.3.34]$$

In this case, the shear rate varies along the radius (in contrast to flow between the cone and the plate, where the shear rate is constant). It is expressed as

$$\dot{\gamma}(r) = \frac{\Omega r}{h} \quad [5.3.35]$$

where Ω is the angular velocity of disk rotation and h is the distance between disks. The variation of the shear rate throughout a volume of a sample being investigated is the main disadvantage of this measuring device. However, if liquid being investigated possesses Newtonian properties, then torque is proportional to the frequency of rotation, and viscosity is calculated from a formula that is analogous in structure to that obtained for other rotational instruments, namely:

$$\eta = \frac{2Th}{\Omega \pi R^4} \quad [5.3.36]$$

where the multiplication factor is the form-factor for this measuring device.

The apparent viscosity of non-Newtonian fluids at the assigned frequency of rotation can be expressed through the maximum shear rate, computed at the edge of disk $\dot{\gamma} = \Omega R/h$. In this case, the calculation of viscosity at this shear rate is reduced to a procedure, analogous to the Rabinowitch-Weissenberg equation in capillary viscometry, namely:¹⁸

$$\eta(\dot{\gamma}_m) = \bar{\eta} \left(1 + 0.25 \frac{d \log \bar{\eta}}{d \log \dot{\gamma}_m} \right) \quad [5.3.37]$$

where $\bar{\eta}$ is the average viscosity computed as

$$\bar{\eta} = \frac{2Th}{\pi R^4 \Omega}$$

Thus, by measuring the dependence of $\bar{\eta}(\dot{\gamma}_m)$ or $T(\Omega)$, it is possible to find the flow curve of non-Newtonian liquid, if, of course, one neglects the edge effects.

The following diagram is an interesting special case of disk viscometers: a thin disk is placed into the infinite medium filled with viscous fluid. Theoretical calculations¹⁹ give the following formula for torque, T , of a disk radius, R , as a function of frequency of rotation, Ω :

$$T = 1.80 R^4 \sqrt{\eta \rho \Omega^3} \quad [5.3.38]$$

where ρ is density of liquid, in which the disk rotates.

According to Eq. 5.3.38, the rotation of a thin disk in viscous fluid is a very special case: the viscosity is defined, not by the ratio of T/Ω , as in all other cases (see Eq. 5.3.13), but by the quantity T^2/Ω^3 .

The *annular viscometer* is a version of the disk viscometer in which the disk is substituted by a ring with an outer radius of R_o and an inner radius of R_i . The apparent viscosity during use of this geometry is also expressed by a formula of the type of Eq. 5.3.13, namely:

$$\eta = \frac{2Th}{\pi(R_o^4 - R_i^4)\Omega} \quad [5.3.39]$$

The advantage of annular viscometers is the fact that the shear rate and stress field in the liquid being investigated can be considered as sufficiently uniform. In this case, the shear stress is calculated as

$$\sigma = \frac{T}{2\pi \bar{R}^2 (R_o - R_i)} \quad [5.3.40]$$

and the shear rate as

$$\dot{\gamma} = \frac{\Omega \bar{R}}{h} \quad [5.3.41]$$

where $\bar{R} = (R_o + R_i)/2$ is the average value of radius and h is the distance between the ring and the plane.

Using Eqs. 5.3.40 and 5.3.41 it is not difficult to find the apparent viscosity and its dependence on the shear rate.

5.3.2.5 Viscometers with spherical surfaces

Two types of viscometers, in which the deformation of liquid being investigated is accomplished by rotation of spherical surfaces, are possible:

- flow between two spheres (or hemispheres) with the same center
- rotation of one sphere in an infinite volume of liquid.

In this case, one of the spheres revolves at a constant angular frequency, Ω , and torque, T , is measured. According to theory, viscosity of Newtonian liquid during flow is calculated as:

$$\eta = \frac{T(R_i^{-3} - R_o^{-3})}{8\pi\Omega} \quad [5.3.42]$$

where R_o and R_i are radii of outer and inner spheres, respectively.

Calculation of apparent viscosity, measured in a spherical viscometer, is also possible for non-Newtonian liquids. But, in order to do so, it is necessary to introduce an assumption regarding the form of the expected flow curve.

The rotating sphere can be placed in a very large (theoretically infinite) volume of fluid. In this case, the wall effect of the vessel on the results of viscosity measurements can be disregarded, and the instrument for viscosity measurements is called a *mono-spherical viscometer*. Then, in the region of low speed of rotation (more precise, the region of $Re \ll 1$), the following formula can be obtained for the calculation of viscosity:

$$\eta = \frac{T}{8\pi\Omega R^3} \quad [5.3.43]$$

where R is the radius of a rotating sphere.

If the rotational speed is not small, then secondary flows appear. In this case, the torque is expressed as follows:²⁰

$$M = 8\pi R^3 \Omega \eta + \frac{\pi}{150} R^7 \Omega^3 \rho^2 \eta \quad [5.3.44]$$

where ρ is density of liquid being investigated.

The second term reflects a contribution of secondary flows to the value of the measured torque, which characterizes viscous properties of liquid. This correction becomes noticeable at sufficiently high values of the Reynolds number.

Eq. 5.3.44 permits finding values of viscosity by measuring torque at different rotational speeds with a subsequent extrapolation in the linear region, in which torque is proportional to the rotational speed.

Mono-spherical viscometers can be of interest as instruments for control of production processes, since it does not represent fundamental difficulties in placing the revolving sphere into an industrial reactor.

5.3.2.6 End (bottom) corrections in instruments with coaxial cylinders

As in the case of capillary viscometry, during the processing of experimental data obtained on the rotational instruments, it is necessary to introduce corrections of different kinds.

Although the geometric form of measuring surfaces in the rotational instruments influences the specific form of corrections, their nature remains one and the same for

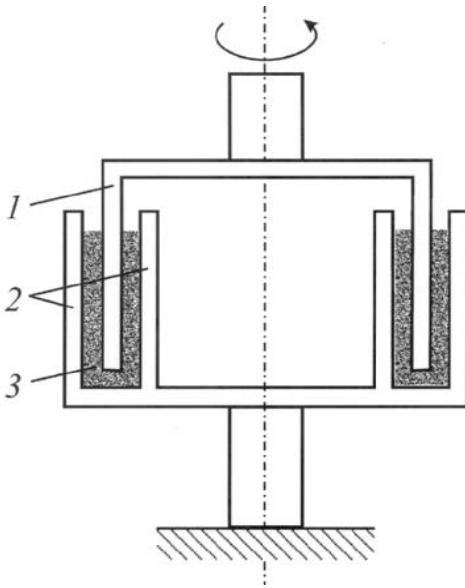


Figure 5.3.6. Rotational viscometer with coaxial cylinders of bell type. 1 – rotating intermediate cylinder; 2 – connected together outer cylinders; 3 – sample.

instruments of different geometry of deformation.

Flow near the bottom and in the bottom region of the coaxial cylinder instrument differs significantly from the theoretical approach utilized for calculating viscosity. Consequently, it is necessary to consider this effect in some manner. Usually this is done by one of the following experimental methods.

The method of two cylinders of different heights. The influence of bottom effect is excluded by the fact that torque is measured at the same frequency of rotation, but using two different cylinders of the same diameter, but having different heights. In this case, the distance from the face of the cylinder to the bottom in both measurements should be identical. The calculation of viscosity is performed based on difference in torques and heights of cylinders inserted into the calculation formula, being

the difference in heights of two cylinders.

The device with guarding cylinders. In this device the outer cylinder revolves. Above and below the inner cylinder are coaxially installed fixed cylinders of the same radii. These cylinders are not rigidly connected with the torque measuring device, but with the stationary casing of the instrument. Therefore, the faces of the measuring (inner) cylinder do not contribute to the measured torque.

The device with bell type cylinders. In this device, shown in Fig. 5.3.6, a pair of hollow cylinders is made in the form of an inverted container, and between them the intermediate revolving cylinder is installed. Due to the small thickness of the wall of this cylinder, the effect of the bottom of the cylinder on torque is negligible. The shear flow of fluid occurs simultaneously in two clearances. The latter must be taken into account in the viscosity calculations.

Arrangement of conical or spherical bottoms. In instruments of this type the bottom is made in the form of a cone or a hemisphere, so that the combination of two rotational viscometers with different geometries of working surfaces is obtained.

5.3.2.7 On a role of rigidity of dynamometer

Measurement of torque is usually accomplished with the aid of elastic elements (*torsional shafts, or dynamometers*) whose deformation serves as a measure of torque. The same scheme is also used in the compensating devices, when deformation of force transducer is compensated by action of external force and this force is measured. In any event, the dynamometer is deformed, and, thus, the conditions of liquid flow are changed. This factor plays no role during the steady-state flow. However, displacement of the dynamometer can have an essential effect on results of measurements of torque in the transient regimes

of deformation before a steady-state flow is achieved and during relaxation (after cessation of flow).

The theory of phenomenon under discussion shows that the greatest error in measurement appears at $t \rightarrow 0$.²¹ Therefore, one should treat the initial stage of transient regime of deformation with special care (see Section 5.3.1).

The general methodical recommendation is to use as rigid dynamometer as possible. In use of the compensating devices, the general requirement is that the response time of the controlling device should be much less than the time of measurement, for example, the characteristic time of a change in the deformation rate in the scanning mode.

5.3.2.8 Temperature effects

At sufficiently high deformation rates, the self-heating of liquid being investigated can be a reason for significant errors. This factor can play a more important role in rotational rheometers than in capillary tube viscometers because of unlimited long stay of the same material under the action of intensive deformation.

During viscous flow of fluid in a rotational instrument different thermal effects are possible, including a rapid increase in temperature that is not compensated by heat transfer (so-called *heat explosion*). More frequent is an increase of temperature to a certain limit, when heat generation is balanced by heat removal. If an increase in temperature is not very high, theory leads to the following formula for calculating apparent viscosity at an assigned temperature of measurement:²²

$$\eta_0 = \frac{\sigma_r h}{u_r} \left(1 + \frac{0.083 h k \sigma_R u_R}{\kappa} \right) \quad [5.3.45]$$

where u_R and σ_R are, respectively, the velocity and shear stress at the boundary surface, κ is the coefficient of thermal conductivity of material being investigated, k is the coefficient characterizing temperature sensitivity of viscosity, h is the clearance between the bounding surfaces in viscometer.

The quantity in front of the brackets in Eq. 5.3.45 is the isothermal value of viscosity, and the second term in brackets is the temperature correction. Then, by measuring values of apparent viscosity at different values of u_R or σ_R and extrapolating the obtained data to zero, it is not difficult to obtain the unknown value of viscosity at an assigned temperature, and, at the same time, the coefficient characterizing temperature sensitivity of viscosity, k .

5.3.3 LIMITATIONS OF ROTATIONAL VISCOMETRY

Possible limitations of rotational viscometry at the low end are related to the design features of experimental techniques used. Thus, while conducting measurements under conditions of imposed strain rates, the required rotational speed is usually created by the power drive with speed control using a system of reducing gears. If such power transfers include many gears, then the natural mechanical imperfection of contacts in gears may lead to inconstancy of the rotational speed, which is expressed by the appearance of shocks. The use of high-quality gears permits shear rates to be as low as 10^{-3} s^{-1} , although the construction of instruments with even lower deformation rates is known.

In using the method of measurement at imposed constant torque, it is necessary to eliminate or compensate resistance caused by friction in moving parts. By using the

method of rotational viscometry, it is possible to measure viscosity of any low-viscosity liquid, and even gas.²³

Basic limitations of rotational viscometry at the upper limit of the high shear rates (and high shear stresses) were indicated above. This, first of all, is an intensive heat generation and it is impossible to maintain a constant temperature of the sample, because of the dissipation of mechanical work at high shear rates and the escape of elastic liquid from a working cell as a result of the Weissenberg effect. The capabilities of rotational rheometry at high shear rates are limited as a result of the appearance of instabilities of flow of different kinds. The physical causes of this phenomenon are the same as described for capillary tube viscometers, although the instability in rotational motion is manifested differently.

Thus, viscosity measurements constitute the right choice only in the region of laminar flow. The critical value of the Reynolds number, Re_c , during the circumferential flow of liquid between coaxial cylinders, for the case when motion is generated by rotation of the inner cylinder, is calculated from the following formula:

$$Re_c = 41.3 \sqrt{\frac{R_o}{R_o - R_i}} \quad [5.3.46]$$

For real dimensions of rotational instruments, this corresponds to a value of Re_c above 100.

If motion is created by rotation of the outer cylinder, then flow remains steady even at the higher values of the Reynolds number.

For viscoelastic liquids, the instability of flow can be caused by their elasticity. This effect may appear as a result of a secondary flow from the eddies arising in the clearance between cylinders, the oscillatory motions of liquid, the detachment of the medium from the walls of the viscometer, the escape of liquid from the working cell, and ruptures inside the sample. In all such cases, measurements are practically impossible. Different types of sample ruptures during the circumferential flows appear at the stresses 5-10 times smaller than the critical stress, σ^* , that corresponds to appearance of elastic turbulence in the capillary flow. It is possible that the reason for this difference is the fact that the rupture is developed with the time of measurement, i.e., σ^* depends on duration of deformation.

Sometimes to eliminate wall slip or ruptures (detachment from walls) in rotational instruments, a hydrostatic pressure is applied. However, the described phenomena are related to elasticity of material, i.e., to its intrinsic properties, and not strictly to phenomena occurring near walls. Therefore, the imposition of additional pressure can be a useful method for warranting the initial adhesive contact of material (especially of high viscosity) with a solid wall. But the stress at which rupture occurs, as a result of deformation, hardly depends on the hydrostatic pressure.

Another recommendation is to corrugate the working surfaces (or increase their roughness). However, the strength of adhesive contact and the cohesive strength of flowing polymeric materials are usually close to each other. Therefore, corrugation of surface, ensuring the best adhesive contact, does not remove slippage at apexes of reefs, because of the cohesive rupture that takes place on the top of reefs.

5.3.4 ROTATIONAL INSTRUMENTS

5.3.4.1 Introduction – general considerations

Rotational viscometry has attracted attention of researchers and designers for many decades. During this time, hundreds of new constructions and many technical improvements of instruments of this type were proposed, described, patented, and found application in research practice. It is worthwhile to note a difference between individual samples of laboratory instruments and viscometers made in a serial production. The latter always appear more attractively made and are supplied with a collection of standard programs for processing experimental results. They are sufficiently simple in operation, so that they do not require a highly qualified experimenter. Instruments of such type are convenient for systematic and repeated measurements to carry out the same tasks each time. However, this does not prevent the possibility of using such instruments for scientific studies, since commercial instruments are frequently supplied with a wide collection of additional options of a high technical level.

At the same time, such instruments are not always suitable for studying new phenomena and refined effects that require additional consideration and understanding of the results of measurements and their possible errors. Certainly, solution of such problems demands a qualified experimenter. Moreover, the data processing systems of some contemporary instruments are designed in such a way that they eliminate possible deviations from “smooth” dependences, considering them as random errors. The apparent (at first glance) random errors in results of measurements can actually be hidden new properties and important results for science.

In spite of a variety of designs and measuring schemes used, it is possible to isolate a number of similar fundamental solutions, common to all instruments. It is possible to identify the basic requirements for rotational viscometers. Thus, for any instrument it is required:

- to have high-quality working surfaces
- to observe coaxiality (for the coaxial cylinders) or strict perpendicularity (for the instruments of the cone and plate type) during their assembly
- to obtain a low parasitic friction in bearing of the rotating part of a working cell (replacement of usual bearings by the gas bearing and use of unsupported construction of the revolving shaft)
- to maintain assigned (constant or adjusted according to the required program) condition of deformation or torque without oscillations and jerks
- to quickly achieve a transient process while imposing the required regime of deformation or load (this requirement is not very important during viscometric measurement, but important during the study of transient processes such as relaxation and creep)
- to control the assigned temperature conditions of tests.

In accordance with these general requirements, the fundamental design of any rotational instrument can be represented in the form of a schematic diagram as depicted in Fig. 5.3.7. All basic elements of the construction of the viscometer are shown in this figure.

The basic element of design is the working cell itself. In Fig. 5.3.7, this is the cylinder with a conical bottom, which revolves around a fixed cylinder that is coaxial with it. Other combinations of axially arranged symmetrical bodies, described above, can be used

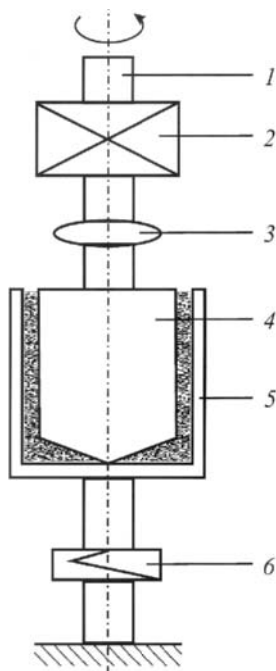


Figure 5.3.7. Schematic representation of rotational viscometer with its basic elements. 1 – rotation drive; 2 – reducer; 3 – angular velocity transducer; 4 – inner (rotating) cylinder; 5 – outer (fixed) cylinder; 6 – torque transducer.

instead. The inner cylinder is subjected to rotation by means of a drive with adjustable speed with the frequency of rotation during the experiment maintained constant or according to a predetermined program. The frequency of rotation is measured by an angular velocity transducer.

In Fig. 5.3.7, the torque transducer is installed on the shaft that connects the outer cylinder with the base of the instrument. This sensor can also be installed on the revolving shaft, measuring the torque experienced by it. Typically, an elastic member torsion shaft is utilized as the working (receiving torque) part of the sensor. The basic requirement for this member is to have a linearity of its performance characteristics, i.e., the dependence of displacement (or angular deflection) on torque. Finally, an important element of the construction of the viscometer (not shown in Fig. 5.3.7) is a temperature chamber since the entire working cell is usually thermostatically controlled. The temperature of the sample is monitored by sensor, which is in direct contact with the material being investigated.

The schematic diagram that is shown in Fig. 5.3.7 can be realized in the existing rotational viscometers in various configurations. However, all basic elements of construction of any viscometer are included in the drawing.

5.3.4.2 Rheogoniometers and elastoviscometers

A large group of instruments with diverse capabilities of rotational rheometry is united under these names. In these instruments, viscosity measurement is augmented by possibilities of determining different characteristics of rheological properties of liquids.

A typical example and the prototype of many instruments of this type is the *Weissenberg Rheogoniometer*, which was manufactured by *Sangamo* (Great Britain).²⁴

In essence, this instrument contains all the basic elements of the diagram, presented in Fig. 5.3.7. The working cell of this instrument is a system consisting of a cone and plate device. The drive (not shown in the figure) is connected with the driving member (lower plate) through a worm gear. The instrument operates in the regime of a constant frequency of rotation at a rotational speed of the main drive of 1,500 rpm. The construction of the gearbox makes it possible to vary shear rate in the range from 7.1×10^{-4} to $9 \times 10^3 \text{ s}^{-1}$ with steps of $10^{0.1} \approx 1.259$. Torque is received by a torsion shaft. The instrument is equipped with a collection of replaceable torsion shafts of different rigidity varying from 1 to 10^3 Nm/rad . By changing the torsion shaft, it is possible to measure shear stress in the range from 10^{-4} to 10^6 Pa .

Temperature control includes both liquid and electrical thermostats permitting tests in the range of temperatures from -50 to 300°C .

In addition to torque measurements, the instrument permits determination of normal stresses using the axial force transducer. In the latest modification of the instrument, the

drive was improved in such a way that it also permits imposition of harmonic oscillations and superposition of low-amplitude harmonic oscillations on steady rotation.

A similar instrument of high level technical capabilities, according to the tasks performed, was produced by *Instron*²⁵ under the name of the *Rotary Rheometer 3250*. At present, several important instrument-manufacturing companies have the capability to produce such instruments. One of them is *Rheometrics Scientific* (now TA Instruments, USA), that makes several high precision instruments. One of these instruments is the *ARES*.²⁶ This is a rotational rheometer with interchangeable working cells: cone-plate, disk-disk, coaxial cylinders. The drive system includes two direct current servomotors. The control system of the instrument allows one to conduct tests in different regimes, at a given shear rate or shear stress as well as periodic deformations. The instrument includes torque and axial force transducers (for measuring normal stresses). The instrument is supplied with a computer having an extensive library of programs.

The same company manufactures other high precision elastoviscoimeters, known under the names *RDA III*, *RFS III*, and *RMS 800*.²⁷ These instruments allow one to conduct measurements in different regimes, including periodic oscillations and steady flow.

The recent achievement of the company in the area of instrument manufacture is the universal rheometer *SR5*.²⁸ This instrument permits implementation of different regimes of tests including relaxation, creep, periodic oscillations, and superposition of different regimes. The instrument is also equipped with a normal stress transducer. The salient capability of this instrument is the wide range of the measured torque, from 10^{-4} to 50 mNm. As in other instruments produced by the company, the frequency can be varied in the range of 7 decimal orders. Temperature range is from -40 to 350°C .

Bohlin manufactures a number of rotational rheometers (general designation of a series C-VOR) with an adjustable frequency of rotation and measured stresses. Several modifications of the instrument are intended for conducting tests in different ranges of torques. Another series of instruments, produced under the designation CVO, is intended for measurements at controlled shear stresses.

Paar Physica (Germany) manufactures a series of instruments. They possess a wide range of technical capabilities. The most complex instrument (produced under the abbreviation MCR) allows one to conduct measurements in different controlled regimes including a constant velocity of rotation, constant stress, varying frequency in the regime of relaxation, and so forth. It can also carry out the measurements in more complex regimes of tests such as the superposition of periodic oscillations on the steady flow.

A number of devices with similar characteristics are manufactured by *Haake* (Germany). In some modifications of the instrument the rheological measurements are augmented by the possibilities of direct observation of structural transformations, caused by the deformation.

Instruments of the type under consideration possess many advantages. But they also have one essential disadvantage – they are expensive. This is due to the complexity of design and technological solutions used for their creation. Therefore, these instruments are not made for mass production, but as measuring systems, intended, first of all, for studies conducted in specialized laboratories.

5.3.4.3 Viscometers with assigned rotational speed

5.3.4.3.1 Laboratory viscometers with adjustable rotational speed

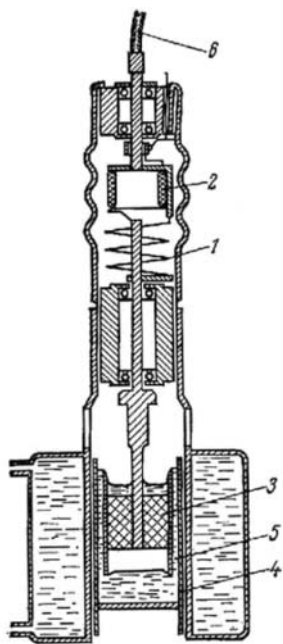


Figure 5.3.8. Typical rotational viscometer operating under imposed rotational speed of rotor. Viscometer *Rotovisco* of cylinder-cylinder type. 1 – torsion (elastic measuring) element; 2 – transducer for measurement of angle of torsional twist (potentiometer); 3 – rotating (inner) cylinder; 4 – fixed (outer) cylinder; 5 – sample; 6 – flexible connector from rotation control drive.

Instruments of such type are simplified versions of rheogoniometers. They are intended exclusively for viscosity measurements. In these instruments, the frequency of rotation is assigned and the torque is measured. Accordingly, they are much simpler in construction in comparison with a rheogoniometer and substantially cheaper. All basic elements shown on the fundamental diagram in Fig. 5.3.7 are used in their design. Also, possibilities of variation of shear rate in these instruments are sufficiently wide.

Some designs of these instruments, which are manufactured on industrial scale, are examined below, as an example.

Fig. 5.3.8 shows the viscometer *Rotovisco* (*Haake*). Usually this instrument is supplied with a cylinder-cylinder type working cell, although in some modifications of the instrument the use of working cells of other geometry is possible (for example, cone and plate).

The torque in this instrument is measured on the drive shaft. The measured shear stress ranges from 1 to 10^5 Pa, the range of shear rate is from 10^{-2} to 10^4 s^{-1} .

A design similar to *Rotovisco* and accordingly close to its technical capabilities (although more limited) is a popular viscometer *Rheotest*, manufactured in Germany.

In the viscometer of *Ferranti-Shirley* the working cell is made in a form of a pair of cone and plate with a very small angle between the generatrix of cone and plate. The special feature of this instrument is the stepless control of frequency of rotation of drive shaft using a direct current electric motor operating according to a diagram of the generator-engine.

A known series of viscometers *Rheomat* are manufactured by *Contraves* (Switzerland). In one of the modifications of the instrument *Rheomat 15T*, a torque transducer allows

one to measure the shear stresses in the range from 0.6 to 2×10^5 Pa with drive allowing one to vary speed (stepwise) to achieve a shear rate from 0.5 to 10^3 s^{-1} . In a more advanced modification of instrument *Rheomat 30*, the lower limit is substantially reduced to 4×10^{-3} s^{-1} . Moreover, in this instrument it is also possible to attain continuous change of rotational speed with the recording of dependence of torque on frequency of rotation.

Of special interest is the version of the instrument known under the name of *Rheomat, Block DC50*. With this instrument, measurements can be carried out in vacuum or under pressure up to 50 bars in temperature range from -50 to 300°C . Measurements can be carried out in the range of shear rates from 2.3×10^{-2} to 170 s^{-1} with viscosity of fluid ranging from 0.1 to 8×10^3 Pa*s. The possibility of measurement under pressure usually is not realized in other serially produced rotational viscometers.

Simple and convenient rotational viscometers are also produced by *Rheometrics Scientific* (TA Instruments, USA). The instrument *RM 100* makes it possible to conduct tests at any of five fixed speeds of rotation²⁹ with a maximum rotation frequency of 600 rpm.

5.3.4.3.2 Viscometers with extension rotor (immersion type)

In these instruments the outer cylinder is absent, and the inner cylinder, fastened to the end of a console, is submerged in liquid being investigated. The rotor can be made not only in the form of a cylinder, but a disk or another body of arbitrary geometric form. The rotor is driven by the electric motor through a reducer with an adjustable frequency of rotation. The measuring element (torsion shaft) is installed on the drive shaft. Such instruments are sufficiently simple in production and operation and are widely used for solving applied problems.

The most common instrument of such a type is the *Brookfield* viscometer. Different modifications of this instrument are produced. They are distinguished by a range of shear rates and by limits of measurements. The technical characteristics of the instrument are defined by rigidity of torsion shaft used, by the gearbox installed, and by the geometry of the utilized rotational member.

The most critical part of viscometers of this type is the twisted spring of the force transducer. This spring is made from beryllium bronze and it is calibrated by the manufacturer. Brookfield viscometers are mainly utilized in technological laboratories for quality control of produced materials with the purpose of comparing production samples with requirements of technical specifications. They are also used at different stages of the technological process of manufacture of materials.

Some modifications of viscometers of this type are intended, in particular, for the measurements of viscosity at high temperatures (up to 1,500°C), for measurements of viscosity of corrosive media, and also for measurements of viscosity at a distance from the location of the technological process. The latter is achieved by application of an adaptor, connected to a spindle of viscometers.

Instruments of the type of the *Brookfield* viscometer are manufactured by various firms under different names. For example: *Contraves* (Switzerland) manufactures a *Process Viscometer TO* and *Haake* (Germany) manufactures several modifications of the instrument, known under the names of *Viscotester VT 181/VT24* and *Viscotester VT 01*. *Rheometrics Scientific* manufactures the instrument with the extension rotor under the name *Rheomat RM 180*.

5.3.4.3.3 Constant torque viscometers

Load viscometers

The use of a measuring scheme in the regime of a constant torque, $T = \text{const}$, has definite advantages in measurements not only of viscosity, but also of viscoelastic characteristics during deformation.

In practice, several different methods of imposition of adjustable torque are used. The most simple method for imposing a constant torque is by use of descending loads, installed at a certain arm with respect to the rotational axis. The speed of rotation of the operating unit or the speed of motion of loads is measured. The instruments in which this method is used are simple in design and experimental procedure. They do not require complex measuring equipment. At the same time, they usually do not give high accuracy of measurement. An increase in accuracy of measurements entails the need of using more

advanced equipment, which is hardly compatible with measurements that are carried out manually. This is characteristic of the simplest viscometers of a fixed torque. At the same time, simplicity of construction and measuring scheme is justified when a fast comparative evaluation of material properties is necessary rather than obtaining precise absolute values of viscosity.

Spring viscometers

The simple measuring scheme for viscosity at an assigned torque is based on use of energy of the initially twisted (loaded) spring, which is done by hand. In the process of measurement, after release of the spring, torque decreases from a given maximum value to zero. The operating unit of the instrument can be made in the form of a rotational body of any configuration. The time required for releasing the spring is a measure of viscosity. The instrument is calibrated on liquid of known viscosity. Then, viscosity is determined by comparing the time of spring release for the standard liquid and the liquid being investigated. This is a very simple measuring scheme that is applicable even under field conditions in the absence of electric power sources. Certainly, because of simplicity and universality, the accuracy of measurements is somewhat lost. Therefore, in this case it is needless to speak about variation of conditions of deformation and other special features if tests are conducted on non-Newtonian liquids. However, even this simplest measuring scheme can be useful under specific test conditions.

The automatic torque control systems

In contemporary instruments the maintenance of the assigned torque, constant or variable according to a predetermined program, is achieved by methods of automatic control, based on the principle of feedback control.

Specifically, rheogoniometers described above and elastoviscometers operate in the stress-controlled regime. These can be both specific instruments and devices in which different conditions of test are performed by adjustment of assigned torque and frequency of rotation.

5.3.4.4 Rotational viscometers for special purposes

The principal capabilities of rotational instruments are frequently realized in viscometers for special purposes. They are intended to solve various scientific problems arising during the analysis of physical properties of liquids. In this case, although the general rules of construction of rotational viscometers are retained, the need for essential modification and custom designs still exists. In the present section, some examples of the above-mentioned approach to technology of rotational viscometry are given.

5.3.4.4.1 High-speed (thin-film) viscometers

High shear rates in rotational viscometers with coaxial cylinders require solution of two basic problems: high accuracy in maintaining a very small clearance between the cylinders and temperature control under conditions of intensive heat dissipation.

The technical tasks confronting the designer of this instrument, were successfully solved during the development of *thin-film flowing viscometer*.³⁰ In this instrument (Fig. 5.3.9) the measurements are accomplished in the scanning regime by continuous change of rotational speed. The clearance between coaxial cylinders is made open, such that the liquid being investigated, supplied with an aid of a press, can flow freely through clearance in a vertical direction. Thus, a continuous change of volume of fluid being investigated is ensured and the effect of heat dissipation is reduced. The gap clearance between

cylinders is 0.15 mm and a radius of the revolving cylinder (rotor) is 2.681 cm. Constant conditions of deformation are reliably maintained by application of rigid radial and axial air bearings. The use of this instrument makes it possible to investigate liquids with viscosity from 0.1 to 100 Pa*s.

In one of the modifications of this instrument the size of clearance between the cylinders is brought to several micrometers. In this case, the clearance between cylinders was calibrated using standard liquids, thus producing a geometric constant of the instrument. Control experiments showed that even in such thin layers, the effects of absorption or orientation of liquid being investigated are absent, so that one succeeds in obtaining reliable values of viscosity with error not higher than 2%.

5.3.4.4.2 Viscometers with noncontact drive (with the very low torque)

For solution of many applied and theoretical problems, it is necessary to know properties of materials at very low shear stresses. Measurements must be conducted in rotational instruments at low torques. Such low shear stresses require imposition of deformation for a long period of time and are important in evaluation of creep of high-viscosity materials, speed determination of fluid runoff on vertical surfaces, etc. It is also needed for evaluation of forces of intermolecular interaction, strength of structural bonding, etc. In all these cases, there is interest in measurements in the shear stress range lower than 1 Pa.

From a methodology point of view, two problems must be solved: creation of very low torque and elimination of friction in bearings.

Air bearings are used. This allows one to achieve torque due to the frictional forces as low as 10^{-11} Nm. Presently, air bearings are traditional elements in the construction of these instruments. In such bearings, the radial clearance does not exceed 0.05 mm with an end clearance of 0.1 mm. Thus, it is possible to decrease friction in bearings to values which correspond to shear stress of the order of 10^{-5} Pa.

A more radical method for further reduction of the measured shear stresses is by elimination of friction using a noncontact method of imposition of torque. The version of such an instrument in which this approach is realized is shown in Fig. 5.3.10. The torque here is created using electromagnetic forces such that it can be conveniently small. The revolving (inner) cylinder made of magnetic iron is weighed in liquid being investigated, i.e., its weight is balanced by an Archimedean force. In a typical instrument of such type the outer cylinder is made in the form of a glass test tube.

Using this viscometer, called the *Zimm-Crothers viscometer*,³¹ it is possible to measure viscosity of low-viscosity liquids and to observe appearance of a yield point in the region of very low shear stresses.

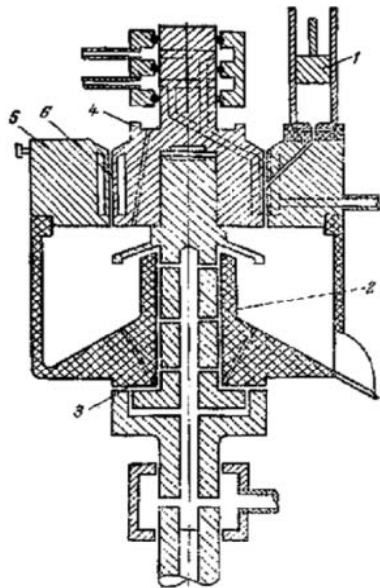


Figure 5.3.9. High speed (thin film) viscometer with continuous flow of sample through working clearance between coaxial cylinders. 1 – ram supplying sample; 2 – radial air bearing; 3 – supporting air bearing; 4 – rotor; 5 – stator; 6 – working clearance between coaxial cylinders.

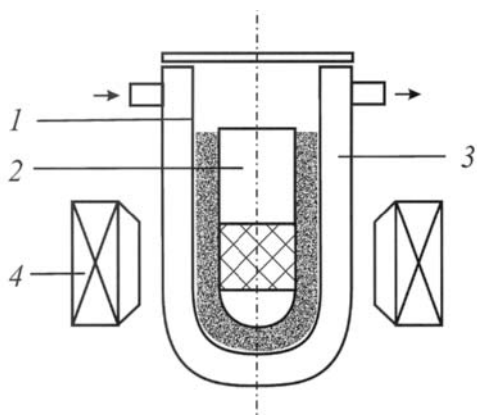


Figure 5.3.10. High sensitivity rotational viscometer having rotor without bearing used for measuring low torque values. 1 – test tube with sample; 2 – rotor with magnetic insert; 3 – thermostat; 4 – stator of electric motor.

This is especially valuable for low-viscosity structured liquids, biopolymers, colloidal systems, and liquid-crystal polymer solutions.

The electromagnetic method of imposing torque for viscosity measurements in the region of low shear rates is quite innovative for testing solutions of electrolytes. In this case, it is generally possible to operate without rotating parts. Flow appears as a result of electromagnetic interaction of the external field with ions of electrolyte.³²

Other variations of the method in question are possible. In particular, using a combination of layers of conducting liquid of high density (for example, a saturated solution of CsCl) and non-conducting liq-

uid, it is possible to measure viscosity of the latter by a differential method.

5.3.4.4.3 Viscometers for electro-rheological liquids

The so-called *magneto- and electro-rheological* liquids are of some interest. These are liquids having a structure which rapidly changes in a magnetic or electric field. Accordingly, their viscosity also changes. For viscosity measurements of such media and control of their change in electromagnetic fields, a number of rotational viscometers with coaxial cylinder can be used. Their basic special feature consists of isolated outer and inner cylinders. This is achieved by modification of the usual rotational instrument by installation of separating bushings made out of nonconducting materials. The instrument itself is an electrical capacitor, because electro-rheological liquids are dielectrics. This design combines viscometric and electrical measurements.

Electrorheological measurements can be carried out also, using instruments with parallel plates (a modification of the rotational viscometer of *Rheometrics System IV*).³³ In this design oscillations were imposed on the disk, but it is also possible to rotate the disk with assigned frequency. The analogous scheme of shear between two parallel electrically isolated disks was realized by some modification of viscometer *RS -50 (Haake)*.³⁴

5.3.4.5 Rotational instruments for technological purposes

The technological evaluation of polymeric materials is one of the basic tasks of rheological measurements. A number of specialized methods, which simulate real technological processes, were proposed. The procedures of measurement and basic geometric parameters of instruments are standardized. This makes it possible to conduct reliable comparative tests of real materials and to rely on previous experiences from processing these materials. Reliable recommendations can be made regarding their application and selection of a technological regime.

5.3.4.5.1 The Brabender Plasticorder

This instrument is a typical example of tools used in technological applications. The *Brabender Plasticorder* is manufactured in large quantities and widely used in the polymer

industry. The instrument is basically a mixer with different mixing elements. Depending on the viscosity of the mixture, the shaft of the kneader arms experiences different torque. This torque is a measure of viscosity. By measuring torque, one can find some characteristics of rheological properties of processed mixtures and trace the evolution of these properties during mixing. Thus, some characteristic values influencing evaluation of material and selection of an optimum technological regime are determined.

Contemporary models of the Brabender Plasticorder are supplied with an adjustable drive allowing one to vary frequency of rotation of rotors in the range from 1 to 400 rpm, although there are modifications of instrument intended for use at a fixed speed of 31.5 or 63 rpm. Torque is measured using a torque transducer. The modifications of instrument are produced for different maximum torque. In a working chamber a vacuum or inert gas atmosphere can be created. The thermostatically controlled chamber makes it possible to conduct measurements up to 400°C.

5.3.4.5.2 The Mooney viscometer

This instrument, in various modifications, is manufactured in many countries, since the *Mooney test method*³⁵ appears in a number of standards for rubber compounds.³⁶

The tested material undergoes shear strains in a closed chamber in clearances between a revolving rotor and the chamber walls. The rotor can be made in the form of a smooth or a serrated disk. During the deformation of material in a chamber due to a complex configuration, the complex fields of velocities and stresses appear, so that the Mooney viscometer gives a conditional characteristic of rheological properties of material being investigated.

The method of torque measurement is the original design feature of the Mooney viscometer. It is determined by measuring force exerted on a spring by the drive shaft.

The rotation of the rotor is achieved by means of a synchronous electric motor through the gear drive and the worm wheel. The material being investigated is located in the chamber under pressure, created during closing of the upper and lower halves of the chamber. Typically, during the first compressing of a sample, the pressure created in the chamber is of the order of 200 Pa, and upon additional compression, with the aid of springs, the pressure is increased to 300-600 Pa. Heaters are installed in both upper and lower halves of the instrument chamber. Usually, tests begin 1 min after compressing the sample, without waiting to achieve steady-state temperature conditions.

Mooney viscometers are manufactured with standard dimensions of working chamber and rotor. The usual frequency of rotation of rotor in the Mooney viscometers is 2 rpm. In some modifications of the instrument, capabilities are augmented by setting frequency of rotation to 4 and 8 rpm, and also by imposing oscillatory motions of the rotor.

The standardized requirements for tests according to Mooney are realized in a number of instruments. A typical example of a modern instrument of such type is the *Mooney-check Compact PC* (Gibitre, Italy).

A combination of possibilities of rotational and oscillatory motions of a rotor is realized in an instrument of the type of Mooney viscometer being manufactured by *Monsanto* (now *Alpha Technologies*). In instrument known as *Rheometer-100*, capabilities exist to measure continuous changes of torque with time (according ASTM D 2084) which makes it possible to follow the kinetics of vulcanization of rubber compounds. *Rheometer-100750* has variable speed of rotation in the range of 1-150 rpm or constant speed at 750

rpm. Additional options permit conducting automatic processing of test results, determining characteristic points on a vulcanization curve – initial and minimum viscosities, curing time, and maximum value of modulus of elasticity of vulcanized rubbers.

Further modifications of this instrument are in *Moving Die Rheometer MDR* (Mon-santo Instrument Company, now Alpha Technologies, USA) and *Rotorless Curemeter* (Goettfert, Germany) in which one platen oscillates. These rheometers use thinner samples of rubber than Rheometer-100. Therefore, less effect of transient heat transfer during curing takes place. The most recent developments are two new instruments – *Rubber Process Analyzer, RPA*, and *Advanced Polymer Analyzer, APA* (Alpha Technologies, USA) allow one to carry out tests over ranges of strain 0.7 to 1200%, frequencies of 0.1 to 2000 cycles per minute and various temperatures. These instruments can measure the storage and loss moduli and $\tan\delta$ during curing of rubber compounds.

5.3.4.5.3 The Goettfert instrument

Goettfert (Germany) developed a series of instruments intended to simulate real technological processes of processing plastics with the purpose of selecting parameters for an optimal regime of processing. One of these instruments is a rotational type viscometer.

5.3.5 MEASURING NORMAL STRESSES

Section 3.4.2 discussed normal stresses in shear flow (the Weissenberg effect). The general stress field produced in shear flow is determined by Eq. 3.4.3. It was also explained that from a rheological point of view, not normal stresses by themselves but two their differences are essential:

$$\begin{array}{ll} \text{the first difference} & N_1 = \sigma_{11} - \sigma_{22} \\ \text{the second difference} & N_2 = \sigma_{22} - \sigma_{33} \end{array}$$

The necessity to operate with the differences of normal stresses but not with absolute values of normal stresses is based on the hypothesis of incompressibility of flowing liquid. Therefore, the addition of hydrostatic pressure (i.e., simultaneous change of all diagonal components of the stress tensor) would not influence the state of shear deformations and N_1 and N_2 values, consequently.

For this reason, an experimenter is interested to know how to measure N_1 and N_2 but not separate components of normal stresses.

5.3.5.1 Cone-and-plate technique

The basic approach to measurements of the first difference of normal stresses is related to the use of the cone and plate technique as in Fig. 5.3.4b.

The balance of force equation for a liquid element can be written (neglecting the mass forces) as

$$\frac{d\sigma_{33}}{dr} = \frac{\sigma_{11} + \sigma_{22} - 2\sigma_{33}}{r} \quad [5.3.47]$$

It is reasonable to suppose that both normal stress differences $(\sigma_{11} - \sigma_{33})$ and $(\sigma_{22} - \sigma_{33})$ do not depend on curvature of stream-lines and are determined by shear rate only. Then, integration of Eq. (3.5.47) gives the following equation for stress distribution:

$$\sigma_{22}(r) = \sigma_{22}(R) + [(\sigma_{11} - \sigma_{33}) + (\sigma_{22} - \sigma_{33})] \ln \frac{r}{R} \quad [5.3.48]$$

The expression inside the square brackets does not depend on the coordinate r . It is reasonable to think (as many experimental works show) that $(\sigma_{22} - \sigma_{33}) \ll (\sigma_{11} - \sigma_{22})$ and that $\sigma_{22}(R) = 0$. The latter reflects the absence of stresses at the free surface. Then, it is seen that the stress distribution along the radius must be logarithmic.

Then, measuring radial distribution of σ_{22} , one can find N_1 as a coefficient in the following dependence:

$$\sigma_{22}(r) = N_1 \ln \frac{r}{R} \quad [5.3.49]$$

Repeating these measurements at different shear stresses, one can obtain the dependence $N_1(\dot{\gamma})$.

The normal stress distribution along the radius was measured as shown in Fig. 5.3.11 by several piezo-tubes.³⁷ This *differential* method of measuring normal stresses was realized in the Roberts-Weissenberg rheogoniometer, model R8. Later this method was not used for practical purposes and normal stresses were measured by the *integral* method. The total force acting perpendicular to the radius of the rotating cone is measured. This force, F , is calculated by integrating Eq. 5.3.48. After some rearrangements, the following relationship is obtained:

$$F = \frac{1}{2} \pi R^2 N_1 \quad [5.3.50]$$

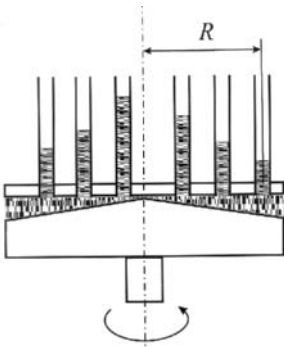


Figure 5.3.11. Measuring normal stress distribution along the radius of a cone-and-plate assembly.

This force, F , is the cause of the Weissenberg effect as described in Chapter 3. The last expression gives a direct method of determination of the first difference of normal stresses by measuring of the total normal force.

This is the most popular method of measuring N_1 , which is realized in several industrial rotational devices. The total force is measured by different transducers but the general rule is: a sensor must be as rigid as possible, because vertical shift (even very small) of a surface in a rotation device leads to distortion of the deformation field in the sample and to essential experimental errors. The maximum vertical shift in the best known units does not exceed several microns and it permits measurement of normal stresses in the range from 0.1 to $1 \cdot 10^6$ Pa at shear rates from 10^{-4} to 10^4 s⁻¹.

Modern rotational devices allow the experimenter to measure normal stress as a function of shear rate not only at steady state flow regimes but also in transient deformation modes and in periodic oscillations as well.

The cone and plate technique gives an adequate and reliable method of measurement of the first normal stress difference and modern experimental devices realize this possibility. One example of such technique is the *Rheometrics RAA rheometer*.³⁸

Using micro-machining technology and miniature pressure sensors positioned along the radius allows one to extend the possibilities of a standard cone and plate rheometer (in

particular *ARES* rheometer described above) and enables one to measure simultaneously the first, N_1 , and the second, N_2 , normal stress differences.³⁹

5.3.5.2 Plate-and-plate technique

This method of measuring normal stresses is almost the same as the previous one, but the rotation of two parallel plates around their common axis is used instead of the cone and plate assembly. The main difference with the previous case is the variation of shear rate along the radius of the measuring device according to formula $\dot{\gamma} = (\omega r)/h$, where r is the current radius and h is the distance between the parallel plates.

Analysis of force balance of liquid element, and assuming that $(\sigma_{22} - \sigma_{33}) \ll (\sigma_{11} - \sigma_{22})$ results in the following relationship directly valid for measuring the first difference of normal stresses:

$$N_1 = \frac{d\sigma_{22}}{d \ln r} \quad [5.3.51]$$

Then, measuring dependence of σ_{22} as a function of r at different shear rates, it is possible to find the dependence of N_1 on shear rate.

Simultaneous application of two geometries of flow (plate-plate and cone-plate) permits finding the second normal stress difference. The final equation is given by:⁴⁰

$$N_2 = \dot{\gamma} \int_0^{\dot{\gamma}} \left[\left(r \frac{\partial \sigma_{22}}{\partial r} \right)_{p-p} - \left(r \frac{\partial \sigma_{22}}{\partial r} \right)_{c-p} \right] \frac{d\dot{\gamma}}{\dot{\gamma}^2} \quad [5.3.52]$$

where subscripts p-p and c-p relate to values measured in plate-plate and cone-plate geometries, respectively.

The alternative form of this equation, which is used in experimental practice, can be written as:⁴¹

$$N_2(\dot{\gamma}_R) = \frac{F_{c-p}}{\pi R_{c-p}^2} - \frac{F_{p-p}}{\pi R_{p-p}^2} \left(2 + \frac{d \ln F_{p-p}}{d \ln \dot{\gamma}_R} \right) \quad [5.3.53]$$

The value $N_2(\dot{\gamma}_R)$ is N_2 as measured at shear rate corresponding to the outer radius of plates.

This is one of the possibilities of measuring N_2 , which has very low value (if not zero) in comparison with N_1 . The application of Eq. 5.3.52 or 5.3.53 gives the best way to measure the second normal stress difference. However, though this method is applicable in principle it should be treated with caution due to uncertain experimental errors because both members of difference in these equations are comparable in value. Therefore, this difference is determined with the largest possible error.

Perhaps the most serious limitation in the application of rotational methods (either cone and plate or plate and plate) for measuring normal stresses is the edge effect including the edge fracture of sample.⁴²

5.3.5.3 Coaxial cylinders technique

Shear flow between rotating coaxial cylinders can be used to measure the second normal stress.⁴³ For this purpose, the difference of radial stresses $\Delta\sigma_{22}$ at the inner and outer cylinders should be measured:

$$\Delta\sigma_{22} \equiv \sigma_{22}(R_i) - \sigma_{22}(R_o)$$

Calculations based on the balance equation show that if the difference between shear rates at inner and outer cylinders is large enough (i.e., the gap between cylinders is large) the following relationship is valid:

$$N_{2,i} = \frac{2}{1 + \frac{d \ln \eta}{d \ln \dot{\gamma}}} \frac{d \Delta \sigma_{22}}{d \ln \dot{\gamma}} \quad [5.3.54]$$

The subscript *i* shows that N_2 determined by this equation is related to the values at the surface of the inner cylinder. The structure of this equation shows that N_2 can be calculated if the flow curve is known and $\Delta\sigma_{22}$ is measured as a function of shear rate.

Another way of measuring the second difference of normal stresses, N_2 , can be realized on the base of axial flow of liquid between two coaxial cylinders.⁴⁴ However, it is necessary to mention that all these methods are more exotic than these in everyday use.

5.3.5.4 Hole-pressure effect

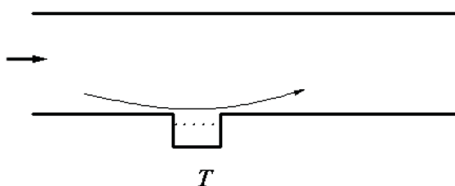


Figure 5.3.12. Measuring normal stresses by the hole-pressure method. Curvature of a streamline near a hole is shown. T – pressure transducer.

There have been several attempts to use flow through a capillary for measuring normal stresses.⁴⁵ A possibility to obtain accurate results by such method is usually strongly dependent on the choice of rheological model and strict control of experimental details. The most widely discussed example is related to measurement of pressure in a hole at the channel wall, as shown in Fig. 5.3.12. The channel should be flat

(i.e., made as a slit) in order to avoid problems related to the wall curvature. The streamlines are distorted near a hole (as shown in Fig 5.3.12). Additional tension is related to elasticity of liquid and its value might be used as a measure of normal stresses. This method is rather controversial: on one hand, a curvature of streamlines must be created, on the other hand, a diaphragm of a transducer should be flash-mounted to avoid uncertain experimental errors.

It was shown that the pressure gradient along a channel, as measured by the hole-pressure method is not only related to shear stresses, but can be used as a method for estimating N_1 .⁴⁶ Possible experimental errors of this method require special rigorous analysis.⁴⁷ The difficulties of correct estimation of details of flow near a hole lead to controversial results in attempts to apply this method to measuring N_2 (even the sign of N_2 appears different depending on not well documented experimental details).⁴⁸ That is why this approach is more of theoretical than applied value, and in modern laboratory practice, simpler (rotational) methods are preferred.

5.4 PLASTOMETERS

5.4.1. SHEAR FLOW PLASTOMETERS

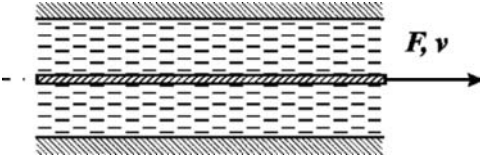


Figure 5.4.1. Sandwich shear flow plastometer.

Instruments of this type provide an ideal model of shear flow experiments, as shown in Fig. 5.4.1. This measuring scheme, most clearly corresponding to the definition of viscosity, seems to be optimal. However, in practice the realization of this scheme of measurements encounters specific methodological difficulties.

If the surface area of the sample being investigated, placed between the plates, is S , and the distance between the plates equals h , then the shear rate is calculated from measured velocity of movement of one of the plates relative to another, V , as $\dot{\gamma} = V/h$. Shear stress is determined through measured force, F , which must be created in order to accomplish the motion of the plate with a required velocity. This shear stress equals $\sigma = F/S$. Hence, according to the general formula, the apparent viscosity is found as a ratio of measured values $\eta = \sigma/\dot{\gamma}$.

Sometimes, shear plastometers are made in the form of a sandwich (Fig. 5.4.1): a moving plate is placed between two fixed ones, and the sample being investigated fills both clearances between the moving plate and each of the fixed plates. The velocity of the plate, V , and force, F , leading to its motion are measured. In this case, the area entering the expression for calculating shear stress is doubled.

Shear plastometers are convenient for measurements of both steady and transient flows during creep under imposed constant shear stress value, σ , elastic recovery (elastic deformations) after removal of external load. The important advantage of shear plastometers is that they permit independent definition of shear rate and shear stress used then for calculation of apparent viscosity, i.e., these instruments can be considered as absolute.

The experiments carried out using shear plastometers can be performed in different regimes, either $F = \text{const}$ or $V = \text{const}$; a possibility also exists (and it is actually used) to impose more complex conditions of deformation, in particular, the oscillatory conditions of deformation. Most frequently, these instruments are used with $F = \text{const}$, since it is easier to carry out experimental work by loading the moving plate with the falling weight.

Shear plastometers are used as simple laboratory instruments, intended for measurement of materials having a high viscosity ($>10^5 \text{ Pa}\cdot\text{s}$), at low shear stresses and shear rates. However, if we make the clearance between plates very small, in the order of a few fractions of cm, then these instruments can also be used for measurements of materials of low viscosity. Shear plastometers permit measurement of viscosity in the range from 10 to $10^{10} \text{ Pa}\cdot\text{s}$. Shear plastometers are very convenient for measurements of yield points, since they allow experimenters to conduct measurements at very low shear stresses.

The accuracy and reliability of results of measurements, carried out on shear plastometers, depend on the quality of their manufacture and adjustment, especially because very frequently these are homemade instruments individually manufactured by the experimenter. Moving and fixed plates of these instruments must be parallel. The variance of

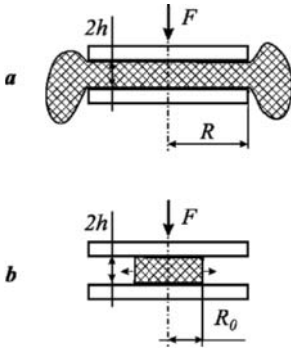


Figure 5.4.2. Squeezing flow plastometers. a – excess of material is squeezed out; b – squeezing sample of constant volume.

thickness must not exceed 20–30 μm , and deviation from parallel alignment may reach several micrometers.

It is important to reduce friction in bearings to a minimum, especially during studies at low loads and speeds. The use of a scheme in which a load is unsupported is optimal. This is achieved, for example, by installation of plates in a vertical position and by direct suspension of the load on one of the plates. At a very low speed of movement of the moving plate, it is sometimes necessary to measure displacement using a microscope. The prolonged maintenance of a uniform temperature field in a sample is an additional problem, which requires a constructive solution.

Shear plastometers permit determination of limiting values of shear rates and shear stresses, which is of interest for experimentalists. But it is usually difficult to obtain reliable results of measurements with an error less than several percent.

5.4.2 SQUEEZING FLOW PLASTOMETERS

In these instruments, a sample, as in the preceding case, is placed between two parallel disks, but the motion of the upper disk occurs, not in parallel to the lower disk, but along the common axis. Thus, the sample being investigated is compressed and spreads along the radius of disks. As shown in Fig. 5.4.2, two cases are possible. In the first case (a), the investigated sample initially fills the entire space between disks. Therefore, during its squeezing, surplus of the sample is extruded from the working volume. In the second case (b), volume of the sample remains constant in the process of tests, and during squeezing it flows between disks, remaining completely between them.

The regime of squeezing can also be different. Tests can be carried out under a constant load, $F = \text{const}$, or under programmed change of force with time. In these cases, either speed of the upper disk is measured (in case a) or a change of radius of the sample is measured (in case b). It is also possible to impose speed of motion to the upper disk and measure an increase in the resulting force as a function of the time, $F(t)$.

The calculation of viscosity according to the test results is simple if liquid has Newtonian properties. The motion of Newtonian liquid between converging disks was described in details in textbooks on hydrodynamics. Therefore, it is expedient here to provide the known solutions.

The basic calculation formula that relates squeezing force and speed of the vertical movement of disk takes the form:

$$F = \frac{3\pi\eta VR^4}{8h^3} \quad [5.4.1]$$

where η is the measured viscosity. Notations of geometric dimensions are shown in Fig. 5.4.2. In this case, the value $2h$ is the variable distance between the disks. The rate of disks closure, V , equals dh/dt .

If the sample volume is $v = 2\pi R_0^2 h_0$ (where R_0 is the initial radius of the sample, and $2h_0$ is the initial distance between the disks), then from Eq. 5.4.1 it is possible to

exclude R , since in the course of experiment the condition of volume constancy, $R_0^2 h_0 = R^2 h$ is satisfied.

Then, it is possible to write the following equation:

$$F = \frac{3\pi\eta R_0^4 h_0^2}{8h^5} \frac{dh}{dt} \quad [5.4.2]$$

This equation is integrated relative to $h(t)$, resulting in the following equation:

$$\frac{1}{h^4} - \frac{1}{h_0^4} = \frac{32tF(t)}{3\pi\eta R_0^4 h_0^2} \quad [5.4.3]$$

Then, by plotting the dependence of $h^4(t)$ versus $F(t)$, it is not difficult to find viscosity from the slope angle of the obtained straight line.

It is usually more convenient to measure dependence of $R(t)$ than $h(t)$. Then Eq. 5.4.3 can be converted after using substitution $h = h_0(R_0/R)^2$. This leads to the following relationship:

$$R^8 = R_0^8 + \frac{32tF(t)R_0^4 h_0^2}{3\pi\eta} \quad [5.4.4]$$

or

$$R^8 = R_0^8 + \frac{32tF(t)V}{3\pi^2\eta} \quad [5.4.5]$$

where V is the constant volume of the test specimen. Using these formulas it is convenient to determine viscosity by plotting dependence R^8 as a function of t at $F = \text{const}$.

If a surplus of liquid being investigated is extruded from the working clearance between the disks, as shown in Fig. 5.4.2a, then integration of Eq. 5.4.1 under the condition $R = R_0 = \text{const}$ gives:

$$\frac{1}{h^2} - \frac{1}{h_0^2} = \frac{16tF(t)}{3\pi\eta R^4} \quad [5.4.6]$$

Then viscosity can be found from the dependence of h^{-2} and $tF(t)$. If the experiment is carried out under condition of $F = \text{const}$, then viscosity is determined by plotting the dependence of h^{-2} versus t .

The above-written relationships and calculation formulas permit determination of viscosity based on experimental data, but with one fundamental limitation that viscosity must be constant. Analogous but more complex formulas can be obtained for other liquids, with rheological properties described by a certain model.

Solution of the hydrodynamic problem requires the assumption that there is no slip along the disk surface. This assumption is correct for Newtonian liquids. However, a squeezing plastometer is very frequently used for rheological analysis of liquids, which can interact with a surface by complex means. Therefore, much attention is given to the theory of liquid spreading during squeezing of disks, using different boundary conditions for the rigid surface.⁴⁹

The absence of friction (slip) on a solid wall (a case opposite to flow when fluid adheres to the solid wall), the equation for calculation of force takes a form:⁵⁰

$$F(t) = \frac{3\pi\eta R_0^2}{h(t)} \frac{dh}{dt} \quad [5.4.7]$$

In many testing machines, the method of measurements is realized under the regime of $V_0 = dh/dt = \text{const}$. Then integration of equation (5.4.7) gives:

$$F(t) = \frac{3\pi\eta R_0^2 V_0}{h(t)} \quad [5.4.8]$$

Hence, the viscosity of liquid being investigated is determined from the measured dependence of $F(t)$ and $h^{-1}(t)$.

The method of velocity measurement of motion of the upper disk is the most critical element of construction of squeezing flow plastometers, since its displacements are small. In the simplest case, this is achieved manually using an indicator of displacement of the dial-type and stopwatch. In more advanced instruments, displacement transducers of induction or capacitor type are used. For precision measurements an interferometric method is used.⁵¹ This method allows one to measure very low speeds, as low as 3×10^{-7} mm/s, although the usual operating range is higher by two orders of magnitude.

The critical element of design of the squeezing flow plastometer is a strictly parallel installation of disks. Analysis⁵² shows that parallel misalignment of even $1-3^\circ$ can give significant errors during processing of experimental data.

As a result of the simplicity of the device and comparatively low cost, squeezing flow plastometers found a wide acceptance in industry. Here, the *Williams plastometer* should be noted. It was proposed in 1924 and until now it is widely used in practice in different modifications. The use of this instrument is standardized for determining the conditional characteristic of viscometric properties of rubber compounds, called *plasticity*.⁵³

The squeezing flow plastometers also received wide acceptance in control of degree of scorching of rubber compounds, for which the *Goodrich plastometer* is used.

The variation of the squeezing flow plastometers are defometers – instruments in which the load, which causes deformation, is measured. By this method the rigidity of natural rubbers and unvulcanized rubber compounds is evaluated.⁵⁴

The diverse variants of plastometers of industrial purpose (first of all, for the rubber industry) are produced by a number of instrument-manufacturing companies in different countries.

5.4.3 METHOD OF TELESCOPIC SHEAR

The shear between parallel planes is shown in Fig. 5.4.3. Here, flow is accomplished between the coaxial cylinders, but in contrast to the rotary instruments, one of the cylinders does not revolve, but moves along the axis. This flow is called *telescopic shear*, and instruments in which this flow is realized are called the *Pochettino viscometers*.⁵⁵

If clearance between coaxial cylinders is small in comparison with their radii, i.e., $[(R_0 - R_i)/R_i] \ll 1$, then curvature of the channel can be disregarded, and telescopic shear proves to be practically identical to shear in plastometers with parallel plates. But if clearance is not small, then the solution of telescopic flow is sufficiently simple only for

Newtonian liquids. The rate of the lowering inner cylinder, V , which moves along axis under its own weight is expressed as follows:

$$V = \rho_l g \frac{R_o^2 - R_i^2}{4\eta} + \frac{(\rho_s - \rho_l)gR_i^2}{2\eta} \ln\left(\frac{R_o}{R_i}\right) \quad [5.4.9]$$

where ρ_l and ρ_s , are, respectively, the density of liquid being investigated and the material from which the inner cylinder is made, g is the acceleration due to gravity.

Hence, by measuring the speed of lowering of the inner cylinder, it is possible to find viscosity.

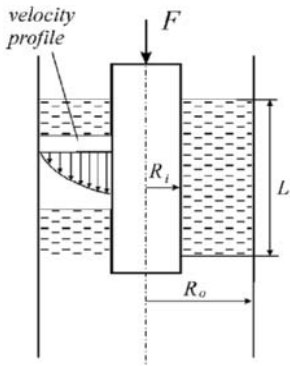


Figure 5.4.3. Plastometer with telescoping flow.

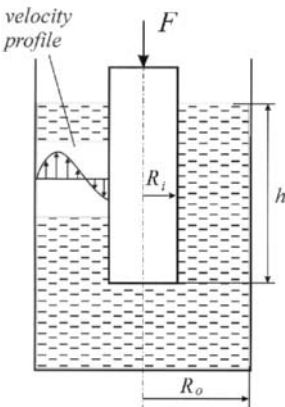


Fig. 5.4.4. Telescoping shear in cylinder with closed bottom ("Penetrometer").

Usually plastometers with telescopic shear are used for viscosity measurements at low deformation rates. This is due to a comparatively small force, created by the weight of the moving cylinder. At the same time, for viscosity measurement of high viscosity materials, such as polymer melts, rubber compounds, asphalts and bitumens (with viscosity in the range of 10^5 – 10^9 Pa*s), this force is insufficient for measurements within a convenient time range. Then, it is expedient to add weight to create an external force, F , as shown in Fig. 5.4.3.

This method was effectively used in laboratory installation, in which the external force was created by a pressure of compressed gas.⁵⁶ With radius of cylinders of the order of 25 mm and the clearance of 0.25 mm between them, a very rapid application of the force using aerodynamic drive created shear rates of the order of 10^5 s⁻¹ for the duration of experiment of about 0.01 s. The speed of movement of the cylinder was measured using an induction sensor, and the force, holding the external cylinder from movement, was measured with a very rigid piezoelectric transducer. Pressure of 1 MPa was reached, which made it possible to measure values of viscosity up to 150 Pa*s.

5.4.3.1 Telescopic shear penetrometer

A *Penetrometer* is a variation of plastometer utilizing a method of telescopic shear. Penetrometers are a separate group of instruments. The operating principle is based on indentation (*penetration*) of a solid body by a tool called the indenter. The instrument, a schematic of which is shown in Fig. 5.4.4, occupies an intermediate position between plastometers and penetrometers. If clearance between cylinders is small, then this measuring device is close to the classical plastometers. A difference in the diagram, shown in Fig. 5.4.4,

from the basic principle of measurements during the telescopic flow, lies in the fact that the outer cylinder is made with a closed bottom. Therefore, the telescopic shear between the cylinders is accomplished because material under study is extruded between the cylin-

ders from the bottom part of the instrument. Liquid resists a movement of the inner cylinder and the telescopic shear of liquid between cylinders occurs. Profiles of velocities of liquid flow between cylinders are different, as shown schematically in Figs. 5.4.3 and 5.4.4.

The basic kinematic feature of telescopic flow in the instrument, shown in Fig. 5.4.4, is that the height of the layer between cylinders changes with time. As a consequence, the rate of motion of the inner cylinder under the assigned force is variable.

The relationship between the force of insertion, F , and the rate of motion of the indenter (inner cylinder), $V = dy/dt$, is established by solving the hydrodynamic problem. Such a solution, known for Newtonian liquids, takes the form:

$$F = V \frac{2\pi y \eta \frac{R_o^2 + R_i^2}{R_o^2 - R_i^2}}{\frac{R_o^2 + R_i^2}{R_o^2 - R_i^2} \left[\ln \left(\frac{R_o}{R_i} \right) - 1 \right]} = 2Ky\eta \quad [5.4.10]$$

where K is the geometric (shape) factor, whose structure is evident from Eq. 5.4.10, and y is variable insertion depth.

Further, using equality $V = dy/dt$, it is possible to obtain the following dependence of insertion depth on time:

$$y(t) = \sqrt{\frac{Ft}{K\eta}} \quad [5.4.11]$$

By plotting the dependence y versus \sqrt{t} , it is possible to find viscosity.

The possible method of viscosity measurement is to specify a certain assigned insertion depth, y_0 , and measuring time, t_0 , required to achieve this depth under assigned load, F . Then, it is pertinent that

$$\eta = kt_0 \quad [5.4.12]$$

where coefficient $k = F/Ky_0^2$ is constant under selected (assigned) conditions of experiment.

In some cases, the resistance, exerted by the bottom surface of the indenter during its penetration into liquid, can be disregarded in comparison with resistance caused by telescopic flow. This happens, for example, when the indenter has the form of a needle with a sharp tip. With this form of the indenter, the shape factor is expressed by simpler means, namely

$$K = \frac{\pi}{\ln(R_o/R_i)} \quad [5.4.13]$$

The above written formulas cannot be used for non-Newtonian liquids. However, if the dependence of $\sigma(\dot{\gamma})$ is known, then the corresponding hydrodynamic problem for telescopic flow can be solved. In practice, the method of telescopic shear, especially in the version of combination with penetrometer, is used only as a relative method of evaluating viscometric properties of material.

Penetrometers have found widespread use in technological practice. They are produced by a number of companies in different modifications. An instrument of such type is known as the *Hoeppler consistometer* (Germany). In the USA, the penetrometers are produced by Gardner. The geometric shape of the indenter can be arbitrary. For determining softness of natural rubber, plastic materials, and unvulcanized rubber compounds, the so-called *Humboldt penetrometer* is used. Tests on this instrument are done as follows. Under a load of 150 g, needle of diameter of 1 mm with rounded apex is pressed into a sample of standard dimensions. Penetration continues for 10 min, after which the indentation depth is measured. The latter value serves as a measure of rheological properties of the material.

In some technical applications, an indenter, prepared in the form of cone, is used. This is especially convenient for tests of high viscosity, filled, polymeric compositions. In this case, measurement of penetration velocity gives the characteristics of viscometric properties of material, and the maximum indentation depth, reached during the application of a specific load, characterizes certain structural strengths of the material. In the simplest case, this strength, F_Y , is defined as

$$F_Y = \frac{F}{Kh^3} \quad [5.4.14]$$

where the shape factor, K , is expressed as $K = \pi \cos^2 \alpha \cot \alpha$ with α being half of the vertex angle of cone.

The main methodological problem arises because of measurements of small deformations (displacements). This difficulty is especially significant when application of large contact loads is inadmissible, since measurements are carried out at low stresses and therefore small displacements. The general solution to such a problem is to utilize noncontact methods of measurements, for example, using optical methods (including interferometry), and also mechano-electronic lamp sensors.

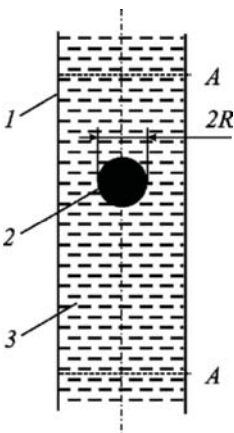


Figure 5.5.1. Scheme of measurements of viscosity by method of a falling sphere. 1 – tube; 2 – sphere; 3 – fluid; A – marks.

5.5 METHOD OF FALLING SPHERE

5.5.1 PRINCIPLES

Experimental methods, considered in this section, are based on measurement of resistance to motion of a solid body in liquid. In contrast to all methods discussed in previous sections, these methods are about external flow around solid bodies. The resistance to motion of a solid body in liquid is determined by its viscosity. Two versions of a method can be envisioned: one is velocity measurement of motion under a given force and another is the force measurement under a given speed of motion. These two versions are completely analogous to methods used in the theory of capillary or rotational viscometry where preselection of one parameter and a measurement of another parameter from a pair pressure/volumetric flow rate or torque/velocity of rotation is used.

A theory of the absolute method of viscosity measurements will be examined below. The theory is based on the simplest measuring scheme: a solid sphere is used as a moving body. The sphere

falls along the axis of a cylindrical tube filled with liquid being tested, and the velocity of the sphere is measured. This is shown in Fig. 5.5.1. It is assumed that the tube is vertical. The theory of motion of a solid sphere, which can be further refined, is valid as the first approximation under the following assumptions:

- the motion is steady, i.e., the rate of sphere descent is constant
- the inertia effects are considered negligible, i.e., motion occurs at low values of Reynolds number, Re ($Re < 1$)
- liquid is Newtonian
- the wall effect on a sphere motion is neglected, i.e., the sphere radius is much smaller than the tube radius
- the sphere moves strictly in a vertical direction.

During the sphere motion of a radius, R , made out of material having density, ρ_s , in liquid having density, ρ_l , under action of the gravitational force, the driving force equals:

$$F = \frac{4}{3}\pi R^3(\rho_s - \rho_l)g \quad [5.5.1]$$

where g is the gravitational acceleration. The force resisting motion of a sphere in viscous fluid is described by the *Stokes formula*:

$$F = 6\pi R U_\infty \eta \quad [5.5.2]$$

where U_∞ is the rate of steady (indicated by subscript ∞) descent of sphere and η is viscosity of investigated liquid.

Under assumption of equality of the two above-written expressions (motion is assumed to be steady), the following formula for determining viscosity from the measured rate of sphere descent is obtained:

$$\eta = \frac{2(\rho_s - \rho_l)gR^2}{9U_\infty} \quad [5.5.3]$$

The measured viscosity is inversely proportional to the steady state velocity of sphere descent and linearly proportional to the difference in densities of sphere and liquid. It is usually considered that this formula is applicable if $Re < 0.1$. The Reynolds number is calculated from

$$Re = \frac{2RU_\infty\rho_l}{\eta} \quad [5.5.4]$$

The shear stress on the surface of moving sphere, σ_R , can be estimated according to the following equation:

$$\sigma_R = \frac{1}{3}R(\rho_s - \rho_l)g \quad [5.5.5]$$

5.5.1.1 Corrections

5.5.1.1.1 Correction for inertia effect

If the condition $Re < 0.1$ is not fulfilled in this experiment, then it means that it is necessary to make correction for the inertia effect using the following expression:⁵⁷

$$F = 6\pi R U_{\infty} \eta \left[1 + \frac{3}{16} Re - \frac{19}{1280} Re^2 + \dots \right] \quad [5.5.6]$$

The expression in brackets is a correction for inertia effect. Eq. 5.5.6 must be used instead of Eq. 5.5.2 to introduce correction. It is sufficient to include the second term in the correction factor. Taking into account this correction, an expression for calculating viscosity takes the form:

$$\eta = \frac{2(\rho_s - \rho_l)gR^2}{9U_{\infty}} \left(1 - \frac{27U_{\infty}^2}{16gR} \frac{\rho_l}{\rho_s - \rho_l} \right) \quad [5.5.7]$$

Correction for the inertia effect is negligible, if an inequality $U_{\infty} \ll \sqrt{gR}$ is fulfilled.

5.5.1.1.2 Correction for wall effect

In many practically important cases, the wall effect of a tube on the results of measurement cannot be disregarded, i.e., an inequality $R \ll R_0$ is not fulfilled. In this case, it is necessary to make correction for the wall effect. If η is viscosity, found from the first approximation, i.e., according to Eq. 5.5.3, then the viscosity η_0 , calculated by taking into account wall effect is determined as⁵⁸

$$\eta_0 = \eta \left[1 - 2.104 \frac{R}{R_0} + 2.09 \left(\frac{R}{R_0} \right)^2 - 0.95 \left(\frac{R}{R_0} \right)^4 \right] \quad [5.5.8]$$

The correction for the wall effect can be neglected only if $(R/R_0) < 0.001$, which is a sufficiently restrictive condition that is usually not satisfied. Therefore, an introduction of correction according to Eq. 5.5.8 is usually necessary.

5.5.1.1.3 Correction for non-Newtonian behavior of liquid

A method of viscosity measurement based on velocity of sphere descent is intended for analysis of Newtonian liquids. However, it is *a priori* unknown, if liquid being investigated exhibits Newtonian or non-Newtonian properties. But if the experiment does show that apparent viscosity, calculated from the above given formulas, is dependent on shear stress, then a basic method is to extrapolate the obtained dependence of apparent viscosity and the shear stress, $\eta(\sigma)$, to a limit $\sigma \rightarrow 0$. For this purpose, it is assumed that the dependence $\eta(\sigma)$ is described by known formulas. For example, it is possible to represent $\eta(\sigma)$ by the following empirical dependence

$$\eta = \frac{\eta_0}{1 + K\sigma^2} \quad [5.5.9]$$

where η_0 the initial Newtonian viscosity, K is the constant.

Then, after presenting experimental data in coordinates of η^{-1} vs. σ^2 and extrapolating them to $\sigma \rightarrow 0$, it is possible to find a value of η_0 . In this case, a constant K is also determined. It can be related to the characteristic relaxation time of non-Newtonian liquid.

An analogous method is used if rheological properties of liquid are described by different equation than Eq. 5.5.9: a selection of form of dependence of $\eta(\sigma)$ is determined by selection of coordinates which permit linearization of experimental data in order to ensure their reliable extrapolation to $\sigma = 0$.

The use of methodology of processing experimental data presented above makes it possible to obtain values of viscosity with an error not exceeding fractions of a percent.

Additionally, the increase in accuracy of measurements is achieved by application of the following recommendations: velocity measurements should be conducted in the middle part of tube (in order to eliminate inertia effect at initial stage of sphere descent and the end effects at the bottom of a tube); averaging data, obtained in repeated measurements after turning a tube by 180° (in order to exclude a non-perpendicularity of tube axis); use of an automatic method of timing motion of a sphere between two markers (in order to exclude a subjective factor in measurements), etc. In measurement of viscosity of Newtonian liquids, by varying material from which a sphere is made, or the sphere radius, it is possible to conduct measurements in the range of shear stresses from ~ 1 to 100 Pa and to measure viscosity in the range from $<10^{-3}$ to 10^2 Pa*s.

5.5.2 METHOD OF ROLLING SPHERE

A cylindrical tube can be used under a preselected angle, φ , in one of the variations of method. The driving force, instead of Eq. 5.5.1, is written as follows:

$$F = \frac{4}{3}\pi R^3(\rho_s - \rho_l)\cos\varphi \quad [5.5.10]$$

Motion of the sphere occurs by rolling and sliding along a wall. The diameter of the tube is made slightly larger than the diameter of the sphere, so that in reality flow of liquid occurs in a comparatively narrow clearance between the sphere and the tube wall. A solution of flow of Newtonian liquid can be written as follows⁵⁹

$$\eta = \frac{Cp}{U_\infty} \quad [5.5.11]$$

where p is pressure exerted by sphere of weight, F , namely $p = F/\pi R^2$, U_∞ is velocity of a steady motion of sphere, C is the instrument constant. The theory gives the following formula for constant, C , expressed through the diameter of the sphere, D , and the clearance, δ , between the tube wall and the sphere:

$$C = 0.18\delta \frac{(D/\delta - 1)^{2.5}}{1 + 0.956(D/\delta - 1)} \quad [5.5.12]$$

Use of Eqs. 5.5.11 and 5.5.12 allows one to consider instruments with the rolling sphere as absolute instruments. However, usually instruments of such type are used for comparative measurements of viscosity. In this case, Eq. 5.5.11 is written in a somewhat different form, namely

$$\eta = \frac{C_0(\rho_s - \rho_l)g\cos\varphi}{U_\infty} \quad [5.5.13]$$

with the instrument constant, C_0 , found during calibration of instrument for each sphere, available in a complete set.

For evaluating shear rates and shear stresses, at which viscosity measurements in instruments with the rolling sphere are made, it is possible to use the following formulas:

$$\dot{\gamma} = \frac{2(U_{\infty}/\delta)}{(1 - \delta/D)^2} \quad [5.5.14]$$

and

$$\sigma = 0.2(1 - \delta/D)^{1/2} \quad [5.5.15]$$

Instruments of the type under consideration are rarely used for measurements of viscosity of non-Newtonian liquids, although the theory of such measurements is known.⁶⁰

5.5.3 VISCOMETERS WITH FALLING SPHERE

Production of instruments with a falling sphere is simple. It is sufficient to have a glass tube, stopwatch, and a sphere of a known diameter.

Commercial viscometers preferably do not use a free fall, but a rolling sphere. This helps in avoiding eccentricity during the free fall and gives reproducible results. Such instruments operate as viscometers for measuring relative viscosity, and their calibration is carried out on standard liquids.

Viscosity measurements by the falling sphere method are standardized in a number of countries (e.g., ISO/DIN 12058, DIN 53015, etc.).

The *Hoeppler viscometer* (Germany) is one of the commercial instruments. The instrument cylinder is made from a heat-resistant glass. The cylinder has a diameter of 16 mm, a length of 200 mm. The cylinder is installed at an angle of 10° to vertical. The cylinder is immersed in a liquid thermostat, maintaining temperature in the range from -35 to 150°C. The experiment consists of measurement of time for sphere to move between two markers, located on the cylinder in its middle part. The viscometer is supplied with a collection of spheres, made of materials of different density, e.g., steel, glass, tungsten. Viscosity can be measured from a few hundredth to 200 Pa*s.

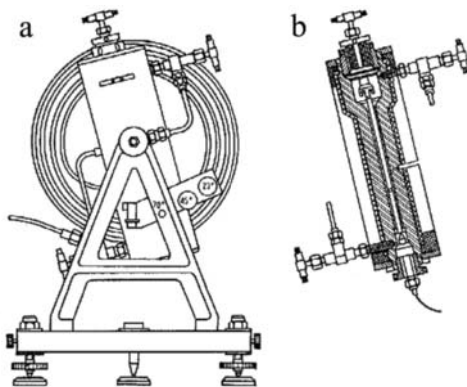


Figure 5.5.2. Rusk viscometer with a rolling ball. a – general view; b – tube placed in a high pressure chamber. (Rusk Instruments, USA).

Many companies produce these instruments. *Physica* produces a portable viscometer, *Anton Paar AMVn*. Special features of this instrument are: a very small volume of the test sample (to 150 ml), a possibility of changing the inclination angle of the cylinder from 15 to 80°, a possibility

of conducting measurements in the range of temperatures from 10 to 100°C, automation of measurements and processing of the obtained results.

An interesting modification of instruments with a falling sphere is the *Rusk viscometer* manufactured by *Rusk Instruments*, USA (see Fig. 5.5.2). Measurements of viscosities can be carried out under high pressures. In a working cylinder of this instrument, a pressure of up to 84 MPa is created. The instrument can work at temperatures up to 350°C. Construction of the instrument makes it possible to vary the angle of inclination of the cyl-

inder. Measurements of ball velocity are accomplished with an electrical detector, which makes it possible to automate the process of measurement.

Laboratory instruments, analogous in designs to the Rusk viscometer, are known in which pressure and temperature can, respectively, reach 500 MPa and 400°C.⁶¹ A working cylinder in this instrument is prepared from a quartz tube with a diameter of 7.125 mm. The tube can be installed at different inclination angles. The velocity measurement is accomplished by a noncontact method using capacitance pickups, which are the Nichrome rings, attached to the tube. For obtaining clear signals, liquid being investigated must have a specific resistance not lower than 10^6 Ohm*cm.

5.5.4 VISCOMETERS WITH FALLING CYLINDER

In the laminar motion of any body in a viscous, Newtonian liquid, a force resisting motion, F , is proportional to viscosity of the medium. Therefore, by measuring F , it is possible to determine viscosity. In viscometers in which this principle is used, sometimes instead of falling sphere, a body of cylindrical form is used.

During motion of a cylinder having radius of R_i along its axis being coaxial with the cylindrical tube having radius of R_o , a flow occurs in the space between two cylindrical surfaces. The velocity profile is described by a known formula, easily obtained from the equilibrium condition of a fluid element by taking into account corresponding boundary conditions. This formula takes the form:

$$V(r) = V_0 \frac{\ln(r/R_o)}{\ln(R_o/R_i)} \quad [5.5.16]$$

where $V(r)$ is the velocity, which depends on the radial coordinate, r , V_0 is the velocity of motion of the inner cylinder.

Hence, the following expression for a force, f , resisting motion per unit length of the cylinder is obtained

$$f = 2\pi R_i \eta \frac{dV}{dr} = \frac{2\pi \eta V_0}{\ln(R_o/R_i)} \quad [5.5.17]$$

and the shear rate (derivative dV/dr) is calculated on a surface of the inner (moving) cylinder.

Eq. 5.5.17 makes it possible to calculate a component of resistance to the motion of the cylinder, that acts on its lateral surface. A complete expression for velocity of a body descending in a liquid under its own weight, V_0 , with a difference in the material densities ($\rho_s - \rho_l$) of the solid body and liquid, takes the form⁶²

$$V_0 = \eta g (\rho_s - \rho_l) \frac{R_i^2}{2} \left(\ln k^{-1} + \frac{k^2 - 1}{k^2 + 1} \right) \chi \quad [5.5.18]$$

where $k = R_i/R_o$, and χ the correction factor due to edge effects, the values of which can theoretically be computed.

Checking this formula for Newtonian liquids with viscosity from 0.08 to 5 Pa*s shows that viscometers under consideration permit one to determine viscosity with error of up to 0.5%, if the Reynolds number does not exceed 25.

In spite of the existence of a theoretical background for viscometers with falling cylinders, they are usually used for relative measurements of viscosity, by calculating viscosity from a measured rate of fall of a cylinder, V_0 , as

$$\eta = \frac{BV_0}{\rho_s - \rho_l} \quad [5.5.19]$$

where B is the instrument constant, determined during its calibration using a standard liquid of known viscosity.

Viscometers with a falling cylinder are very simple to construct, but their use in practice is limited, since they do not possess essential advantages of viscometers with the falling sphere. These instruments are used for measuring viscosity of foaming liquids under conditions of high hydrostatic pressure.⁶³ For this application, the instrument has an enclosed high-pressure chamber with noncontact measurement (by induction sensor) of rod velocity (rod is rigidly connected to the falling cylinder). The cylinder, lifted to a given height falls under its own weight. Measurements of viscosity at pressures up to 15 MPa are possible.

5.6 EXTENSION

5.6.1 GENERAL CONSIDERATIONS

Important and unique methods of determining viscometric properties of liquids are measurements that are carried out by uniaxial extension. Mechanical properties of solid materials and rubbers under stresses are measured by uniaxial extension. A basic methodological difficulty exists for liquid measurements. Integrity of the stream has to be maintained in order to make successful measurements. This is difficult or even impossible with low viscosity liquids, such as water. But for high-viscosity fluid (e.g., polymer melts) integrity of a measured sample can be maintained for the duration of measurement. The method is mostly used for polymeric materials.

General theoretical considerations, related to the extensional flow, were examined in Section 3.7. Total deformation has to be separated into irreversible and elastic components. For Newtonian liquids, there is correlation between viscosity measured during shear flow and longitudinal viscosity (the *Trouton law*). The same is correct for a linear viscoelastic body, since viscoelastic characteristics, measured in shear flow, with factor 3 are equal to the analogous characteristics, measured by elongational flow (see Eq. 3.7.2). Results of testing elongational flow in the nonlinear region give new independent information about rheological properties of material, which cannot be obtained from shear flow measurements. For these reasons, linear extension is an important independent type of experiment. The information has theoretical value in rheological studies and it is important for many practical applications, for example, in analysis of processes of fiber spinning, film drawing, etc.

Uniformity of deformation is of fundamental importance in uniaxial extension experiments. During extension experiments with viscous fluids, the sample retains its integrity because viscosity is very high ($\sim 10^9$ Pa*s). But the sample decreases its surface of cross-section, which eventually leads to its rupture. With extension of polymeric viscoelastic

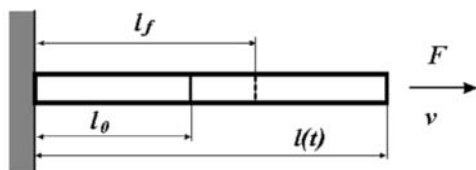


Figure 5.6.1. Typical diagram illustrating uniaxial extension.

length, l . Then, the external force is removed, and the sample restores its length to l_f . The difference between l_f and l_0 is a strain experienced during viscous flow. Measuring this strain in time, t , the strain rate is obtained. By measuring the reversible component of strain, i.e., the difference $(l - l_f)$, elasticity of material under study can be determined.⁶⁴

5.6.2. EXPERIMENTAL METHODS

5.6.2.1 The simplest measuring schemes

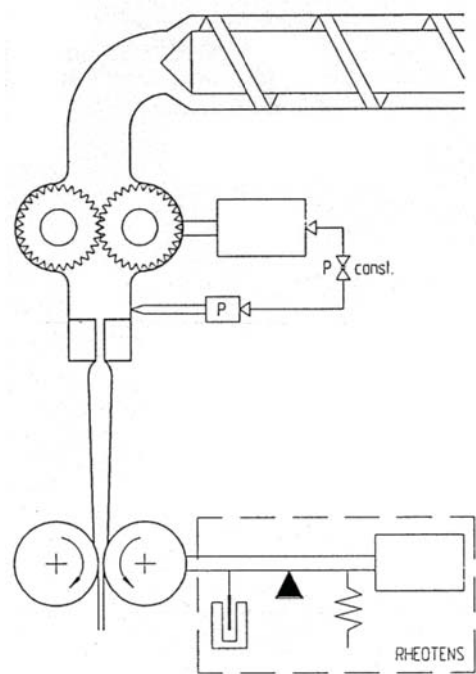


Figure 5.6.2. Instrument Rheotens for qualitative evaluation of extensibility and strength during elongation of polymer melts. [Adapted, by permission, from M. F. Wagner, B. Collington, J. Verbeke, *Rheol. Acta*, **35**, 117 (1996)].

Melt is supplied by an extruder into the head. Then, extrudate is pulled from the head by rotating rollers. The speed of roller rotation can be varied. Pressure, P , at the entrance of the head and the force with which rollers pull the extrudate are measured (a block diagram

liquids uniformity of sample shape along the length results from material elasticity, which is a stabilizing factor.

Let us examine a diagram of a sample, that, at one end is fixed in a clamp, and the other end is extended at a certain speed, v , by force, F , (Fig. 5.6.1). The initial length of the sample equals l_0 . The length of the sample after extension for time, t , has

In a simple experiment, a sample is attached to a fixed clamp and a load is attached to another end of the sample. Measuring rate of extension gives strain rate and known load gives stress. Using these data, an apparent viscosity can be calculated as a measure of sample resistance to elongation, although, in a strict sense, calculated apparent viscosity is not true viscosity but a relative characteristic of rheological properties of material in uniaxial extension. This characteristic is useful for technological evaluation of materials.

Molecular weight of ultra high molecular weight polyethylene was estimated by uniaxial extension.⁶⁵ Stress at extension of up to 600% was measured with different samples at 150°C for 10 min. The change of molecular weight from 2×10^5 to 10^7 (about 2 decimal orders) increases stress by 4 decimal orders.⁶⁶

*Rheotens*⁶⁷ (Fig. 5.6.2) is a commercial instrument used for measurements of viscosity in extension. This instrument permits determination of two basic parameters of polymer: apparent longitudinal viscosity and the maximum extension to rupture.

of the latter is shown in the dash rectangle). By changing the feed rate of melt and roller rotation rate, the deformation rate can be varied. A maximum permissible speed of drawing characterizes the melt strength properties during the extension.

5.6.2.2 Tension in a controlled regime

Quantitative measurements of elongational viscosity in uniaxial extension consist of controlled extension through imposition of constant strain and measurement of stress, or an imposition of constant stress and measurement of strain rate. In essence, the methodology here is the same as in any other rheological experiment, in which one parameter (kinematic or dynamic) is maintained constant and the other is measured.

The end of extrudate in Fig. 5.6.1 is moved with velocity of $v(t)$, which is varied with time in such a manner that strain rate (or similarly a gradient of the longitudinal velocity) remains constant. At the initial length of sample, l_0 , the initial strain rate equals v_0/l_0 , where v_0 is the initial extensional velocity.

As extension progresses, the length of the sample increases according to the following expression

$$l(t) = l_0 + \int_0^t v(t) dt \quad [5.6.1]$$

In order for strain rate to remain constant and equal to the initial value of $\dot{\epsilon}$, it is necessary that the rate of extension increases according to the equation

$$v(t) = \dot{\epsilon}_0 l_0 e^{\dot{\epsilon}_0 t} \quad [5.6.2]$$

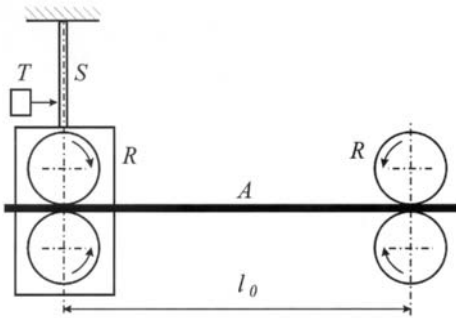


Figure 5.6.3. Principal scheme of testing of sample in uniaxial elongation under controlled conditions. A – sample; R – two pairs of drawing rollers; S – elastic element; T – force transducer.

If stress is constant, then the initial tensile force, F_0 , must decrease proportionally to elongation, since elongation is accompanied by a decrease of the cross-section of the sample. Thus, if the sample was stretched λ times, then the tensile force must decrease to the value of F_0/λ .

An automatic control of force or rate of extension must be used to conduct extension under controlled conditions. Early attempts used various mechanical devices, but now only electronic control systems are used. Measurement of longitudinal viscosity is shown in Fig. 5.6.3. Extension is accomplished using clamps with the speed

of their rotation (also the strain rate) regulated by a drive system. The force is measured by a sensor connected to an elastic element.⁶⁸ In order to avoid sample bending, the sample is placed on the surface of liquid. This liquid bath also serves as a thermostat.

The imposed strain rate is controlled by selection of rotation frequency of driving rollers. If it is necessary to conduct tests under constant stress, then the force transducer controls speed. Dimensions of the instrument permit measurements of extension up to 50 times the initial length of the sample.

These instruments can measure strain rates from $\sim 10^{-3}$ to 10 s^{-1} . Detailed analysis of errors confirmed reliability of results and possible limitations of the method.⁶⁹

The latest version of the extensional rheometer intended for high tensile stresses can create tensile stresses of up to 0.3 MPa for time shorter than 0.02 s. Total deformation ratio can be as high as 100 (it corresponds to Hencky deformation of approximately 4.6). These parameters are achieved using a pneumatic loading system.⁷⁰

5.6.2.3 Tubeless siphon instruments

In a uniaxial extension of viscoelastic liquids a so-called *siphon effect*, described in Section 3.7.4 and shown in Fig. 3.7.10, is observed.

A complex velocity profile, arising during flow, does not permit us to consider this as an absolute method. However, direct measurements demonstrated that at a certain length of jet, the velocity gradient remains constant.⁷¹ The latter gives basis for quantitative calculations of elongational viscosity according to experimental data obtained in the regime of siphon flow. The strain rate is controlled by variation of speed of winding of the liquid jet. The force of extension is created either by connecting the free end of the capillary to a vacuum (as in Fig. 3.7.10), or by measuring the force acting on the winding roller (as in Fig. 3.7.10).

In known instruments of such type, the frequency of roller rotation is in the range from 0.1 to 170 s^{-1} , which gives velocity gradients of up to 200 s^{-1} . Such high rates of the elongational deformation cannot be created in instruments with controlled regimes of extension. The attractiveness of this method is also related to the fact that with siphon flow

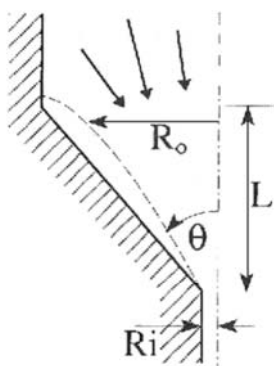
it is possible to investigate comparatively low viscosity (but elastic), moderately dilute, polymer solutions that cannot be studied in instruments with controlled regimes of extension. At the same time, this method and instruments based on this principle should be considered as relative, since during the siphon flow it is difficult to separate viscous flow from the elastic deformation.

5.6.2.4 Flow in convergent channels

During an abrupt change in the cross-section of a channel, the longitudinal acceleration of flow is developed at the entrance to a small channel. It was proposed to use this special feature of flow for evaluation of longitudinal viscosity.⁷²

The diagram of flow in a converging channel is shown in Fig. 5.6.4. It is evident that upon transfer from a tube having radius, R_o , to a capillary having radius, R_i , the cone-shaped flow is formed with an angle, θ , and length, L . In this zone, shear and elongational flows are superimposed.

Figure 5.6.4. Flow in converging channel – longitudinal velocity gradient.



In order to estimate the elongational viscosity, a pressure difference, Δp , at the entrance into a capillary should be measured. This difference is responsible for the elongational flow and determination of the normal stress. The rate of stretching deformation is found from rates of flow in tube, V_o , and in a capillary, V_i , as

$$\dot{\epsilon} = \frac{V_i - V_o}{L} = \frac{Q}{\pi L} \left(\frac{1}{R_i^2} - \frac{1}{R_o^2} \right) \quad [5.6.3]$$

Hence, it is possible to find a relative value of the elongational viscosity, η_E .

However, a problem that remains undetermined during this evaluation is the contribution of shear strains. For stricter calculations of the velocity field and, correspondingly, the elongational viscosity, the approach of a lubricating film layer is used. According to this model it is assumed that shear occurs in a very thin (lubricating) layer, and in the material bulk uniaxial extension occurs.⁷³ The problem with this concept is that correct theoretical calculation is possible only if the model of rheological behavior of investigated material is *a priori* known, which is not always possible.

5.6.2.5 High strain rate methods

Several methods of studying elongational flow were proposed for analysis of elongational deformations of dilute solutions, in the limit for studying extension of individual macromolecules.⁷⁴ A diagram of four-rollers method is shown in Fig. 5.6.5. A liquid is taken into the interroller space and then it is drawn out of it. There is a certain region where flow occurs in a pure shear mode that is equivalent to two-directional (planar) elongation (see Section 1.2.4.2).

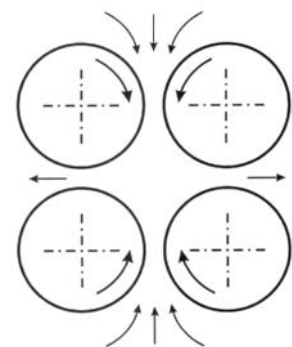


Figure 5.6.5. Four-rollers method for creation of longitudinal flow.

Using optical methods (birefringence) it is possible to estimate the gradient of longitudinal velocity and stress, and thus the elongational viscosity of polymeric solutions at deformation rates of the order of hundreds s^{-1} . This method is very informative for evaluating some physical properties of macromolecules (for example, see Fig. 3.7.11 and discussion in Section 3.7.5). This method also allows one to observe instabilities due to elasticity of polymeric strands in dilute solutions.

Another optical method of investigation of the longitudinal flow of dilute polymer solutions includes flow of liquid in two coaxial capillaries moving towards each other. Here, in a certain flow region, the uniaxial longitudinal flow is realized. Deformation rates can exceed $10^3 s^{-1}$. Both methods can be used for studies in the field of polymer physics, in particular to observe the coil-to-stretch transition of flexible macromolecules.

5.6.2.6 Capillary breakup elongational rheometry

The interest in extension properties of low viscosity substances (polymer solutions, emulsions) lead to the creation of a new type of instruments.⁷⁵ The method consists of extension of a small liquid droplet placed between parallel plates. This liquid droplet has a cylindrical shape. Then, the plates are rapidly moved apart from each other. This type of deformation can be treated as a step strain. The evolution of the liquid bridge between plates is treated in the terms of viscous and viscoelastic properties of a matter. The final stage is the break-up of the sample. This method can be applied to liquids with viscosities down to several tens mPa*s.

However, there are some difficulties in treating experimental results because of an uncertainty of the shape of the sample surface. The calculations of relaxation times and other quantities are easy when and if the initial shape of the sample is cylindrical and the

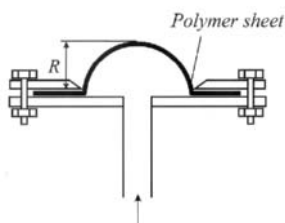


Figure 5.6.6. Schematic of bubble inflation rheometer. [Adapted, by permission, from C. D. Denson, R. J. Gallo, *Polym. Eng. Sci.*, **11**, 174 (1971)].

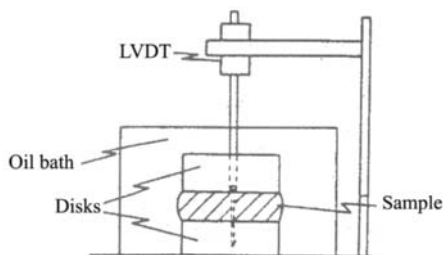


Figure 5.6.8. Schematic of lubricated squeezing flow instrument. [Adapted, by permission, from S. Chatraei, C. W. Macosko, H. H. Winter, *J. Rheol.*, **25**, 433 (1981)].

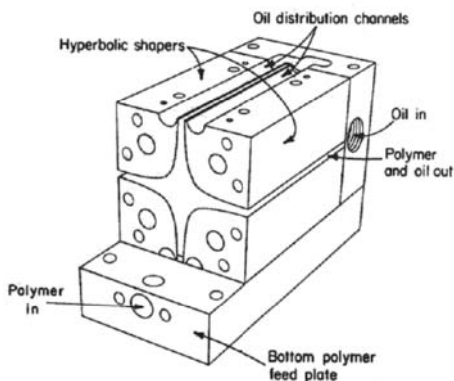


Figure 5.6.7. Schematic representation of die for creating lubricated planar stagnation flow of a polymer melt. [Adapted, by permission, from H. H. Winter, C. W. Macosko, K. E. Bennet, *Rheol. Acta*, **18**, 323 (1979)].

diameter of a cylinder decays exponentially in time. In this case, the deformation is uniform and proceeds at constant strain rate. Besides, the choice of a simple rheological model used for calculations is important. Moreover, experiments and numerical calculations demonstrated that the situation is more complex.⁷⁶

5.6.3 BIAXIAL EXTENSION

Material testing using the biaxial extension (at equal or different strain rates in two mutually perpendicular axes), just as in a uniaxial extension, gives independent information about rheological properties of materials, and therefore, it is of interest. Biaxial extensional flow occurs in several polymer processing operations such as film blowing, blow molding, and vacuum forming. Therefore, the rheological behavior of polymers subjected to biaxial extension is of prime importance in understanding and improving such processes. Significant research in biaxial rheology has occurred, primarily during the last two decades.

A number of methods are used to obtain biaxial extension of polymer melts including sheet inflation,⁷⁷ axisymmetric and planar stagnation,⁷⁸ lubricated squeezing flow,⁷⁹ and sheet elongation.⁸⁰

Sheet or bubble inflation involves a circular sample that is clamped around its perimeter (Fig. 5.6.6). Inert gas or silicone oil under pressure is introduced to one side of the sheet, causing inflation of the bubble. An equal biaxial elongation occurs at the top of the bubble. The strain rate is calculated by measuring the deformation of grid marks made on the sample. The stresses in the inflated bubble are related to the internal pressure by controlling which one can impose a constant stress or a constant elongation rate.

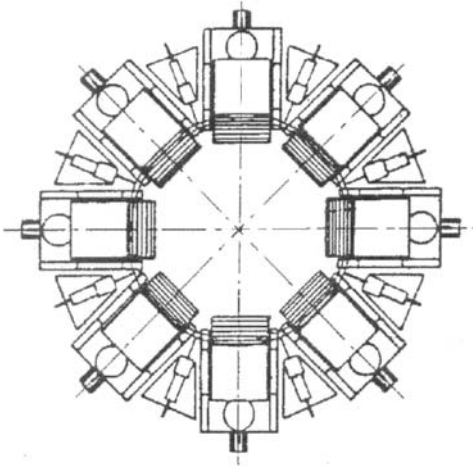


Figure 5.6.9. Instrument with rotary clamps for measurement of biaxial viscosity. [Adapted, by permission, from J. Meissner, S. E. Stevenson, A. Demarmels, P. Portmann, *J. Non-Newt. Fluid Mech.*, **11**, 221 (1979)].

force during squeezing flow and therefore biaxial viscosity can be measured.

A sheet elongation is achieved by stretching a sheet of polymer along its periphery using specially designed rotary clamps (Fig. 5.6.9). The rotary clamps are able to pull the sample at a controlled rate in two directions. The pulling force is measured on clamps. Depending on the arrangement of clamps, equal biaxial stretching or planar elongational flow can be achieved.

5.7 MEASUREMENT OF VISCOELASTIC PROPERTIES BY DYNAMIC (OSCILLATION) METHODS

5.7.1 PRINCIPLES OF MEASUREMENT – HOMOGENEOUS DEFORMATION

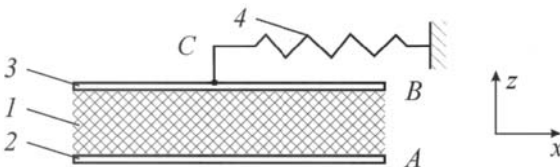


Figure 5.7.1. Principal scheme of measurements in forced oscillating mode. 1 – sample; 2 – driving plate A; 3 – plate B connected with a measuring device; 4 – spring of a measuring device with rigidity Z .

Let a uniform isotropic sample be placed between two parallel plates A and B (Fig. 5.7.1). The gap between the plates is small in comparison with the size of plates. The edge effects are assumed to be negligible.

The plate A is subjected to forced oscillations in accordance with a harmonic law:⁸¹

$$x_A(t) = x_{0A} e^{i\omega t} \quad [5.7.1]$$

where x_A is a displacement of plate A depending on time t , x_{0A} is the amplitude, and ω is frequency of oscillation.

It is assumed that slip on the boundaries of the plate is absent. Stresses appearing as a result of movement of plate A are transferred *via* sample to plate B. The latter is joined to a stationary fixed frame of the measuring device through an elastic element – a spring of rigidity, Z .⁸² The displacement of the upper plate is a measure of stresses in the sample which characterize rheological properties of the material. It is assumed that a layer of material is thin enough to suppose that stresses inside the sample are uniform and the mass of the sample is negligible. The last suppositions will be formulated quantitatively below in Section 5.7.2.

If properties of material do not change in time, the movement of plate B will occur by a harmonic law with complex amplitude $x_B^* = x_{0B} e^{i\alpha}$ and with the same frequency, ω , as the movement of plate A:

$$x_B(t) = x_B^* e^{i\omega t} = x_{0B} e^{i\alpha} e^{i\omega t} = x_{0B} e^{i(\omega t + \alpha)} \quad [5.7.2]$$

In this expression, x_{0B} , is the amplitude of oscillations of plate B and α is the *phase angle* – phase difference between displacements of both plates.

For material with arbitrary properties, the relationship between shear stresses, σ , and deformations, γ , can be written as

$$\sigma = G^* \gamma = G^* \left(\frac{dx}{dz} \right)$$

where G^* is the complex dynamic modulus depending on frequency.

The main experimental goal is to calculate $G^* = G' + iG''$ based on pre-set value of x_{0A} , and measured values of x_{0B} and α and known sizes of the measuring device at different frequencies.

In the ideal scheme of deformation considered here, the equation of motion of the point C in Fig. 5.7.1 is written as

$$m \frac{d^2 x_B}{dt^2} + Z x_B + \frac{S}{h} G^* (x_B - x_A) = 0 \quad [5.7.3]$$

The value $(x_B - x_A)/h$ is deformation dx/dz , S is the surface area of plates, h is the gap between plates, the ratio $K = S/h$ is the form-factor and m is mass of plate B. This equation is solved by substitution of expressions for x_A (Eq. 5.7.1) and x_B (Eq. 5.7.2). The final result obtained after rearrangements is

$$G^* = \frac{(Z - m\omega^2)x_{0B}e^{i\alpha}}{K(x_{0A} - x_{0B}e^{i\alpha})} \quad [5.7.4]$$

By separating real and imaginary parts of the expression for G^* , one obtains the following formulas for the components of the dynamic modulus:

$$G' = \frac{(Z - m\omega^2)(p \cos \alpha - 1)}{K[(p - \cos \alpha)^2 + \sin^2 \alpha]} \quad [5.7.5]$$

$$G'' = \frac{(Z - m\omega^2)p \sin \alpha}{K[(p - \cos \alpha)^2 + \sin^2 \alpha]} \quad [5.7.6]$$

and

$$\tan \delta = \frac{G''}{G'} = \frac{p \sin \alpha}{p \cos \alpha - 1} \quad [5.7.7]$$

The factor p is the amplitude ratio: $p = x_{0A}/x_{0B}$.

Eqs. 5.7.5 and 5.7.6 are the solutions of the formulated problem. A particular case of this solution is important when $Z \gg m\omega^2$. The last inequality means that the inertia of the moving parts of plate B is negligible in comparison with the force of the deforming spring. High rigidity of the spring also provides its small displacement. So it can be assumed that in this case $p \gg 1$. This leads to the most simplified expressions for the components of dynamic modulus:

$$G' = \frac{Z}{Kp} \cos \alpha \quad [5.7.8]$$

$$G'' = \frac{Z}{Kp} \sin \alpha \quad [5.7.9]$$

The phase angle, α , equals loss angle, δ . However, this is not so in a general case, as seen from Eq. 5.7.7.

Eqs. 5.7.5 and 5.7.6 are valid in the whole frequency range except for resonance frequency of measuring device, ω_0 , which is calculated as

$$\omega_0 = \sqrt{Z/m} \quad [5.7.10]$$

The results of measurements in the vicinity of ω_0 are unreliable because even a slight error in measuring phase angle and amplitude ratio leads to a large error in calculating components of dynamic modulus.⁸³

In application of the principal scheme of the complex modulus calculation, a problem arises as to how to correctly measure small phase angles. One possible solution of the problem is to use controlled amplification of signals of a measuring device.⁸⁴ This method permits measurement of phase angles as low as $1 \cdot 10^{-4}$ rad. The other approach is based on the *correlation method* – removing noise of signals by measuring the angle in a number of cycles of oscillations. This improves reliability in calculating components of dynamic modulus.⁸⁵ In both cases, this problem is solved by application of known electronic means and using computer techniques.

5.7.2 INHOMOGENOUS DEFORMATIONS

An ideal scheme of measurements, as discussed in Section 5.7.1, did not take into account possible inhomogeneity in the sample deformation. However, a general case must include consideration of stress distribution inside a sample if a gap size between plates in Fig. 5.7.1 is not very small. Besides, it is necessary to give a strict definition of the limitation of the gap size in order to consider it to be small. The solution is based on analysis of equi-

librium of an infinitesimally thin layer of material of thickness, dz , which is parallel to the plates. The equilibrium equation for this layer is

$$\rho \frac{d^2 x}{dt^2} - G^* \frac{\partial^2 x}{\partial z^2} = 0 \quad [5.7.11]$$

where ρ is density of material under investigation.

The displacement x depends on time as well as on the distance from plate A designated by coordinate z (for plate A, $z = 0$). The general solution of Eq. 5.7.11 is

$$x(z, t) = x_0^*(z) e^{i\omega t} = x_0 e^{i\alpha} e^{i\omega t} \quad [5.7.12]$$

where x_0^* is the complex amplitude of oscillations in a layer located at position z and α is the phase angle in this layer (depending on z).

Substituting Eq. 5.7.12 into Eq. 5.7.11 gives the linear second-order differential equation for x_0^*

$$G^* \frac{d^2 x_0^*}{dz^2} + \rho \omega^2 x_0^* = 0 \quad [5.7.13]$$

The integration constants are found from boundary conditions:

$$x_0^* = x_{0A} \text{ at } z = 0$$

and the equilibrium conditions for forces acting at plate B:

$$\frac{\partial x_0^*}{\partial z} = \frac{x_B^*(m\omega^2 - Z)}{SG^*} \text{ at } z = h.$$

The solution of Eq. 5.7.13 with these boundary conditions gives the function $x(z, t)$ and its particular case at $z = h$: $x(h, t) \equiv x_B^*(t)$. Then, the ratio x_{0A}/x_B^* is found which is expressed in the following manner

$$\frac{x_{0A}}{x_B^*} = \cosh(kh) - \frac{m\omega^2 - Z}{SG^*} \cosh(kh) \quad [5.7.14]$$

where $k = \omega \sqrt{-\rho/G^*}$

Eq. 5.7.14 is the complete solution of the problem under discussion, because it is an equation for G^* including all necessary parameters – x_{0A} and x_B^* , the latter being determined if amplitude, x_{0B} , and phase angle, α , have been measured.

However, this equation is not convenient for practical applications because the unknown value G^* enters not only the coefficient of the second term at the right-hand side of Eq. 5.7.14 but also constant k . Therefore, approximations based on this equation are ordinarily used. For this purpose, the functions entering this equation are presented as the Taylor series and the higher order terms of G^* , other than $(G^*)^{-1}$, are omitted. Then, the *linear approximation* leads to

$$G^* \left(1 - \frac{p}{e^{i\alpha}}\right) = \frac{m\omega^2 - Z}{K} + \frac{\rho\omega^2 h^2}{2} \quad [5.7.15]$$

A possibility to use Eq. 5.7.15 instead of exact solution Eq. 5.7.14 is determined by the condition $(kh)^2 \ll 5$ or $G^* \gg 0.2\rho\omega^2 h^2$, i.e., the gap h must not be too large.

Practical application of Eq. 5.7.15 is based on separating it into real and imaginary parts.

Eq. 5.7.15 can be written in a form equivalent to Eq. 5.7.4, if one writes the right-hand side of Eq. 5.7.15 as

$$\frac{m\omega^2 - Z}{K} + \frac{\rho\omega^2 h^2}{2} = \frac{m_0\omega^2 - Z}{K} \quad [5.7.16]$$

where $m_0 = m[1 + (m_s/2m)]$ is called the *reduced mass* and the value $m_s = \rho Sh$ is mass of the deforming sample. The value $m_s/2$ is called the *coupled mass*. Using m_0 instead of m in Eq. 5.7.4 accounts for inertia of the sample.

The physical meaning of approximation, Eq. 5.7.15, and neglecting the stress distribution inside a sample, can provide a clear understanding of the meaning of the product kh . If the displacement of plate B is very small such that $x_{0B} \ll x_{0A}$, then it is possible to show that the initial amplitude of deformation, x_{0A} , damps by e times at a distance δ from plate A determined by equality $(k\delta) = 1$.⁸⁶ The value δ in the theory of oscillations is called attenuation. Damping is negligible (or deformations in sample can be considered as uniform) if the following strong inequality is valid: $h \ll \delta$. This inequality shows that the term “small gap” means such a gap thickness along which damping oscillation inside sample is negligible.

5.7.3 TORSION OSCILLATIONS

This type of deformation mode is realized for rigid materials if the sample is prepared in the form of a long rod that can maintain its shape. Also, this deformation mode is realized in all rotational devices, which were described in Section 5.3 for measuring rheological properties of fluid materials, if one uses oscillations instead of rotation. In this case, the sample fills a gap between coaxial cylinders, cone and plate, or two parallel disks in rheometer. In all these cases, the angle of torsion is assumed to be small enough to exclude axial deformations.

An equation describing torsional oscillations of cylindrical sample caused by twisting of one of its ends is written as

$$G^* \frac{d^2 \theta_0^*}{dt^2} + \rho\omega^2 \theta_0^* = 0 \quad [5.7.17]$$

where $\theta_0^*(z) = \theta e^{i\alpha}$ is a complex amplitude of twisting. Both amplitude and phase angle are varied along the vertical axis z .

This equation is identical to Eq. 5.7.13 with evident changes of linear sizes for circular ones. Then, all details of the solution and discussion of results of calculations are the same, if one changes mass, m , to the moment of inertia, I , rigidity, Z , to the twisting rigid-

ity of a torsion bar and the form-factor to $K = \pi R^4/2H$, where R is radius and H is the cylinder height.

If the experiment is carried out in a cone and plate device, then again nothing changes, though the form-factor becomes $K = 2\pi R^3/3\phi$, where R is the radius of the cone and ϕ is the angle between the cone and the plate.

In measuring rheological properties of viscoelastic liquid-like materials, the deformation of a hollow cylindrical sample is often studied. Such sample is formed by material filling gap of height, H , between two coaxial cylinders. One of the cylinders (let it be the outer cylinder with radius R_o) is oscillating with a frequency, ω , and an angular amplitude, θ_{0A} . The angular displacement of the other cylinder, θ_B , (with radius R_i) is measured. If the gap between cylinders is small, the curvature of the sample can be neglected and this is similar to shear deformation shown in Fig. 5.7.1. This situation takes place when the strong inequality $(R_o - R_i) \ll R_i$ is satisfied. In this case, all discussion is the same as in Section 5.7.1 and the form-factor is expressed as

$$K = \frac{2\pi R_i^2 H}{R_o - R_i} \cong \frac{2\pi R_o^2 H}{R_o - R_i}$$

The arbitrary size of the gap between coaxial cylinders can be an interesting case. The theory of this experimental method in its principal features is the same as described in Section 5.7.2, though an equilibrium equation, written in cylindrical coordinates, looks somewhat different than Eq. 5.7.13:

$$\frac{d^2 \theta_0^*}{dr^2} + \frac{3}{r} \frac{d\theta_0^*}{dr} + \frac{\rho \omega^2 \theta_0^*}{G^*} = 0 \quad [5.7.18]$$

where θ_0^* includes an amplitude and a phase angle, both depending on current radius, r .

The complete solution and analysis of this equation is possible⁸⁷ but practical interest is limited by the linear approximation, which gives:

$$\frac{\theta_{0A}^*}{\theta_B^*} = 1 + \frac{1}{G^*} \quad [5.7.19]$$

Then, by separating complex numbers into real and imaginary parts, the following expressions for components of dynamic modulus are given by:

$$G' = \frac{L(p \cos \alpha - 1)}{(p - \cos \alpha)^2 + \sin^2 \alpha} \quad [5.7.20]$$

$$G'' = \frac{L p \sin \alpha}{(p - \cos \alpha)^2 + \sin^2 \alpha} \quad [5.7.21]$$

The analogy between these equations and Eqs. 5.7.5 and 5.7.6 is quite evident, if one takes into account that $p = \theta_{0A}/\theta_{0B}$, and coefficient L is expressed as

$$L = \left[\frac{I\omega^2 - Z}{4\pi H} + \frac{\rho\omega^2(R_o^2 - R_i^2)R_i^2}{8} \right] \frac{R_o^2 - R_i^2}{R_o^2 R_i^2} \quad [5.7.22]$$

This coefficient is equivalent to the factor $(Z - m\omega^2)/K$ that enters Eqs. 5.7.5 and 5.7.6 with an appropriate choice of form-factor. Besides, the coefficient L includes the inertia of moving elements coupled with a torsion element and inertia of the moving material. Therefore, similar to Eq. 5.7.16 reduced moment of inertia must include the coupled inertial term.

An expression for loss tangent, derived from Eqs. 5.7.20 and 5.7.21, is equivalent to Eq. 5.7.7. It is essential that both equations for $\tan\delta$ do not include any geometrical factors. Also, $\tan\delta$ is calculated by measuring p and phase angle only. It is useful for measurements in some applied problems where the main interest is in finding mechanical losses, but not for dynamic modulus.

5.7.4 MEASURING THE IMPEDANCE OF A SYSTEM

One of the versions of oscillating measurements is fixing plate A and applying force $F(t)$ to plate B varying as

$$F = F_0 e^{i\omega t} \quad [5.7.23]$$

where F_0 is the force amplitude and ω is frequency.

Displacement of the plate B, as well as its velocity, v , follows harmonic law. The characteristic of such a system is its *mechanical impedance*, Y_m^* , determined as

$$Y_m^* = \frac{F}{v} = R_m + iX_m \quad [5.7.24]$$

and consisting real (active), R_m , and imaginary (reactive), X_m , components.

In the scheme shown in Fig. 5.7.1

$$X_m = \frac{G''}{K\omega} \quad [5.7.25]$$

and

$$R_m = -\frac{G'}{K\omega} - \frac{Z}{\omega} + m\omega \quad [5.7.26]$$

Now it is reasonable not to measure force and velocity separately but to measure their ratio. It permits calculation of components of dynamic modulus from mechanical impedance. Some experimental devices directly measure mechanical impedance and thus this is a simple way to calculate G' and G'' .

This experimental scheme can also be realized in torsion deformation if one fixes one boundary surface and varies torque by a harmonic law. One of the possible versions of this method of measurement of viscoelastic properties is by subjecting a tube-like sample placed between two coaxial cylinders to an axial displacement. The velocity of oscillations is given by equation:

$$v = v_0 e^{i\omega t} \quad [5.7.27]$$

Then, by measuring mechanical impedance it is possible to find components of dynamic modulus. The theory for arbitrary shape of the measuring device is not difficult, but the final equations are rather bulky. However, in the linear approximation (which is applicable in the majority of real experimental schemes), the result of calculation is very simple as indicated by the following formula:

$$Y_m^* = \frac{F_0^*}{v_0} = \frac{F_0 e^{i\alpha}}{v_0} = \frac{KG^*}{\omega} \quad [5.7.28]$$

where the form-factor K is

$$K = \frac{2\pi H(R_o^2 + R_i^2)}{(R_o^2 + R_i^2) \ln \frac{R_o}{R_i} - (R_o^2 - R_i^2)} \quad [5.7.29]$$

Then, very simple equations for G' and G'' are derived:

$$G' = \frac{F_0 \omega}{K v_0} \cos \alpha \quad [5.7.30]$$

and

$$G'' = \frac{F_0 \omega}{K v_0} \sin \alpha \quad [5.7.31]$$

which are analogous in their structure to Eqs. 5.7.8 and 5.7.9, respectively.

5.7.5 RESONANCE OSCILLATIONS

There is a very special case of oscillation, when amplitude of deformation is at maximum. This is called *resonance oscillations*.

The theory of resonance oscillations is based on the analysis of movement of the upper plate B in Fig. 5.7.1, which is loaded by the oscillating force, as described by Eq. 5.7.23. The equilibrium equation in this case is written as

$$m \frac{d^2 x}{dt^2} + Zx + KG^* x = f_0 e^{i\omega t} \quad [5.7.32]$$

where f_0 is the amplitude of force, all other notations are similar to previously used.

The solution of this equation for components of dynamic modulus is

$$G' = \frac{1}{K} \left[\frac{f_0}{x_{0B}} \cos \alpha - (Z - m\omega^2) \right] \quad [5.7.33]$$

$$G'' = \frac{1}{K} \left(\frac{f_0}{x_{0B}} \sin \alpha \right) \quad [5.7.34]$$

Then, excluding the phase angle, it is possible to obtain the following expression for the amplitude of oscillations of plate B:

$$x_{0B} = \frac{f_0}{\sqrt{(KG' + Z - m\omega^2)^2 + (KG'')^2}} \quad [5.7.35]$$

Resonance corresponds to the maximum of x_{0B} as a function of ω . However, it is impossible to obtain the exact solution for x_{0B}^{\max} from Eq. 5.7.35 because G' and G'' are unknown functions of ω . The analysis becomes easier if rigid viscoelastic materials with low losses are considered, i.e., if $G'' \ll G'$. In this case, the minimum value of the denominator (and consequently, maximum of x_{0B}) is reached at the *resonance frequency*, ω_0 , which is calculated as

$$\omega_0 = \sqrt{\frac{KG' + Z}{m}} \quad [5.7.36]$$

Then, the components of dynamic modulus are easily found at this frequency as

$$G' = \frac{m}{K} \left(\omega_0^2 - \frac{Z}{m} \right) \quad [5.7.37]$$

and

$$G'' = \frac{F_0}{Kx_{0B}^{\max}} \quad [5.7.38]$$

The experimental procedure consists of varying frequency and measuring amplitude of oscillation until a maximum x_{0B}^{\max} is reached. Additional information can be obtained by measuring the width of a resonance curve. This width is the difference of frequencies $\Delta\omega = \omega_1 - \omega_2$ at half of the height of the resonance value, x_{0B}^{\max} . In the case of low losses and sharp resonance, this value characterizes the loss modulus, which is calculated as

$$G'' = \frac{\Delta\omega G'}{\sqrt{3}\omega_0} \frac{1}{1 - Z/(m\omega^2)} \quad [5.7.39]$$

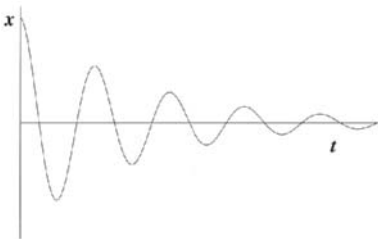


Figure 5.7.2. Damping oscillations.

The resonance method is applicable for measuring G' and G'' at a single resonance frequency for low loss materials. In fact, the resonance frequency can be changed (though not within a wide range) by varying the front-factor, K , and mass, m . A possible version of this method consists of measuring modulus at overtones of the resonance frequency.

5.7.6 DAMPING (FREE) OSCILLATIONS

The oscillations of plate B in Fig. 5.7.1 are supported by the applied force. If the force is imposed on a plate to initially shift its position from an equilibrium state, the plate will approach this state either monotonously or in the mode of *damping oscillations* (Fig. 5.7.2).

The equation of motion of the point C in Fig. 5.7.1 is the same as in all previous cases with the difference in the boundary conditions used for solution. The equilibrium equation can be written as

$$m \frac{d^2 x}{dt^2} + Zx + K \left(G'x + \eta' \frac{dx}{dt} \right) = 0 \quad [5.7.40]$$

where the term in the parenthesis reflects both components (elastic, G' , and damping, η') of the reaction of liquid.

The solution of Eq. 5.7.40 has the form

$$x(t) = x_{0B} e^{(i\omega - \alpha)t} \quad [5.7.41]$$

or

$$x(t) = x_{0B} e^{-\alpha t} \cos \omega t \quad [5.7.41a]$$

where ω is frequency of oscillations and α is a damping factor. The substitution of Eq. 5.7.41 into Eq. 5.7.40 and dividing the resulting expression into real and imaginary parts gives

$$G' = \frac{m}{K} \left[(\omega^2 + \alpha^2) - \frac{Z}{m} \right] \quad [5.7.42]$$

$$G'' = \frac{2m\omega\alpha}{K} \quad [5.7.43]$$

and

$$\tan \delta = \frac{2m\omega\alpha}{m(\omega^2 + \alpha^2) - Z} \quad [5.7.44]$$

The important characteristics of a measuring system is its *natural frequency* $\omega_0 = \sqrt{Z/m}$, which is determined in experiment without a sample. Using this value, the final expressions for the components of dynamic modulus are written as

$$G' = \frac{m\omega^2}{K} \left[1 + \left(\frac{\alpha}{\omega} \right)^2 - \left(\frac{\omega_0}{\omega} \right)^2 \right] \quad [5.7.45]$$

$$G'' = \frac{2m\omega^2\alpha}{K\omega} \quad [5.7.46]$$

and

$$\tan \delta = \frac{2(\alpha/\omega)}{(\alpha/\omega)^2 + [1 - (\omega_0/\omega)^2]} \quad [5.7.47]$$

These equations allow one to find G' and G'' by determining the parameter of a measuring device, ω_0 , and two experimental values ω and α .

The frequency of oscillations is easily observed and found from experiment. The value of a damping factor, α , is related to the so-called *logarithmic decrement of damping*, Δ , which is determined as

$$\Delta = \ln \frac{X_{n-1}}{X_n} = \alpha(t_n - t_{n-1}) \quad [5.7.48]$$

where X_i are the maximum values of displacement (of the function $x(t)$) reached at the moments t_i . The difference $(t_n - t_{n-1})$ is the period of oscillations and equals $2\pi/\omega$.

In the simplest case (which is valid in many real experimental situations), $\alpha/\omega \ll 1$ and $Z/m\omega^2 \ll 1$. Then, the following equations for G' , G'' and $\tan\delta$ can be used

$$G' = \frac{m\omega^2}{K} \left(1 + \frac{\Delta^2}{4\pi^2} \right) = \frac{m}{K} (\omega^2 + \alpha^2) \quad [5.7.49]$$

$$G'' = \frac{m\omega^2 \Delta}{K \pi} \quad [5.7.50]$$

$$\tan\delta = \frac{\Delta}{\pi} \quad [5.7.51]$$

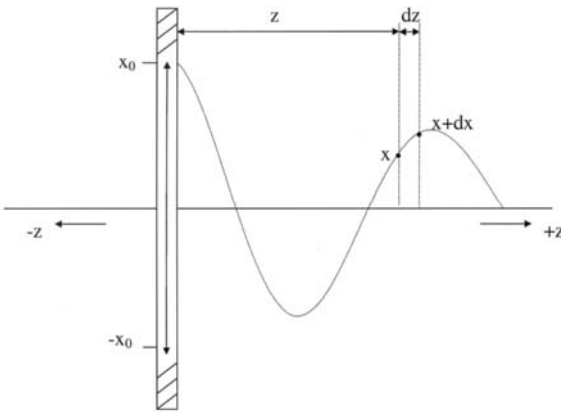


Figure 5.7.3. Oscillation of plate along its plane in material.

above discussed cases. The equations derived in this section are valid, if $\omega \ll (1/h)\sqrt{G^*/\rho}$, where ρ is density of material under study.

Damping oscillations are often realized using the torsion mode of deformations. If sample is cylindrical, Eqs (5.7.45) – (5.7.47) as well as Eqs (5.7.49) – (5.7.51) are valid with a change of mass, m , for moment of inertia, I , and form-factor is $K = 4\pi R_0^2 R_1^2 H / (R_0^2 - R_1^2)$.

Samples of other geometrical forms can also be used in the damping oscillation experiment utilizing torsion. Formulas for calculating G' and G'' are much more complicated due to contribution of out-of-plane bending and twisting.⁸⁸

Parameters of material determined by damping oscillation method are measured at a single frequency. This frequency can be measured or roughly estimated from Eq. 5.7.49 as $\omega \approx \sqrt{KG'}/m$ assuming that $\alpha \ll \omega$. However, frequency can be varied (though not within a wide range) by changing the parameters of the measuring system – form-factor, K , and moving mass, m .

The basic theory of damping oscillations does not take into account sample inertia. The situation here is quite the same as in the

5.7.7 WAVE PROPAGATION

In these methods,⁸⁹ the propagation of waves is directly observed for samples of large thickness such that several wave lengths are present within the material. If the damping characteristics of materials are not high, the wavelength and attenuation can be measured. These methods are different from the previously discussed methods. In the former methods, the effect of a wave is detected on the surface of instruments with sample thickness being much smaller than the wavelength. Typically, shear and longitudinal waves are used for measurements of viscoelastic properties of materials.

5.7.7.1 Shear waves

In this case, a plate is placed in material. The plate is subjected to oscillations in its own plane along x axis, as indicated in Fig. 5.7.3. The wave propagates in the direction of the z-axis. The amplitude and frequency of oscillations is x_0 and ω , respectively. At some distances z and $z+dz$ from the plate, the displacements in material are x and $x+dx$, respectively. Then, the shear strain and shear stress at the position z in material is, respectively:

$$\gamma(t, z) = \frac{\partial x(t, z)}{\partial z}, \quad d\sigma(t, z) = \frac{\partial \sigma(t, z)}{\partial z} dz \quad [5.7.52]$$

Equation of motion is

$$\rho \frac{\partial^2 x}{\partial t^2} = \frac{\partial \sigma}{\partial z} \quad [5.7.53]$$

with the shear stress, σ , being

$$\sigma = G'\gamma + \frac{G''}{\omega} \frac{d\gamma}{dt} \quad [5.7.54]$$

Substitution of Eq. 5.7.54 in Eq. 5.7.53 leads to

$$\rho \frac{\partial^2 x}{\partial t^2} = G' \frac{\partial^2 x}{\partial z^2} + \frac{G''}{\omega} \frac{\partial^3 x}{\partial t \partial z^2} \quad [5.7.55]$$

Since the solution of Eq. 5.7.55 is proportional to $e^{i\omega t}$, one obtains

$$\rho \omega^2 x = G' \frac{\partial^2 x}{\partial z^2} + iG'' \frac{\partial^2 x}{\partial z^2} = G^* \frac{\partial^2 x}{\partial z^2} \quad \text{or} \quad \frac{\partial^2 x}{\partial z^2} = \Gamma^2 x \quad [5.7.56]$$

with $\Gamma = -(\rho \omega^2)/G^*$. The solution of Eq. 5.7.56 is

$$x(z, t) = (k_1 e^{\Gamma z} + k_2 e^{-\Gamma z}) e^{i\omega t} \quad [5.7.57]$$

with k_1 and k_2 being integration constants that are determined based on the geometry of experiment. In a semi-infinite medium, $k_1 = 0$ and Eq. 5.7.57 becomes

$$x(z, t) = x_0 e^{-\Gamma z} e^{i\omega t} \quad [5.7.58]$$

It is convenient to replace Γ in Eq. 5.7.58 by

$$\Gamma = \frac{1}{z_0} + i2\pi\lambda \quad [5.7.59]$$

Then, Eq. 5.7.58 becomes

$$x(z, t) = x_0 e^{i(\omega t - 2\pi z/\lambda) - \frac{z}{z_0}} \quad [5.7.60]$$

where λ is the wavelength.

It is seen that at $z = z_0$, the amplitude of wave in material decreases by a factor e and the value of $\alpha = 1/z_0$ is attenuation (Fig. 5.7.4). Then, the dynamic moduli are as follows:

$$G' = \frac{\rho\omega^2(4\pi^2/\lambda^2 - \alpha^2)}{(4\pi^2/\lambda^2 + \alpha^2)^2} \quad [5.7.61]$$

$$G'' = \frac{\rho\omega^2 4\pi\alpha/\lambda}{(4\pi^2/\lambda^2 + \alpha^2)^2} \quad [5.7.62]$$

$$\tan\delta = \frac{G''}{G'} = \frac{4\pi\alpha\lambda}{4\pi^2 - \alpha^2\lambda^2} \quad [5.7.63]$$

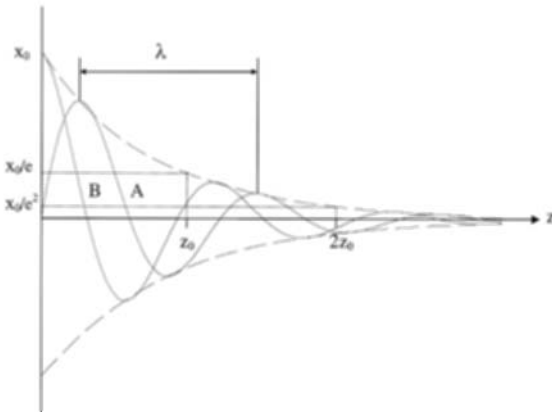


Figure 5.7.4. Propagation of a shear wave of wavelength, λ , and attenuation, $1/z_0$, in the direction z : A at time $t = 2\pi n/\omega$ and B at $t = (2\pi n + \pi/2)/\omega$.

It is pertinent from Eqs. 5.7.61, 5.7.62, and 5.7.63 that, by measuring wavelength and attenuation, the dynamic properties of material can be measured. However, if attenuation is small the wave propagates over a long distance and reflection from walls may cause the measured damping to be magnified. At the other extreme, if attenuation is large, the shear wave decays over short distances and this causes a difficulty in measurement of wavelength. Thus, an upper limit is typically $\lambda\alpha = 3$. This technique can be used in the range of frequencies from 4

to 5000 Hz. At high frequencies from 3 kHz to 3 GHz, the reflection of propagating waves in a quartz crystal against the interface between the quartz and a thin film of liquid is used.

5.7.7.2 Longitudinal waves

In this case the oscillation of the plate is in the z direction. The material is subjected to oscillatory extension and compression. The dynamic longitudinal moduli, E' and E'' are measured according to the following equations:

$$E' = B' + \frac{4}{3}G' \quad [5.7.64]$$

$$E'' = B'' + \frac{4}{3}G'' \quad [5.7.65]$$

$$E^* = B^* + \frac{4}{3}G^* \quad [5.7.66]$$

where B' and B'' are the components of the complex dynamic bulk modulus B^* .

5.7.8 VIBRATION VISCOMETRY

Viscosity (more exactly – Newtonian viscosity) of inelastic liquids is frequently measured by various versions of the oscillation methods. They are based on a very well documented theory of oscillations and simplicity of apparatus is their realization. The main field of application of *vibration viscometry* is to relatively low viscous fluids.

The basic theory of viscosity measurements by oscillation methods is a particular case of a more general theory of measuring viscoelastic properties as discussed above in this chapter. However, the general theory can be substantially simplified if it is *a priori* known that $G' = 0$. Then, viscosity equals G''/ω , and, therefore, it is necessary to measure losses only.

The basic equations of equilibrium for viscous inelastic liquid, according to the scheme shown in Fig. 5.7.1, is

$$m \frac{d^2x}{dt^2} + Zx + \frac{S}{h} \eta \frac{d(x - x_0)}{dt} = 0 \quad [5.7.67]$$

instead of Eq. 5.7.3, where the term $(1/h)[d(x - x_0)/dt]$ is deformation rate. Solution of this equation gives two equivalent expressions for viscosity

$$\eta = \frac{Z - m\omega^2}{K\omega} \frac{1}{\sqrt{p^2 - 1}} \quad [5.7.68]$$

$$\eta = \frac{Z - m\omega^2}{K\omega} \cot \alpha \quad [5.7.69]$$

where the notations are the same as before.

For the limiting case $Z \gg m\omega^2$ and $p \gg 1$, Eq. 5.7.68 leads to

$$\eta = \frac{Z}{K\omega p} \quad [5.7.70]$$

which is equivalent to Eq. 5.7.9 because for inelastic liquid $\alpha = \pi/2$ and $\sin \alpha = 1$.

If oscillations of the plate take place in a vessel of arbitrary size, the equilibrium equation is

$$m_0 \frac{d^2x}{dt^2} + Zx + k_u \frac{dx}{dt} = f_0 e^{i\omega t} \quad [5.7.71]$$

where m_0 is a reduced mass, as in Eq. 5.7.16, and the coefficient $k_u = S\sqrt{\eta\rho\omega/2}$.

The solution of this equation is well known. It is an equation of harmonic oscillations with amplitude, x_{0A} , and phase angle, α , which are expressed as

$$x_{0A} = \frac{f_0}{\sqrt{(m_0\omega^2 - Z)^2 + k_u^2}} \quad [5.7.72]$$

$$\tan \delta = \frac{\omega k_u}{m_0\omega^2 - Z} \quad [5.7.73]$$

Any of these equations allows calculation of viscosity from measured values of x_{0A} or $\tan \delta$ because viscosity enters expression for k_u . However, these equations are not convenient in real practice. Therefore, the main interest is in the limiting cases. If a plate is vibrating in a large volume (such that $h \gg \delta$ or $h \gg 3.2\sqrt{\eta/\rho\omega}$; the meaning of parameter, δ , was explained in Section 5.7.2, then Eqs. 5.7.72 and 5.7.73 have the following form:

$$\frac{A}{f_0} = \left\{ \left[\left(m + S\sqrt{\frac{\rho\eta}{2\omega}} \right) \omega^2 - Z \right]^2 + \frac{S^2\rho\eta\omega}{2} \right\}^{-1/2} \quad [5.7.74]$$

$$\tan \alpha = \frac{\omega S \sqrt{\frac{\rho\eta}{2\omega}}}{\left(m + S\sqrt{\frac{\rho\eta}{2\omega}} \right) \omega^2 - Z} \quad [5.7.75]$$

For further analysis of these equations it is convenient to use the dimensionless variables:

dimensionless frequency: $\lambda = \omega/\omega_0$, where $\omega_0 = \sqrt{Z/m}$ is the natural frequency of a measuring device

dimensionless amplitude: $a = AZ/f_0$

dimensionless viscosity: $\gamma = (S/m)\sqrt{\rho\eta/2\omega_0}$

After some rearrangements Eqs. 5.7.74 and 5.7.75 become:

$$a = \left[\left(\frac{1 + \gamma\sqrt{\lambda}}{\lambda^2} \right)^2 + \frac{\gamma^2}{\lambda^3} \right]^{-1/2} \quad [5.7.76]$$

and

$$\tan \alpha = \frac{\gamma}{\gamma - \frac{\lambda^2 - 1}{\sqrt{\lambda}}} \quad [5.7.77]$$

The dependencies of a and α on the dimensionless parameters γ and λ are called the *amplitude* and *phase characteristics* of a vibrating system. These dependencies, built in accordance with Eqs. 5.7.76 and 5.6.77, are presented in Fig. 5.7.5.

Some important particular cases are worth of special discussion.

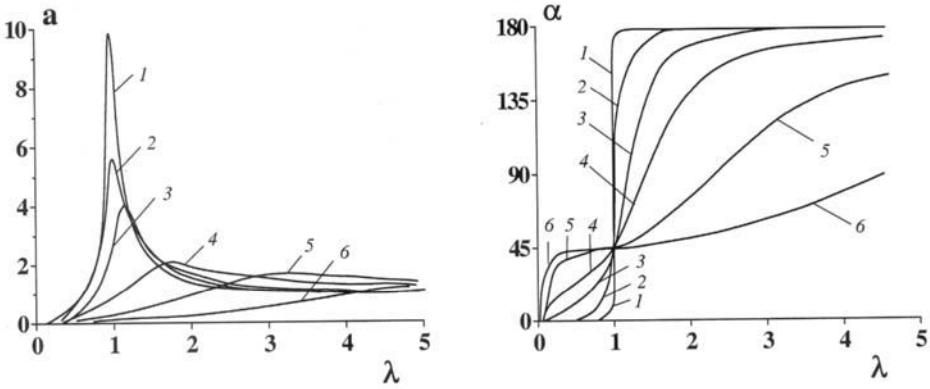


Figure 5.7.5. Amplitude $a(\lambda, \gamma)$ (left) and phase $\alpha(\lambda, \gamma)$ (right) characteristics of oscillations of flat plate inside viscous liquid (in dimensionless variables). Values of γ are: 0.01 (curves 1); 0.1 (curves 2); 0.3 (curves 3); 1 (curves 4); 5 (curves 5); 10 (curves 6).

Measurement of resonance amplitude. If viscosity is low ($\gamma \ll 1$), then the resonance in Fig. 5.7.5 is reached at $\lambda = 1$. Viscosity is directly related to the resonance amplitude, x_0^{\max} , as

$$\rho\eta = k(x_0^{\max})^{-2} \quad [5.7.78]$$

where coefficient k can be calculated or found by calibrating a measuring system.

If viscosity is not low, the maximum is not sharp. Then, it is necessary to use the complete equation instead of Eq. 5.7.78.

Measuring amplitude at arbitrary frequency. Viscosity can be calculated from the amplitude characteristics of a system at an arbitrary measured amplitude, though it is not convenient. Moreover, if viscosity is not low this method becomes unreliable because at large values of λ , an amplitude equals ~ 1 for all values of γ .

Measuring amplitude at a defined frequency. There exists such a value of frequency at which the relationship between a and γ is rather simple. Indeed, let $\alpha = \pi/2$. According to Eq. 5.7.77, $\gamma = (\lambda^2 - 1)/(\sqrt{\lambda})$ and $a = \lambda^{3/2}/\gamma$. Then

$$\gamma = [a^{1/3}(a - 1)]^{-3/4} \quad [5.7.79]$$

For low viscosity materials this condition is close to the resonance ($\lambda \approx 1$), but in a general case this method does not give reliable results because even a slight variation of frequency near the resonance results in large changes in viscosity.

Measuring frequency at a chosen phase angle. Viscosity is calculated from Eq. 5.7.77. If $\alpha = \pi/2$, then $\gamma = (\lambda^2 - 1)/\sqrt{\lambda}$ and

$$\rho\eta \propto \frac{\lambda^2 - 1}{\lambda} \quad [5.7.80]$$

The dependence of viscosity on λ is strong, especially in the range of high values of viscosity, where condition $\alpha = \pi/2$ corresponds to high values of dimensionless frequency.

Measuring resonance frequency. This method is invalid for low γ because resonance is achieved at $\lambda = 1$ for liquid of any viscosity. However, this method can be used for high viscosity liquids, though it is not sensitive as the resonance maximum is not distinctly expressed.

Measuring phase angle. As seen from Fig. 5.7.5, this method can be used for high values of γ . A particular case of this method is measuring the phase angle at the resonance frequency. The condition $(\partial x_0 / \partial \lambda) = 0$ leads to relationship between α and γ . Numerical analysis shows that noticeable changes in α take place in the range of γ between 0.1 and 10. It corresponds to the phase angle changes by about 20° . Beyond this range of γ this method is not applicable, due to the very small variation of α .

5.7.8.1 Torsion oscillations

Similar to the above discussed cases of measuring dynamic modulus, the transition from plane shear to torsion does not change basic equations, except for the use of circular displacements instead of linear ones.

For example, if liquid is placed between two coaxial cylinders and one of them is under torsion oscillations, viscosity can be calculated from one of the following equations:

$$(K_1 \omega^2 - ZK) \frac{1}{\eta} = \omega p \sin \alpha \quad [5.7.81]$$

$$(K_2 \omega^2 - ZK) \frac{1}{\eta} = p \cos \alpha \quad [5.7.82]$$

where p is the ratio of amplitude of oscillations of inner and outer cylinders, Z is rigidity of measuring device, and K_1 , K_2 , and K are form-factors. Their values can be calculated without any problems, though the final formulas are rather bulky. They can also be measured by calibrating a measuring device. By measuring either $\omega p \sin \alpha$ or $(p \cos \alpha - 1)$ as a function of ω^2 , viscosity can be found through an experimental procedure according to Eq. 5.7.81 or Eq. 5.7.82.

5.7.8.2 Oscillation of a disk in liquid

A plane disk of radius, R , is making torsional oscillation around its axis according to harmonic function $\theta(t) = \theta_0 \cos \omega t$, where θ_0 is an angular amplitude and ω is its frequency. If a disk is moving in a sufficiently large vessel, an equilibrium equation is written as

$$T = k_\omega \Omega + I_s \frac{d\Omega}{dt} \quad [5.7.83]$$

where M is torque and Ω is angular displacement. The coefficients in this formula are expressed as

$$\begin{aligned} \text{coefficient of resistance:} \quad k_\omega &= \pi R^4 \sqrt{\rho \eta \omega / 2} \\ \text{jointed (coupled) moment of inertia:} \quad I_s &= \pi R^4 \sqrt{\rho \eta / 2 \omega} \end{aligned}$$

If liquid is placed on both sides of a disk, a multiplier 2 must be introduced in both coefficients, k_ω and I_s .

These equations permit us to find viscosity by measuring parameters of the disk movement. If the gap between an oscillating disk and stationary walls is small, the expressions for the coefficient should be modified but the scheme of calculations remains intact.

5.7.8.3 Oscillations of sphere

In torsion oscillations of sphere around its diameter, torque appears, due to the resistance to movement of the sphere. The equilibrium equation is the same as Eq. 5.7.83, though the expressions for the coefficients are different:

$$k_{\omega} = \frac{8\pi R^3(3 + 8a + 6a^2 + 2a^3)}{3(1 + 2a + 2a^2)}\eta \quad [5.7.84]$$

$$I_s = \frac{16\pi R^3 a^2(1 + a^2)}{3\Omega(1 + 2a + 2a^2)}\eta \quad [5.7.85]$$

where $a = R/\delta$, R is the sphere radius and Ω is the angular velocity. The physical meaning of δ was explained in Section 5.7.2.

Of special interest is a particular limiting case when $a \gg 1$. In this case, Eqs. 5.7.84 and 5.7.85 become:

$$k_{\omega} = 8.38R^4 \sqrt{\frac{\rho\eta\omega}{2}} \quad [5.7.86]$$

$$I_s = 8.38R^4 \sqrt{\frac{\rho\eta}{2\omega}} \quad [5.7.87]$$

An analogy between these expressions and the corresponding equations obtained for an oscillating plate is obvious with evident changes of coefficients.

A special case is the oscillation of a sphere filled with liquid. Liquid impedes the oscillation of the sphere and it can be used as a method of viscosity measurement. This method was proposed as a very sensitive, absolute method of measurement. In this case, many methodical contrivances were used.⁹⁰

5.7.8.4 Damping oscillations

Damping oscillations in liquid depends on its viscosity. Therefore, by measuring damping oscillations it is possible to find viscosity. The basic equation of equilibrium is Eq. 5.7.40 with $G' = 0$ and $\eta' = \eta$. Then viscosity can be found from Eq. 5.7.46 as

$$\eta = \frac{G''}{\omega} = \frac{2m\alpha}{K} \quad [5.7.88]$$

This equation is valid for any mode of damping oscillations (including torsional oscillations) by appropriate choice of form-factor, K . The corresponding values of K for different geometrical shapes of sample were discussed above (in this chapter in connection with rotational instruments of different types). All these expressions can be used in Eq. 5.7.88. However, an exact solution for damping oscillations of a sample of arbitrary shape in a vessel of arbitrary size may be complicated. However, there are no principal difficulties in obtaining such a solution. Nevertheless in real practice, it is preferable to take into account the limitations of applicability of Eq. 5.7.88 or to calibrate a measuring system using standard liquids.

5.7.9 MEASURING VISCOELASTIC PROPERTIES IN NON-SYMMETRICAL FLOWS

Viscoelastic properties of material are measured during unsteady motion with deformation changing in time. A different approach was developed based on changes of deformation in space, when small harmonic perturbations of velocity are superimposed on steady flow.⁹¹

Let us consider circular flow with radial and axial velocity components equal to zero. Small angular periodic perturbations are superimposed on the main circular flow, so that the velocity field is described as

$$u_r = u(r, z)e^{i\varphi} \quad [5.7.89a]$$

$$u_\varphi = \omega r + v(r, z)e^{i\varphi} \quad [5.7.89b]$$

$$u_z = w(r, z)e^{i\varphi} \quad [5.7.89c]$$

and the values u , v , and w are small in comparison with ωr .

In this formulation, the equation of motion is exactly the same as for viscous liquid if Newtonian viscosity is replaced by a complex viscosity, η^* . Then, the problem consists of solving dynamic equations for a defined geometry of flow and calculating η^* for different experimental schemes.

Parallel disks with shifted axes. Small radial shift of axes leads to periodic changes of velocity. As a result, radial forces F_x and F_y appear. Analysis of possible approximation based on the exact solution of problem gives the following (linear approximation) formulas for components of dynamic modulus

$$G' = KF_y/a \quad [5.7.90]$$

$$G'' = KF_x/a \quad [5.7.91]$$

where the form-factor K is

$$K = \frac{h}{2\pi R^2} \quad [5.7.92]$$

R is radius of disks, h is the distance between disks, and a is radial shift of axes.

Parallel cylinders with shifted axes. Theoretical analysis of deformation gives (in linear approximation) the same equations as Eqs. 5.7.90 and 5.7.91 for components of dynamic modulus, where the form-factor K is

$$K = \frac{\ln(R_o/R_i) - \frac{R_o^2 - R_i^2}{R_o^2 + R_i^2}}{4\pi H} \quad [5.7.93]$$

R_o and R_i are the radius of outer and inner cylinders, respectively, H is the height of a liquid layer in a gap between cylinders and a is the radial shift of cylinder axes.

Rotation between surfaces with a small angle between them. There are three types of the simplest geometries of such kind:

- coaxial disks with inclined surfaces
- cylinders with inclined axes
- cones with inclined axes.

In all these cases, the angle between the inclined axes, ϵ , is small.

Equations for calculating the components of dynamic modulus are the same in all cases. They are:

$$G' = KF_y/\epsilon \quad [5.7.94]$$

$$G'' = KF_x/\epsilon \quad [5.7.95]$$

and the form-factor depends on the geometry of deformation.

Rotation of spherical surfaces. There are two principal schemes of rotating spheres with small perturbations of the velocity field:

- flow between two spheres with slightly shifted centers
- flow between two spheres with the common center but slightly inclined axes of rotation.

For the first case, Eqs. 5.7.90 and 5.7.91 are valid, while in the second case equations analogous to Eqs. 5.7.94 and 5.7.95 can be used. The front factors are different in the cases under discussion.⁹²

5.7.10 ABOUT EXPERIMENTAL TECHNIQUES

Many hundreds of experimental devices have been constructed for measuring viscoelastic properties of different materials. In particular, many designs of vibration viscometry were described during the last century. It is impossible here to give even a short survey of all units. Therefore, only the main features of design of experimental devices are presented below.

5.7.10.1 Rotational instruments

Essentially, these are rotational devices (rheogoniometers, rheometers, elastoviscometers, and so on) as described in Section 5.3. Instruments should be capable of oscillating measurement, in addition to steady rotation. These types of devices are instruments with variable mechanical drive. In modern versions of such instruments, frequency can be changed in the range of more than 7 decimal orders.⁹³ The amplitude of deformations can also be changed in a wide range, providing a possibility to follow the non-linear effects of dependence of viscoelastic properties on deformation and to find the boundaries of linearity in mechanical behavior of material.

Rotational instruments produced by some companies (*Rheometrics*, *TA Instruments*, *Imass*) are also equipped with techniques for measuring viscoelastic properties in non-symmetric flows, commonly using a scheme with shifted axes.⁹⁴ *Contraves* has made an instrument of this type that is called a *Balance Rheometer*, in which flow occurs between two spheres with inclined axes of rotation.

5.7.10.2 Devices with electromagnetic excitation

This type of experimental technique initially used a method of impedance measurements.⁹⁵ Instruments of this type were proposed primarily to study rigid materials.

Another approach is based on separate measurements of forces and deformations, and measurement of properties of various fluid materials, including dilute solutions with

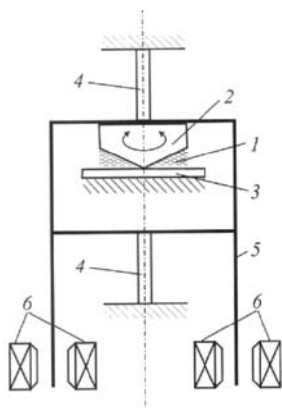


Figure 5.7.6. Rotational instrument with electromagnetic excitation. 1 – sample; 2 – cone surface; 3 – plate; 4 – two torsion rods; 5 – frame-rotor; 6 – force coils of electrodynamic drive.

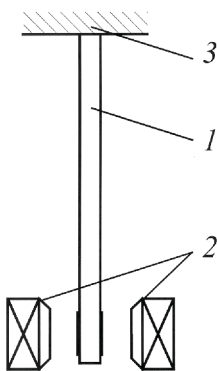


Figure 5.7.7. Vibrating reed method of measurement. 1 – sample; 2 – electro-magnets; 3 – sample holder.

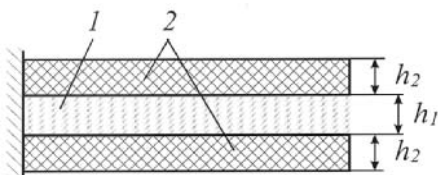


Figure 5.7.8. A sandwich-type sample: layers (2) of a soft material are placed on a hard support (1).

modulus varying in the range from 0.1 to 10^4 Pa and viscosity varying from 0.2 to 10^3 Pa*s.⁹⁶

A promising development along this line of constructing instruments for measuring viscoelastic properties was the application of a multi-frequency resonator placed in liquid media.⁹⁷ This instrument makes measurements at ten different frequencies in the range from

10^2 to 8.3×10^8 Hz. The optical system of measurement was used to measure amplitudes as small as 10^{-3} degree. This instrument can measure modulus in the range from 0.1 to 10^3 Pa for liquids with viscosity not less than 0.2 Pa*s.

Electromagnetic excitation is also convenient in instruments for torsion deformation, where different modes of deformation are possible – forced oscillations, damping oscillations, creep, elastic recoil, and steady flow.⁹⁸ An example of instruments of this type is shown in Fig. 5.7.6.⁹⁹ A sample is placed between a cone and a plate or between two disks. A moving part is fixed by torsions, which provide reliable alignment of the working unit. A frame is made of aluminum. It works as the rotor of an electrodynamic drive. By varying the electrical parameters, one can vary the regime of deformations.

Electromagnetic excitation is also widely used in the *vibrating-reed method* (shown in Fig. 5.7.7). Excitation of oscillation (periodic or damping) is created by means of a charge placed on the sample surface and an electromagnetic drive. Frequency may vary in a wide range, practically from several to hundreds Hz. Deformations are followed and registered by an optical method (not shown here). This version of method is applicable to materials with modulus from 10^5 to 10^{11} Pa. The devices of this type can be combined with very different measuring techniques. These instruments are also very convenient for the resonance method of measurement. These devices are simple and they are used either as home-made versions or produced by specialized companies.

This method is very convenient in different applications. In particular, the vibrating reed method was used at very low temperatures down to 4K and allowed measurement of loss tangent as low as 10^{-3} .¹⁰⁰

Free bending oscillation (as in Fig. 5.7.7) can be applied to many materials. However, when testing mild materials an experimental scheme must be modified. An example of modification of a sample is shown in Fig. 5.7.8. Here, two layers (with the thickness h_2) made of a soft material (it might be rubber, gel, or a viscoelastic solution) are placed on a

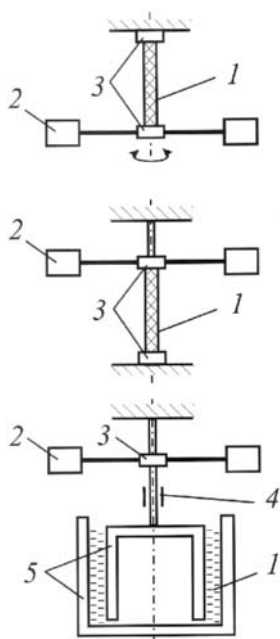


Figure 5.7.9. Three versions of torsion pendulum: direct (upper), reverse (middle), and for liquid samples (bottom). 1 – sample; 2 – inertial masses; 3 – holder; 4 – gas bearing; 5 – measuring cell of a cylinder-cylinder type.

surface of a rigid support (with thickness, h_1). The whole sandwich construction oscillates together. Measurement of properties of support and sandwich sample separately permits calculation of rheological characteristics of a soft material. The reverse scheme – a soft material between two rigid layers – is also possible.

A sandwich construction can be used in a different system. For example, it was proposed to prepare sample as a hollow cylinder and other cylindrical body, made of different material. They were placed inside a hole.¹⁰¹

5.7.10.3 Torsion pendulums

Torsion pendulums are the most popular and widely used instruments for centuries to solve different fundamental physical problems.¹⁰² In the practice of measuring viscoelastic properties, torsion pendulums were introduced in the 1950s,¹⁰³ though earlier they were widely used in viscometry. Now devices of this type are frequently used as home-made instruments as well as being produced by several companies.

Principal schemes of torsion pendulums are shown in Fig. 5.7.9 in three different versions: upper scheme – direct pendulum, central one – reverse pendulum, and bottom scheme – pendulum for liquid samples. There are a lot of different designs of torsion pendulums differing in methods of deformation measurement, mode of load application, construction of a holder, material of a torsion bar, design of thermo- and/or cryo-chamber, geometry of measuring cell,

and so on. However, all reproduce the main design feature of the instrument shown in Fig. 5.7.9. Depending on design, special torsion pendulums can work at frequencies between 0.01 and 80 Hz, at temperatures from liquid nitrogen up to $>1500\text{K}$. They can measure modulus in the range from 10^2 up to 10^{12} Pa and $\tan\delta$ from 10^{-4} (or even lower values, though the latter requires very accurate measurements) up to about 3.¹⁰⁴ Different optical or photo-electronic systems of measuring deformation are used.

Torsion pendulums can be used for the monitoring process of oligomer curing. This is realized by using a torsion element made as a braid (prepared from quartz, glass, silk, carbon fibers, and so on) impregnated with liquid. Then, evolution of viscoelastic properties of such complex sample is measured, which gives important technological information about relative changes in the sample.¹⁰⁵ The advantage of this method consists of a possibility to use a very small quantity of sample, as low as 0.1 g, and to study unstable materials.

5.8 PHYSICAL METHODS

5.8.1 RHEO-OPTICAL METHODS

5.8.1.1 Basic remarks

The term “*rheo-optics*” contains of two words: rheo (flow) and optics. Rheo-optics is a method of study of deformations and stresses during flow of transparent polymeric systems by means of optical techniques that measure the difference of the *refractive indices*, n_{ij} . The refractive index is determined by the polarizability of atomic groups and bonds in molecules.

When a parallel beam of light is incident to the surface separating two transparent media, part of the light is reflected back into medium and part is transmitted into the second medium. These are the *reflected* and *transmitted rays*. The direction of the transmitted ray does not coincide with that of the incident ray and the transmitted ray is said to be *refracted*. The angles that the incident, reflected, and refracted rays make with a normal to surface at the point of incidence are known as the angles of incidence, reflection, and refraction and they are denoted as i , R , and r , respectively. Reflection and refraction in isotropic media obey *Snell's law* such that $i = R$ and $\sin i / \sin r = n_{12}$. If light enters a medium from a vacuum, the above ratio is called the absolute refractive index of the medium. If c is the velocity of light in a vacuum, v_1 and v_2 are velocities of light in media, the absolute refractive indices are $n_1 = c/v_1$, $n_2 = c/v_2$, and $n_{12} = v_1/v_2 = n_2/n_1$. The frequency f of waves, $f = v/\lambda$, is unchanged when light travels through various media. Therefore, the wavelength, λ , changes. If λ_1 and λ_2 denote the wavelengths in the two media, then

$$n_1 = \lambda_0/\lambda_1, n_2 = \lambda_0/\lambda_2, n_{12} = \lambda_1/\lambda_2 = v_1/v_2 \quad [5.8.1]$$

Polymer molecules are typically anisotropic. However, if molecules are in a coiled state and randomly oriented in space, they form optically isotropic materials. If molecules are oriented under deformation of material, the material becomes anisotropic, causing a phenomenon of double refraction (*birefringence*) due to dependence of the refractive index on direction. The degree of anisotropy of the refractive index is characterized by a symmetrical tensor of the refractive index, n_{ij} :

$$n_{ij} = \begin{bmatrix} n_{11} & n_{12} & n_{13} \\ n_{12} & n_{22} & n_{23} \\ n_{13} & n_{23} & n_{33} \end{bmatrix} \quad [5.8.2]$$

This tensor is analogous to the stress or strain tensor. The components of the tensor of refractive indices follow the same rules as the components of other tensors during transformation from one coordinate system to another. In particular, one can find three mutually perpendicular directions in which the diagonal components of tensor, n_{ij} , attain the maximum values of n_I , n_{II} , and n_{III} . These are the principal values of tensor n_{ij} .

Optical quantities related to this tensor can be determined by using a polarization optical technique. Through a transparent model (plate, channel, etc.), a transmitted beam of polarized light and reflected light give an *interference picture*, which characterizes the stress-strain state of the model.

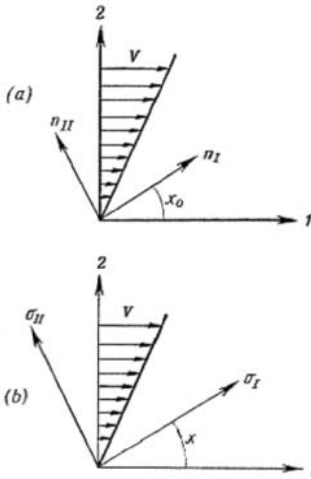


Figure 5.8.1. Coordinate system with axes of stresses and refractive indices in simple shear flow.

Brewster¹⁰⁶ was the first to discover this phenomenon and suggested its use to study the stress state in glasses. Later it was proven that for a wide class of planar elastic problems, the distribution of stresses is independent of elastic constants of materials. Thus, the stress distribution can be determined using transparent models with elastic constant different from material of objects. This fact opened an avenue for use of polarization-optical techniques to study stresses and deformations in solids. This area of studies is called *photoelasticity*. Good examples of the use of photoelastic techniques are investigations of the stress state in models of bridges and dams made from glasses.

By means of interference, differences in the principal stresses and their directions, but not the stress components, can be determined. In some cases, this information is sufficient to solve practical problems, but usually one needs to determine separate values of principal stresses.

For these purposes, methods of separation of stresses are used.¹⁰⁷

In the beginning of the 20th century, work was initiated to study the relationship between the refractive index tensor and stresses during plastic deformation of transparent models. In particular, a method of coating received wide acceptance. According to this method, photoelastic transparent coating covers a model. Coating deforms together with the surface, and using reflection technique, stresses can be determined on the studied object. This is a fertile area of research related to solid materials.

However, the main interest here is application of optical techniques to study the flow of polymeric melts and solutions. The major boost of research in the application of these techniques to flowing polymeric melts and solutions was received in the middle of the 1950s. This was due to the theoretical work done by Lodge,¹⁰⁸ and the experimental work carried out by Philippoff,¹⁰⁹ Janeschitz-Kriegl,¹¹⁰ and their co-workers.

At the present time, methods of rheo-optics are used in various areas, such as studies of stresses and strains in solids, residual stresses and structure in solids, stresses in fluids, rubbers, products made by polymer processing, etc.

The most extensive information concerning measurement of birefringence of polymeric fluids is available for simple shear, as shown in Fig. 5.8.1. Here 1 designates the direction of shear, 2 is the direction of the velocity gradient. Hence, shear occurs in plane 1-2. The third is known as a neutral direction, which is normal to the plane of drawing and corresponds to the direction of light propagation. For simple shear, the principal directions of a birefringence tensor are defined by vectors n_I and n_{II} . They characterize orientation of the birefringence ellipsoid in space.

Experimental determination of this orientation is carried out as follows. Use is made of a system of crossed polarizing devices – the planes of polarization of light in a polarizer and analyzer are arranged at an angle of 90° (*cross Nicols*); in this case light does not reach an observer situated after the analyzer. The object under study is placed between the analyzer and the polarizer. The plane-polarized light of wavelength, λ , passing through a bire-

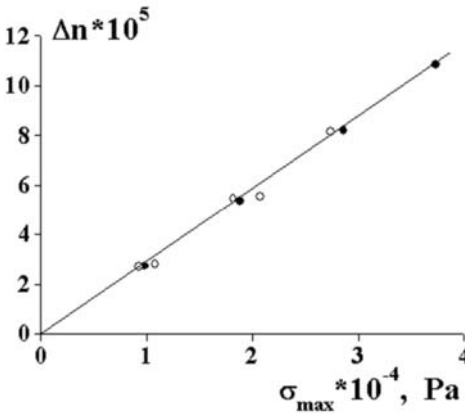


Figure 5.8.2. Birefringence vs. maximal tangential stress, σ_{\max} , in a slit die during polyisobutylene flow. Stress-optical coefficient, $C = 1414$ Br. [Adapted, with permission, from A.I. Isayev and R.K. Upadhyay, *J. Non-Newt. Fluid Mech.*, **19**, 135 (1985)].

fringent material of thickness, d , is split into two beams, which propagate along the principal directions of the refractive index ellipsoid. Having passed through the analyzer, these two beams interfere with a phase shift of $\delta = 2\pi d(\Delta n/\lambda)$. Here $\Delta n = n_I - n_{II}$. It is this quantity that is a measure of birefringence.

Upon synchronous rotation of the crossed polarizer and analyzer, light will be annihilated. The angle of complete light extinction (the *extinction angle*) is taken to be the smaller of the two angles between the plane of polarization and the direction of shear. Then, by definition, the angle, χ , is smaller than or equal 45° . For low-molecular-mass liquids the angle χ is 45° within ordinary values of shear stresses and

shear rates. For polymer melts and solutions the angle, λ , equals 45° only at very low shear stresses. As the stress increases, the refractive index ellipsoid rotates relative to the neutral axis and the extinction angle diminishes. In the limiting case, the refractive index ellipsoid is found to be oriented in the direction of axis 1 and the angle equals zero.

5.8.1.2 Stress – optical rules for polymer melts

The method of quantitative measurement of stresses in polymeric fluids is based on a linear stress-optical relationship, which is sometimes called the *stress-optical law*. According to this rule, birefringence is linearly proportional to difference of principal stresses and the directions of optical axes, χ_{op} , and mechanical stress axes, χ_{mech} , coincide such that

$$\Delta n = n_i - n_j = C \Delta \sigma = C(\sigma_i - \sigma_j), \chi_{\text{op}} = \chi_{\text{mech}} \quad [5.8.3]$$

This rule holds true for a large group of industrially important polymers, such as polyethylene, polystyrene, and many other thermoplastic melts and solutions, uncured and randomly crosslinked (cured) elastomers. This rule is obeyed by polymeric systems consisting of linear flexible-chain molecules. The stress-optical rule means that the principal axes of stress and refractive index ellipsoids coincide. This relationship is expressed through a proportionality factor, C , called the stress-optical coefficient, which is a fundamental characteristic of a polymer:

$$C = \frac{2\pi}{45kT} \frac{(n^2 + 2)(\alpha_1 - \alpha_2)}{n} \quad [5.8.4]$$

where n is the mean value of refractive index, which is determined from the relation $3n = n_I + n_{II} + n_{III}$; α_1 and α_2 are the longitudinal and transverse polarizabilities of the Kuhn random link of a chain molecule, k is Boltzmann constant, T is the absolute temperature. The above expression for C and the stress-optical rule follow from the classical the-

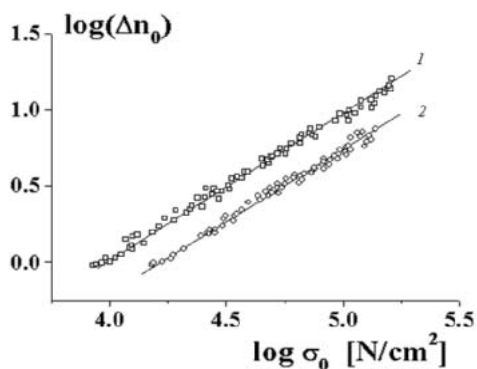


Figure 5.8.3. Dependence of birefringence amplitude, Δn_0 , on shear stress amplitude, σ_0 , for various polybutadienes (1) and polyisoprenes (2) at different frequencies. Lines are drawn according to the stress-optical coefficient of the respective polymers. [Adapted, with permission, from G.V. Vinogradov, A.I. Isayev, D.A. Mustafaev and Y.Y. Podolsky, *J. Appl. Polym. Sci.*, **22**, 665 (1978)].

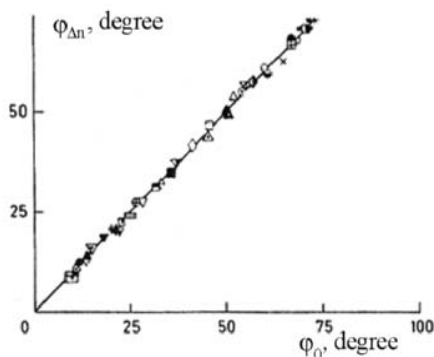


Figure 5.8.4. Phase angle by which oscillatory birefringence leads the oscillatory strain against phase angle. Line is drawn according the equality of these phase angles. [Adapted, with permission, from G.V. Vinogradov, A.I. Isayev, D.A. Mustafaev and Y.Y. Podolsky, *J. Appl. Polym. Sci.*, **22**, 665 (1978)].

ory of an ideal network of rubber elasticity.¹¹¹ There are many examples¹¹² where the condition of $C = \text{const}$ has been observed. It is measured in *Brewsters* ($1 \text{ Br} = 10^{-12} \text{ Pa}^{-1}$).

The use of the stress-optical rule for estimation of stresses in polymeric fluids is based on Lodge's idea of the existence of a fluctuating entanglement network, which manifests itself like a network formed by covalent bonds in crosslinked elastomers. Then the macromolecular chains between the entanglement points undergo numerous conformational transformations during the time required for small displacements of centers of gravity of macromolecules. The most important criterion of applicability of the stress-optical rule to uncured polymers must be the existence of a random entanglement network.

A remarkable feature of the stress-optical rule is that, over a wide range of stresses, the quantity C does not depend on deformation and rate of strain. At the same time, it is well-known that in simple shear, the shear rate depends strongly on shear stress. The constancy of C under simple shear for high-molecular-mass polymeric liquids may be explained by proceeding from the earlier discussed concept that the nonlinear relation between shear rate and shear stress for polydisperse polymers is due to successive transition of the highest molecular mass fractions to the rubbery state (Section 3.3.5). This reduces hydrodynamic losses, thereby changing viscosity of polymers, but the transition of polymer from fluid to rubbery state is not accompanied by a change in the quantity C .

As an example, Fig. 5.8.2 shows the dependence of birefringence, Δn , on maximum tangential stress, σ_{max} , which equals half of the difference of the principal stresses during flow of polyisobutylene melt in a slit die.¹¹³ The linear relationship between birefringence and stress is fulfilled in a wide range of stresses indicating that C is constant. It should be noted that the linear stress-optical rule is also satisfied for oscillatory flow of polymeric melts if the frequency of oscillations and temperature imposed are in fluid and rubbery states of polymer. These are shown in Figs. 5.8.3 and 5.8.4 for series of polybutadienes

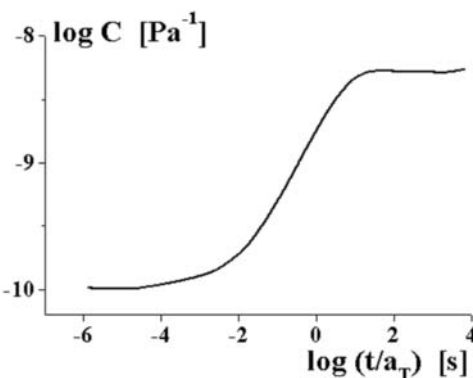


Figure 5.8.5. Master curve of stress-optical coefficient for polycarbonate at reference temperature of 147.5°C indicating the dependence of the coefficient on the time and temperature in the transition region from rubbery to glassy state. [Adapted, with permission, from G.D. Shyu, A.I. Isayev and C.T. Li, *J. Polym. Sci., Phys. Ed.*, **39**, 2252 (2001)].

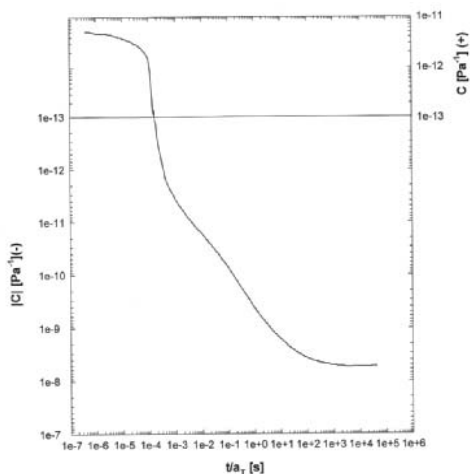


Figure 5.8.6. Master curve of the stress-optical coefficient for polystyrene at the reference temperature of 97°C indicating the dependence of the coefficient on the time and temperature in the transition region from rubber to glassy state. [Adapted, with permission, from G.D. Shyu, A.I. Isayev and C.T. Li, *J. Polym. Sci., Phys. Ed.*, **39**, 2252 (2001)].

and polyisoprenes of various molecular weights.¹¹² In particular, Fig. 5.8.3 indicates that the birefringence amplitude as a function of the stress amplitude is linear. The lines drawn in this figure are based on the stress-optical constant of polymers obtained in steady shear flow. Fig. 5.8.4 compares phase shifts between oscillatory birefringence and strain, $\varphi_{\Delta n}$, and between oscillatory stress and strain, φ_0 . It follows from this figure that $\varphi_{\Delta n} = \varphi_0$, i.e., phases of birefringence and stress with respect to the assigned deformation coincide and hence they coincide with respect to one another as well.¹¹⁴

In the transition region from rubbery to glassy state, the stress-optical rule is no longer valid.^{115,116} In this region, the stress-optical coefficient becomes a function of time and temperature, as shown in Fig. 5.8.5 for polycarbonate in the form of a master curve.¹¹⁵ With increasing and decreasing time and temperature the stress-optical coefficient approaches respective constant values corresponding to their values in the fluid and rubbery states and the glassy state. This non-constancy of the stress-optical coefficient between the glassy and rubbery states is generally observed for many polymers. It should be noted that for polycarbonates, as seen from Fig. 5.8.5, the stress-optical coefficient exhibits its positive value at any time and temperature. However, such a behavior is not generally true for all polymers. In particular, for polystyrene the stress-optical coefficient is positive in the glassy state and negative in the rubbery and fluid states, as shown in Fig. 5.8.6.¹¹⁵ Such a behavior of the stress-optical behavior of polystyrene was explained as follows. The birefringence of polystyrene is mainly determined by the orientation of the phenyl groups. Upon deformation in the glassy state, the motion of polymer chains is restricted. The phenyl groups are tilted toward the stretching direction, resulting in a positive birefringence. However, in the rubbery and fluid state, polymer chains are able to move freely and tend to align along the stretching direction to some extent. Thus, the phe-

nyl groups lie preferentially perpendicular to the stretching direction, leading to a negative birefringence. Therefore, the positive value of C comes primarily from the tilting of side phenyl groups and the negative value of C results from the chain segmental orientation. The stress-optical coefficient of polymers is also affected by the strain level, especially when a polymer is in the glassy state. As shown for polycarbonates its stress-optical coefficient is a decreasing function of the strain.¹¹⁶ This time, temperature and strain dependency of optical behavior is a general feature of various polymers.

In addition, the stress-optical rule is not applicable to filled polymers even in cases when they exhibit high optical transparency and the light depolarization is insignificant. This also applies to some copolymers with a heterogeneous microstructure.

Turning to the quantitative aspect of the stress-optical rule, it is useful to refer once more to Fig. 5.8.1 which, apart from the geometrical characteristic of relationships between simple shear and birefringence, shows a graph that gives an idea of a system of acting forces. Assuming a linear relationship between birefringence and stress tensors, one obtains the following system of equations:

$$\begin{aligned}\Delta n \sin 2\chi &= 2n_{12} = 2C\sigma_{12} \\ \Delta n \cos 2\chi &= n_{11} - n_{22} = C(\sigma_{11} - \sigma_{22}) \\ n_{22} - n_{33} &= C(\sigma_{22} - \sigma_{33}) \\ n_{11} - n_{33} &= C(\sigma_{11} - \sigma_{33}) \\ \cot 2\chi &= \frac{n_{11} - n_{22}}{2n_{12}} = \frac{\sigma_{11} - \sigma_{22}}{2\sigma_{12}} = \cot 2\chi_m\end{aligned}\tag{5.8.5}$$

where χ is the extinction angle measured by the optical technique and defining the direction of the principal refractive indices, χ_m is the mechanical angle measured by mechanical means and defining the direction of the principal stresses.

The determination of the stress optical coefficient, C , and tests of its constancy are usually carried out by using the relationship

$$\Delta n = \frac{2C\sigma_{12}}{\sin 2\chi}\tag{5.8.6}$$

or

$$C = \Delta n \sin 2\chi / 2\sigma_{12}\tag{5.8.6a}$$

Though measurements of stresses by optical method are not direct, they are of great interest for the following reasons. The method makes it possible to conduct measurements in a polymer stream by a non-invasive method, without flow perturbations that could be caused by any measuring mechanical devices. The optical method is of special importance for estimation of the first and the second normal stress differences. Such measurements can be made in rigid measuring devices. In measurement of these values by means of mechanical devices, considerable difficulties arise, due to deformation of various force transducers.

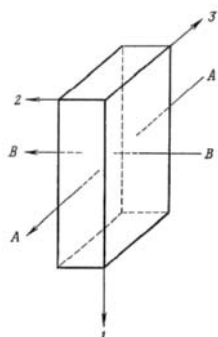


Figure 5.8.7. Scheme of birefringence measurement in slit die.

Let us consider briefly the latter method of measurement. Fig. 5.8.7 shows the scheme of measurements of the normal stress differences in a slit instrument. Measurements of the quantities $n_{11} - n_{22}$ and $n_{11} - n_{33}$ in the AA and BB directions, respectively, can be carried out. The second normal stress difference, N_2 , can be found (see Section 3.4.2), which is proportional to $(n_{11} - n_{22}) - (n_{11} - n_{33})$. According to results of these measurements, $N_2 < 0$ and it is about 10 percents of N_1 . This is in good agreement with data obtained by direct mechanical measurements of N_1 and N_2 .¹¹⁷

The rheo-optical method can also be used for measuring quasi-equilibrium compliance, J_s^0 , phase angle, δ , and recoverable deformation, γ , corresponding to steady-state flow. This is based on the following equation:

$$\frac{\sigma_{11} - \sigma_{22}}{2\sigma_{12}} = J_s^0 \sigma_{12} = \cot 2\chi_m = \cot 2\chi = \cot \delta = \gamma$$

However, determination of recoverable deformation based on polarization-optical measurements can yield satisfactory results only at relatively low values of σ_{12} .

5.8.1.3 Stress-optical rule for polymer solutions

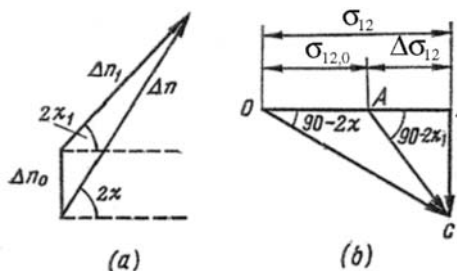


Figure 5.8.8. Vector diagram of the plane stress state for a polymer solution: the difference of refractive indices (a) and stresses (b) for solution and polymer.

The quantity C remains constant over the entire range of polymer concentrations, from infinitely dilute solutions up to molten polymers.¹¹⁸ At a low content of polymer in solution the properties of solvent begin to play an important role. Then, estimation of the observed optical properties must be carried out by taking into account the contribution of stresses on optical anisotropy of solvent compared with optical anisotropy of solution. As an example, it may be pointed out that, whereas the stress optical coefficient of polyisobutylene has a value

close to 1,500–1,600 Br, solvents, such as cetane and methylnaphthalene, have C values equal to 1,100 and 1,900 Br, respectively. Therefore, depending on ratio of optical properties of polymer and solvent, the stress optical coefficient may vary with change of concentration of polymer solution.

The general method of determining normal stresses in solutions using optical measurements consists of separating the total observed birefringence into contributions of polymer and solvent. They are added up as vectors (in the case of a biaxial stress) since deformation of solvent is accompanied by appearance of only shear stresses and that of polymer by development of both shear and normal stresses. The difference of the refractive indices of a system, Δn , is expressed in terms of the difference between the refractive indices of solvent, Δn_0 , and polymer, Δn_1 , using vector equality of $\Delta n_1 = \Delta n - \Delta n_0$. This is shown in Fig. 5.8.8a, which also gives an observed angle, χ , and angle, χ_1 , associated with

stresses that arise because polymer is in solution. The angle χ due to deformation of solvent equals 45° because no normal stress arises during its flow. The diagram of stresses developing in solution is shown in Fig. 5.8.8b, where σ_{12} is the total shear stress acting in the system and σ_{12}^0 is the component of the total stress, which is due to the flow of pure solvent. The difference, $\Delta\sigma_{12} = \sigma_{12} - \sigma_{12}^0$, is the contribution introduced by the presence of polymer in solution to the shear stress (and, hence, to viscosity of system). The vector BC corresponds to the normal stress difference $\sigma_{11} - \sigma_{22}$ and the vector OC is the difference between the principal stresses acting in solution. It is important to note that the angle χ between direction of shear and direction of principal stresses in solution is not equal to χ_1 . Of special interest in the case of dilute solutions is the question of the relation between the angle χ_1 and the stress-optical properties of polymer. Experimental investigation of this problem has shown that the extinction angle of polymer melt $\chi_m = \chi_1$, but $\chi_m \neq \chi$. The stress-optical rule for the polymer melt is written in the following form:

$$\Delta n_1 = \frac{2C\Delta\sigma_{12}}{\sin 2\chi_1} \quad [5.8.7]$$

where C is the stress-optical coefficient of the polymer melt, which is independent of the concentration of solution and solvent type.

The obvious difference between Eqs. 5.8.7 and 5.8.6 is that, instead of the total difference between the refractive indices, Δn , measured experimentally, in Eq. 5.8.7 use is made of the quantity Δn_1 , and the total shear stress, σ_{12} , is replaced by the quantity, $\Delta\sigma_{12}$, which refers to shear stresses that arise additionally because of the polymer presence in the system.

Calculations using the above relationships require knowledge of two parameters of solvent: viscosity, η_s , and stress-optical coefficient, C_0 . Then

$$\sigma_{12}^0 = \dot{\gamma}\eta_s, \Delta n_0 = 2C_0\sigma_{12}^0 = 2C_0\dot{\gamma}\eta_s$$

The quantities Δn and χ are determined experimentally and the method of determining Δn_1 and χ_1 using vector triangle is pertinent from Fig. 5.8.8a. The difference of normal stresses arising during shear flow of solution is then calculated from equation:

$$N_1 = 2\Delta\sigma_{12}\cot 2\chi_1 \quad [5.8.8]$$

In concentrated solutions, solvent makes a negligibly small contribution to stress and birefringence, and therefore $\chi_m = \chi = \chi_1$ and the decisive role is played by the stress-optical properties of polymer.

If the stress-optical coefficient of polymer is unknown, then, according to Eq. 5.8.7, it can be found from results of measurements carried out in dilute solutions.

5.8.1.4 Viscometers for optical observations

Study of structural transformations in liquid medium under action of deformation represents a special field of research. The methodological basis of such studies is a combination of viscometers and optical measurements. Depending on purpose, different methods are used.

Extensive research is devoted to measurement of birefringence in flow of dilute polymer solutions based on the so-called *dynamo-optic Maxwell effect*. Birefringence

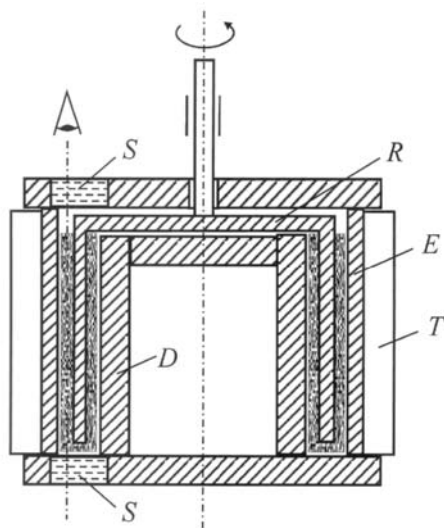


Figure 5.8.9. Bell-type viscometer as a rheo-optical instrument. R – rotating cylinder (rotor); D and E – fixed inner and outer cylinders; S – windows for visualization through the outer clearance. [Adapted, with permission, from E.B. Frisman, V.N. Tsvetkov, *Zh. Teor. Exp. Fiz.* (J. Theor. Experim. Phys. – in Russian), **23**, 690 (1952)].

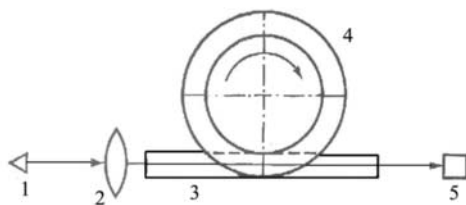


Figure 5.8.10. Diagram of measurement of cloud point of polymer solution flowing between coaxial cylinders of rotational viscometer. 1 – monochromatic light source; 2 – lens; 3 – optical tube; 4 – working cell; 5 – photocell. [Adapted, with permission, from A.Ya. Malkin, S.G. Kulichikhin, G.K. Shambilova, *Vysokomol. Soedin.* (Polymers – in Russian), **33B**, 228 (1991)].

appearing in a shear field results from structural transformations of macromolecules, caused by deformation. During polymer solution flow, the Maxwell effect depends on geometrical, mechanical and optical properties of dissolved macromolecules, i.e., on their structure. Therefore measurements of birefringence in flow is an effective method of structural studies of macromolecules.¹¹⁹

Instruments, in which birefringence during flow is measured, are called *dynamooptimeters* or *rheo-optical instruments*. The range of instruments of such type is distinguished by two basic elements of construction, namely viscometric and optical parts. The typical example, which illustrates the experimental measuring scheme is shown in Fig. 5.8.9. Rotational viscometer with a bell type intermediate revolving cylinder is used. The shear of liquid being investigated is accomplished in narrow clearances between the revolving cylinder and two fixed cylinders. For the optical measurements during flow in the outer clearance in the upper base of rotor perforation in the form of a system of annulus is arranged along the circumference. In the lower and upper bases, observation windows, S, are made.

The viscometric part of the rheo-optical apparatus does not differ from usual viscometers. The specific attribute of such instruments is optical measurement. The corresponding diagrams are described in the specialized monograph.¹²⁰ Essentially, these diagrams give the possibility of measuring two basic parameters – birefringence and orientation (extinction) angle during flow of polymer melts and solutions.

Instruments in which the viscometric and optical observations are combined are also used for study of shear-induced phase transition in polymers (see Section 3.5.3). For the realization of such studies, a rotational viscometer with the coaxial cylinders is applied with a transparent outer cylinder.

The onset of phase transition is detected by the classical method of cloud point.¹²¹ A monochromatic light beam passes tangentially through a transparent outer cylinder, then

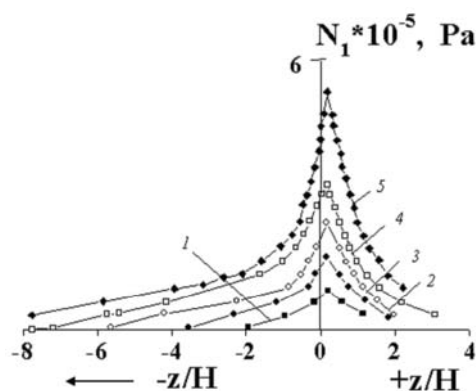


Figure 5.8.11. The first difference of normal stresses along flow axis at the entrance into a slit die for broad MMD polybutadiene (molecular mass 2.4×10^5 ; 25°C). The arrow indicates the direction of flow. The curves correspond to shear stresses at wall in the zone of developed flow: 0.051 (1); 0.098 (2); 0.141 (3); 0.21 (4); 0.25 MPa (5). [Adapted, with permission, from V.I. Brizitsky, G.V. Vinogradov, A.I. Isayev and Y.Y. Podolsky, *J. Appl. Polym. Sci.*, **21**, 751 (1977)].

through flowing solution, and the exiting beam is detected by a photomultiplier (Fig. 5.8.10).¹²² In another version of this method, the light beam is sent along a radius of cylinders, then it is reflected from the polished surface of the inner cylinder, and, after passing twice through the solution being investigated, it is captured by photomultiplier. Appearance of intensive light scattering (cloudiness) depends on shear rate.

A combination of viscometric and optical schemes of measurements is especially effective for observation of transient regimes of deformation, when structural transformations due to deformation occur in multi-component systems.¹²³

Commercial instruments supplied with optical devices, manufactured by specialized companies, can be used. Rheometer *Rheometrics RMS 800* (TA Instruments,

USA) equipped with the optical system *Rheo-optical Analyzer* is equipped with an He-Ne laser. The working cell is equipped with cone and plate or parallel disks. The light beam is oriented in a direction parallel to the velocity gradient. The observed picture of light scattering at small angles gives a very good image of structural processes taking place during deformation of a mixture of incompatible polymers.

5.8.1.5 Polarization methods for measuring stresses

Stress-optical measurements are the most effective and interesting in the study of polymer flow through channels and dies of different types, including capillaries. Experimental instruments are used for this purpose. As an example of the use of the polarization-optical method, let us consider measurement of normal stresses arising when polymer flows from a reservoir into a rectangular die.¹²⁴

Fig. 5.8.11 shows dependence of the first difference of normal stresses (extensional stress), N_1 , on the dimensionless length, Z/H , i.e., the distance along the flow axis referred to the die width. Each curve corresponds to a constant value of shear stress on the die wall in the region of a fully developed velocity profile. The positive values of Z/H refer to the pre-entrance region, and their negative values refer directly to the die. The value of $Z/H = 0$ corresponds to the die edge. Inspection of Fig. 5.8.11 shows that in the pre-entrance region of die, the extensional stresses increase, reaching a maximum. The position of the maximum of extensional stresses is located over the die entrance at a distance of $(0.2-0.3)H$ from the die edge. Then relaxation begins and terminates inside the die.

The rheo-optical method can also be used to measure stresses under conditions of sinusoidal oscillatory shear.¹²⁵ It has been shown that the normal stresses measured by the dynamic method consist of two components: the constant steady state term, $N_{1,c}$, and the oscillating term of doubled frequency, $N_{1,2\omega}$ as compared with frequency of specified

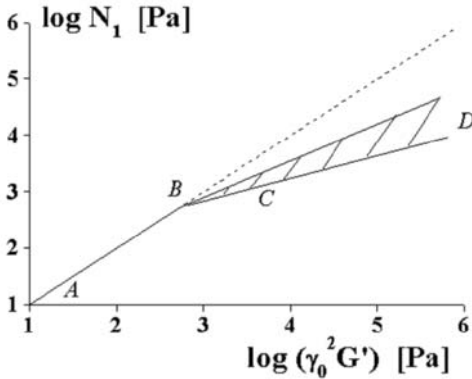


Figure 5.8.12. Master curve showing dependence of the steady state component of the first difference of normal stresses on the amplitude of strain in oscillation regime of deformations. The portion of the curve ABC refers to polystyrene solutions according to data by H. Endo and M. Nagasawa, *J. Polym Sci., A-2*, **8**, 371 (1970); the band CD refers to a series of polybutadienes and polyisoprenes. [Adapted, with permission, from G.V. Vinogradov, A.I. Isayev, D.A. Mustafayev and Y.Y. Podolsky, *J. Appl. Polym. Sci.*, **22**, 665 (1978)].

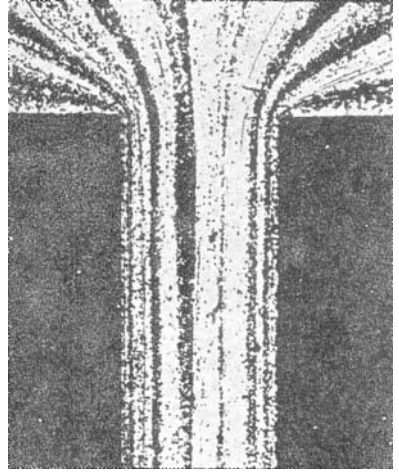


Figure 5.8.13. Flow lines of polybutadiene at shear stresses of 6.31×10^4 Pa (at a wall of rectangular channel). [Adapted, with permission, from G.V. Vinogradov, *Rheol. Acta*, **12**, 357 (1973)].

shear stresses. The constant component reflects the long-time end of the relaxation spectrum since the stress has no time to relax during each deformation cycle.

The quantity $N_{1,c}$ in the linear deformation domain equals $\gamma_0^2 G'$, where γ_0 is the amplitude of deformation and G' is the storage modulus. Fig. 5.8.12 shows this relation for various polymeric materials. At low oscillatory amplitude, $N_{1,c}$ is proportional to $\gamma_0^2 G'$. At higher amplitudes there is a deviation from proportionality between these two quantities, but a master curve can be constructed.

5.8.1.6 Visualization of polymer flow in dies

In Section 3.6.3, the critical deformation regimes for flexible-chain linear polymers and the associated spurt of their stream (loss of fluidity) in dies was discussed. It is very important to have experimental information explaining what happens to polymers during spurt and under above-critical regimes of occurrence of the elastic instability. Rheo-optical technique is useful for visualization of polymer stream. It is also particularly useful in investigation of polymer flow through channels of complicated geometrical forms.¹²⁶

What can be achieved by the method of visualization of polymer flow can be illustrated by data presented in Fig. 5.8.13. The streamlines were recorded by observing a movement of 10-20 μm glass beads in polymer. Flow at low shear rates is associated with the regular nature of streamlines in a die and at its entrance.

What can be achieved by observation of flow of polymer under circularly polarized light was demonstrated in Figs 3.6.12 and 3.6.13. (see discussion of results in Section 3.6.3).

5.8.2. VELOCIMETRY

One evident consequence of non-Newtonian flow properties of liquid is a non-parabolic velocity profile in round channels. This statement can also be formulated in an inverse

form: if a velocity profile along the channel radius is non-parabolic, then liquid is non-Newtonian. Measurement of velocity near a channel wall in order to confirm the concept of polymer adhesion to a wall or to observe slip along the wall surface is a separate problem. Both effects require measurements of velocity profile in order to carry out calculations of rheological properties of liquid.

This approach (called *velocimetry*) is successfully realized by utilizing several physical phenomena. The most popular phenomena used as a base for velocimetry are:

- the Doppler effect¹²⁷
- Nuclear magnetic resonance (NMR) imaging.¹²⁸

The *Doppler effect* is a change of frequency of vibration as a function of velocity of relative movement of a source of vibrations and an observer. Measuring a shift in frequency, a motionless observer can measure the velocity of movement.¹²⁹

NMR¹³⁰ flow imaging (used in different versions) is the most interesting method because it allows the experimenter to obtain velocity values at many points across the radius of a channel approaching the wall of the channel (about 0.2 mm). This is especially interesting for measuring near-wall effects. NMR technique of velocimetry has many applications in medical studies as well as in investigations of flow of thixotropic suspensions.¹³¹

Other versions of optical methods for measuring velocity include creating an interference pattern by means of laser system and measuring intensity of reflected light that varies as small particles cross the interference pattern.¹³²

Velocimetry can be useful to obtain data on velocity evolution in transient flow. Velocity profile in a steady laminar flow reflects shear rate distribution. The latter can be calculated if velocity profile is measured. This is a typical inverse problem (analogous to some other mentioned in this book), which is solved by a standard procedure, e.g., by Tikhonov regularization method.¹³³

5.8.3 VISCOMETERS-CALORIMETERS

Measurement of thermal effects, which accompany viscous flow, can be of definite interest for studying some physical phenomena, for example, detection of phase transitions or other structural transformations caused by deformation. These measurements are carried out using a combination of viscometers with a calorimetric device, i.e., strictly viscometric measurements are supplemented by measurement of heat fluxes.

As mentioned above (see Section 3.2.5), thermal effects always accompany viscous flow in view of energy dissipation of external forces. Therefore, it is important to separate structural phenomena from a trivial energy dissipation of forces of viscous friction. In practice this is achieved by combination of a rotational viscometer with a calorimeter into which the working cell of viscometers is placed.¹³⁴

Calorimetric measurements are accomplished by the installation of heat flux sensors on fixed and rotating cylinders. Calibration of the instrument is accomplished based on heat emission measured for standard Newtonian liquid. The intensity of heat emissions is proportional to the square of shearing rate: $W = k\dot{\gamma}^2$. Thus, the instrument constant, k , is determined. Then, heat emissions during shear flow of non-Newtonian liquid are measured. The component of heat flux due to structural transformation is evaluated based on deviation of observed dependence $W(\dot{\gamma})$ from quadratic dependence indicated by viscous flow.

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QUESTIONS FOR CHAPTER 5

QUESTION 5-1

Melt flow index, MFI, was measured using a capillary with the following dimensions: diameter $d = 2.16$ mm, length $L = 8.0$ mm. Diameter of barrel was $D = 9.5$ mm. Density of melt was $\rho = 0.8$ g/cm³. Let the weight of a load be $G = 2.16$ kg. Estimate the shear stress attained in this experiment and calculate the apparent viscosity if a measured value of MFI was 2 g/10min.

Additional question

Give a general formula for calculation of apparent viscosity for some arbitrary weight of a load, G , and melt flow index, MFI.

QUESTION 5-2

How do you calculate shear rate at a wall for liquid with viscous properties described by a power-law type equation?

QUESTION 5-3

Experimental study of the tube flow of suspension gave the following results:

for tube I: $D_1 = 2$ cm, $L_1 = 20$ cm, output $G_1 = 42$ g/min under pressure $P = 4$ bar;

for tube II: $D_2 = 4$ cm, $L_1 = 40$ cm, output $G_2 = 294$ g/min (pressure $P = 4$ bar).

Density of suspension was $\rho = 1.4$ g/cm³.

Explain the results and estimate the rheological parameters of material.

QUESTION 5-4

Calculate the velocity profile in flow of Newtonian liquid through an annulus produced by two coaxial cylinders of length, L . Flow is induced by a pressure gradient, ΔP , at the ends of annulus. The radii of an inner and outer cylinders are R_i and R_o , respectively.

Additional question

How does one obtain the form-factor for this type of annular flow?

QUESTION 5-5

For a rotational viscometer of a coaxial cylinders type, what should be the diameter of an inner cylinder if the diameter of an outer cylinder is 40 mm and the acceptable inhomogeneity of the stress field is 5%?

QUESTION 5-6

In Section 5.7.3, a portable viscometer was described that measures viscosity *via* time of turn of a light cylinder from the initial position by a constant angle, the initial deformation is set by twisting of a torsion spring. What is the relationship between measured time and viscosity?

QUESTION 5-7

In the principal scheme of measuring viscoelastic properties of material, a spring is used (Fig. 5.7.1) that is not ideal elastic but viscoelastic (has some losses in deformation). How do you calculate viscoelastic properties of material under investigation?

QUESTION 5-8

In Section 5.7.2, the condition of uniform deformation of sample in oscillation was formulated as $h \ll \delta$. Analyze this condition for inelastic viscous liquid.

QUESTION 5-9

Prove that Eq. 5.7.39 is valid for materials exhibiting low losses.

QUESTION 5-10

The value of maximum displacement X_{0B} appears in solution of Eq. 5.7.41 of an equilibrium Eq. 5.7.40, but this value does not appear in Eq. 5.7.44 and other equations for G' and G'' . Explain why?

QUESTION 5-11

Prove that Eqs. 5.7.5 and 5.7.6 give Eqs. 5.7.53 and 5.7.54 for inelastic liquid.

QUESTION 5-12

In Section 5.7.6 deformations of sample were treated as damping oscillations. Is it a unique case of damping deformations? Explain the answer.

Additional question

In which case does the deformation of inelastic liquid become aperiodic but not oscillating?

QUESTION 5-13

Eq. 5.3.49 is valid as an approximation only. What should be the exact solution?

Answers can be found in a special section entitled Answers.