

APPLICATIONS OF RHEOLOGY

6.1 INTRODUCTION

Rheological measurements provide us with *properties* of materials. Fundamental rheological theories show how to treat results of measurements of these properties and how to use them in solving applied problems. This is similar to measurements of any other properties of materials. How to apply knowledge of rheological properties to solve real technological and applied problems depends mainly on our understanding of the physics of these problems. Rheological characteristics of materials determine their behavior in many applications and they are important, together with various other material properties.

With this background, it is possible to point out several main directions of application of rheology in practice:

- Rheology is a ***physical method*** of characterization of the *structure* of matter. Rheology gives unambiguous, physically meaningful, quantitative parameters of materials. These parameters can be correlated with the structure of matter, either chemical (molecular structure of a compound, length and architecture of a molecule, and so on) or physical (physical intermolecular interactions, phase state, size and distribution of components in multi-component systems, and so on) structure. Rheological parameters *correlate* with the structure of material and can be used for structure characterization.
- Results of rheological characterization of various similar materials give a basis for ***comparison*** of these materials. Rheology does not answer questions as to whether materials under test are “good” or “bad”. The answer depends on expert estimation and previous experiences in the application of similar materials. The latter allows us to establish what parameters characterize the “ideal” material, with which other materials of a similar type can be compared. This line of application results in a great number of *standards* and *standardized test methods* developed for the main types of commercial materials. Thus, rheology proposes methods for quality control of materials.
- Description (and ***modeling***) of the dynamic behavior of different materials, including their flow in technological equipment. Description is based on solving *field equations* and rheological (material) properties enter these equations as coefficients and/or functions. Predicted dynamic behavior strongly depends on rheological properties of matter.
- Special ***rheological effects***, i.e., phenomena, which do not exist in Newtonian liquids, but can be used for some practical application. Such rheological phenom-

ena as, e.g., deformation induced transition from liquid to rubbery state, elasticity of flowing liquids might be of theoretical and engineering interest.

The most important and impressive examples of such effects are:

- The Toms effect (suppressing turbulence at high Reynolds numbers)
- The Weissenberg effect (rubbery elasticity and appearance of normal stresses in shear flow)
- expandability of liquid streams due to superposition of elasticity and fluidity of material
- superposition of liquid- and solid-like properties providing stability of shape at rest and fluidity at intensive loading
- memory of pre-history of loading and deformation
- thinning or thickening effects as a result of flow accompanied with deformation-induced structure rearrangements
- solidification (liquid-to-solid transition) in intensive deformations, which may lead to stabilization of a liquid stream in various applications
- electro- (or magneto-) rheological effects (influence of electric or magnetic fields on rheological properties of liquid).

All these effects can be used (and are used) in engineering practice. Their limitless applications depend on the inventiveness of engineers.

6.2 RHEOLOGICAL PROPERTIES OF REAL MATERIALS AND THEIR CHARACTERIZATION

Rheology as an independent branch of natural sciences has come into existence as a method of characterizing deformation properties of real materials, which are far from idealized models of Newtonian liquid and Hookean solid.

Properties of numerous real materials are so diverse that it is impossible to invent a single or even a few different models. However, it is reasonable to try to classify numerous real materials into several principal groups or classes, depending on their nature or the similarity of their rheological behavior. Such classification cannot be absolute, because the same material can be treated as belonging to different groups, depending on the approach to classification. For example, paint with polymeric binder can be regarded as a polymeric material, or a colloid system, or dispersion. Blood is a special liquid, though it can be treated as a substance that belongs to a much wider class of dispersions. The same is true for numerous food pastes, creams, pharmaceuticals, and so on.

Below, the main peculiarities of rheological properties of different groups of materials will be discussed with reference to the above mentioned directions of application of the results of rheological studies.

6.2.1 POLYMER MATERIALS

This is a large group of different materials including polymer melts, solutions, filled materials, and multi-component blends.¹ The main difficulty in the application of rheological methods for characterizing these materials is encountered because practically none of them is an individual material. In the best case, a real polymer consists of fractions of macromolecules of different length of the same chemical nature, i.e., real polymers are always *polydisperse*. This is the reason why possible correlations between rheological

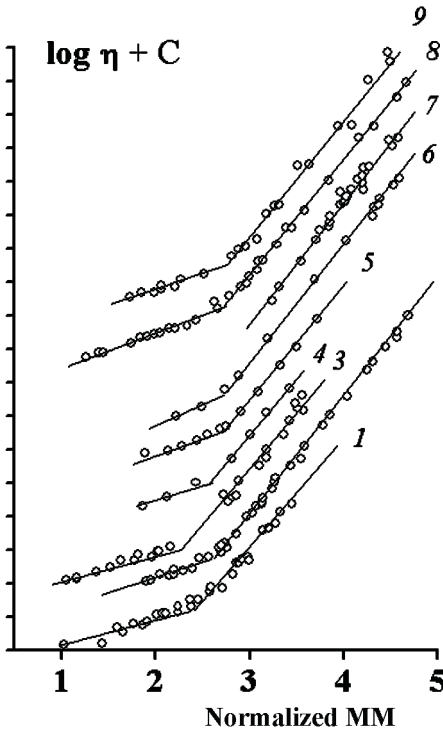


Figure 6.2.1. Relationship of viscosity and length of molecular chain (normalized MM) for: 1 – polystyrene; 2 – polyvinylacetate; 3 – polyethyleneglycol; 4 – polymethylmethacrylate; 5 – poly(tetra-methyl p-silphenil siloxane); 6 – polybutadiene; 7 – polyethylene; 8 – polyisobutylene; 9 – polydimethylsiloxane. Viscosity values are shifted along the Y-axes by the arbitrary values. One division on the Y-axis corresponds to one logarithmic unit. [Adapted, with permission, from G.C. Berry, T.G. Fox, *Adv. Polymer Sci.*, **5**, 261 (1968)].

As was established for many polymers, the initial Newtonian viscosity, η_0 , is very sensitive to the average molecular mass (see section 3.3.4). One illustration of this fact was shown in Fig. 3.3.2. The other illustration is the molecular mass dependence of initial Newtonian viscosity of different polymer melts (Fig. 6.2.1). The transition from a low-molecular-mass branch of the $\eta_0(\bar{M}_w)$ dependencies to a high-molecular-mass part of the curves is pertinent. The most important experimental fact here is the universality of a slope of a high-molecular-mass part of dependencies, which is close to 3.4-3.5.

Another impressive illustration of the relationship between viscosity and molecular mass is shown in Fig. 6.2.2 for polydimethylsiloxane covering 11 (!) decimal orders of viscosity changes. The slope of the curve changes more smoothly in this relationship.

It is pertinent from these examples that viscosity of polymers depends on their molecular mass, but the exact form of this dependence may differ for a specific polymer.

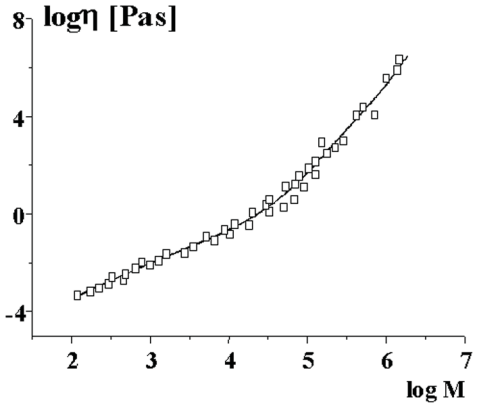


Figure 6.2.2. Molecular mass dependence of viscosity for polydimethylsiloxane. Collection of experimental data of T. Kataoka and S. Ueda. [Adapted, by permission, from *J. Polym. Sci., Polym. Lett.*, **4**, 317 (1966).]

properties and molecular parameters are based on averaged characteristics of molecular mass distribution, MMD.

The most important correlations based on vast experimental data are dependence of viscosity on average molecular mass, M , and between flow properties (non-Newtonian behavior) and MMD. This was discussed in detail in section 3.3.4 because analysis involves different aspects of rheology fundamentals. However, experimental results on which this analysis is based, including Fig. 3.3.2 and Eqs. 3.3.14, 3.3.15, 3.3.18, can be equally treated as a part of this section.

This is important in practical applications, because the “universal” value of the slope is only a rough approximation.

As was shown in section 3.4, the dependence of coefficient of normal stresses, Ψ_0 , on molecular mass is even more pronounced than the $\eta_0(M)$ dependence (see Eq. 3.4.7).

The dependence of intrinsic viscosity $[\eta]$ on molecular mass is usually expressed by a power-type equation (see Eq. 3.3.18). However, the exponent in the $[\eta](M)$ dependence is much smaller than the exponents in $\eta_0(M)$ and $\Psi_0(M)$ dependencies, i.e., the order of sensitivity of rheological parameters to molecular mass is:

$$\{\Psi_0\} > \{\eta_0\} > \{[\eta]\}$$

In practical technological applications, direct determination of molecular mass is based primarily on measurements of intrinsic viscosity. The reasons for using the least sensitive quantity (in comparison with viscosity and normal stress variations) is partly because of tradition but mainly because of simpler experimental technique and on the possibility of measurements of small size samples.

Rheological measurements can be used for determination of the average molecular mass of polymer. As discussed in section 3.3.5, it is possible to determine molecular mass distribution based on non-Newtonian flow curve measurements. However, this relates to practical reliability of method, which is always in doubt, because even strong variations of MMD are only slightly reflected by the shape of a flow curve. The ratio of viscosity values measured at two different shear stresses (i.e., measuring two points on a flow curve) can be used as a qualitative measure of the width of MMD and this method can be useful in comparing materials synthesized at analogous technological processes.

MMD of polymer is more effectively reflected in the elasticity of melt. A typical example was shown in Fig. 3.4.3. Addition of a even small amount of high-molecular-mass fraction immediately causes a rapid increase of compliance (decrease of rubbery modulus). No complete theory relating the elasticity of melt to MMD exists, though the correlation between these two properties does exist and can be used in practice for estimation of MMD. This correlation is expressed in the form of some empirical relationships relating steady-state compliance, J_s^0 , to ratios of average molecular mass, including higher values of MMD. The following structure of such relationships is the most popular and can be used in practical applications:²

$$J_s^0 = K \left(\frac{\bar{M}_w}{\bar{M}_z} \right)^\beta \quad [6.2.1]$$

However, it is more likely that elasticity of polymer solutions and melts is determined by higher values of MMD, though it is difficult to separate the role of different MMDs. For a monodisperse sample ($\bar{M}_n = \bar{M}_w = \bar{M}_z = \bar{M}_{z+1}$) compliance does not depend on molecular mass. This is experimentally well-known.

According to these or similar empirical relationships, and based on measurements of melt elasticity, qualitative estimation of width of polymer MMD is possible. Using the relationship between molecular mass parameters and viscosity or elasticity, it is possible to regulate MMD to obtain required properties of material.

Rheological methods are also sensitive to the structure of the polymer chain. However, only qualitative estimations are possible. Also, a choice of experimental method depends on experience and its successful use by the experimenter. The central point here is a choice of parameter or dependence which is the most sensitive to structure details of interest.

Comparison of linear and branched polymers in uniaxial extension (see section 3.5.3 and Fig. 3.7.8) is an important example of application of rheological methods for characterizing a structure of polymer chains. This is a qualitative comparison only. It is uncertain what quantitative measure of branching of polymer chains can be used because it depends on polydispersity, molecular mass, distribution of branches, their length, and their position along a chain.

Activation energy of viscous flow (or the temperature coefficient of viscosity) is a rheological parameter which is sensitive to the presence of side branching. There is almost a two-fold difference between activation energy for high density (linear) polyethylene and conventional low-density (branched) polyethylene. Intermediate cases were also observed.³ Analogous effect was also described for linear and branched polystyrenes.⁴

The effect of long chain branching can be characterized by following concentration dependence of viscosity of the polymer melt with variable solvent concentrations.⁵ This dependence is different for linear and branched polyethylenes. The example demonstrates that correlation between results of rheological measurements and structure parameters can be unusual and unexpected, but useful in practical applications if known.

Rheological properties are also sensitive to peculiarities of chain structure, such as composition of copolymers, side group content, and so on. The results of rheological measurements can be used for polymer structure characterization. The kinetics of polyvinylacetate conversion to polyvinylalcohol is one example. It is discussed in section 6.3. However, this area of rheology application is still more a potential possibility than a real technological method.

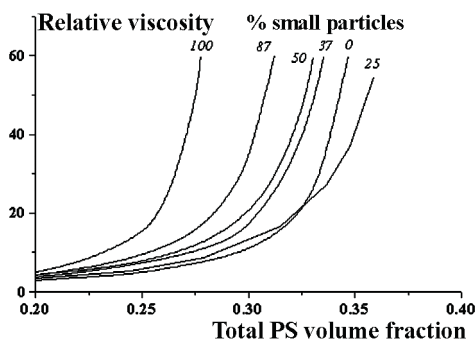


Figure 6.2.3. Particle size distribution effect on viscosity of polystyrene, PS, latex: relative zero shear viscosity as a function of the total PS volume fraction for a mixture of two monodisperse particles. Salt in water concentration $[KCl] = 0.1$ mM. Original experimental points are omitted. [Adapted, with permission, from F.M. Horn, W. Richtering, *J. Rheol.*, **44**, 1279 (2000)].

Polymeric materials are processed with a variety of other materials. Use of filler is commonplace (see example in section 3.2, Fig. 3.2.4). Polymer melt is a continuous phase in this case, but polymeric substances may also be a disperse phase – latex is an example. Polymer dispersions are mainly stabilized by colloid size. Viscosity of such systems can be estimated as for any other dispersion (see section 3.3.4). Viscosity of dispersions depends not only on the total concentration of a dispersed (polymer) phase, but on particle size distribution. This is illustrated in Fig. 6.2.3, where results of viscosity measurements of latex-containing mixtures having fractions of two sizes with the same total concentration are presented. Control of the particle

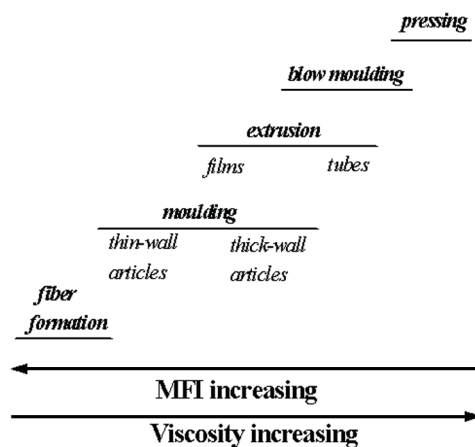


Figure 6.2.4. Primary correlation between viscosity (expressed by MFI) of a polymer melt and recommended processing method.

size distribution of a dispersed phase is a sensitive method of changing rheological properties of material.

The above-discussed measurements are treated in terms of absolute parameters of rheological properties, such as viscosity and compliance. There is a lot of standardized rheological methods, which do not give *absolute* values of molecular parameters of polymer but some *technological characteristics* related to molecular mass and (in some cases) concentration of polymer in solution. All these rheological methods give valuable information concerning technological properties and quality of polymeric material used in engineering practice.

Melt flow index, MFI, (see section 5.2.6) is a characteristic of viscosity directly related to molecular mass of polymer. However, MFI by itself is not suitable for determining any molecular parameter; it is only useful for technical description of polymers produced by industry and many polymers are classified according to their MFI. This rheological parameter determines the recommended method of polymer processing, and *vice versa*, selection of the suitable polymer grade for a particular processing method is based on a value of MFI. This is illustrated in Fig. 6.2.4.

A large number of different qualitative methods based on rheological measurements were proposed, standardized, and used in technological practice of characterizing polymer melts and solutions.

A list of the most popular methods includes:

- Melt Flow Index (MFI) – according to ISO 292; ASTM D 1238; BS 2782 (the amount of extruded melt in ten minutes under specified conditions, such as, temperature, load, and size of capillary)
- Rossi-Peaks Test – according to ASTM D 569 (a thermoplastic material flows a specified distance under a specified pressure when tested in a standard apparatus)
- Davenport Extrusion Rheometer (for shear rates up to 10^4 s^{-1})
- Ubbelohde Viscometer (for dilute polymer solutions)
- Brabender Plastograph (for materials with changing properties)
- Castor-Severs Viscometer (for plastisols and organosols at high shear rates)
- Brookfield Viscometer (the same but for low shear rates, also for other polymer solutions and gelling materials)
- Cup Flow Method (for thermosetting polymeric materials)
- Mooney Shearing Disk Viscometer – according to ISO 617 (a multi-purpose device for testing rubbery materials)
- Humboldt Penetrometer
- Hoeppler Consistometer
- Meissner Drawability Tester
- Williams Plastometer
- Goodrich Plastometer
- Defoe Plastometer
- Convey Extrusion Machine
- Agfa Vulcameter
- Ring-and-Ball Method (for synthetic rubbers of Novolac type)

Hot Plate Method (for polyamide and fluoropolymers)

Rebound Method (ASTM D 1054; DIN 53512) (estimating elasticity)

Ford Cup Method (ASTM D 1200) (for paints and lacquers)

Stormer Viscometer (ASTM D 562) (for polymer solutions).

It is important to stress two terms always present in description of any method – *specified conditions* and *standard apparatus*. Only because of these limitations is any such method useful for testing and qualifying polymeric materials.

Application of results of rheological analysis of polymeric materials is based on the following concepts:

- polymers can be characterized by definite molecular values – molecular mass, molecular mass distribution, and branching. There are different empirical or model correlations between these values and rheological properties; therefore, when measuring rheological properties it is possible to make a prediction of molecular parameters of a polymer chain
- there is a large number of standardized methods which permit characterization of technological properties of polymers and defining grades of industrial products; therefore, rheological methods are widely used for technological and processing control.

6.2.2 MINERAL OILS AND OIL-BASED PRODUCTS

Mineral oils are natural materials obtained from various sources. Oil is a mixture of liquid hydrocarbons and other chemical compounds. These are waxes, paraffins, sulfur derivatives, organic aromatic compounds, solid components, etc. The composition of crude oil differs depending on origin. Consequently, rheological properties of crude oils are different ranging from viscous liquids to viscoplastic materials with yield stress. Rheological properties of many oils are temperature dependent, because temperature of processing and transportation overlaps with temperature of crystallization of some components, mainly waxes and paraffins. Temperatures of crystallization of these components are in the range from 40 to 80°C. It means that under processing conditions (usually below 40°C) crude oils are either multiphase or unstable systems.

Measurement of rheological properties of crude oils has practical importance for their transport properties and pipeline and pump station design. Composition of crude oils of different origin dictates the necessity of measuring rheological properties and methods of their quantitative description for any oil well.

Investigation of oils demonstrates that diverse rheological behaviors can be observed. Viscosity characteristics (flow curve) are the most frequently applied rheological properties because oil transportation through pipelines is its main engineering problem. Crude oil is an unstable material and its rheological properties and transport characteristics also depend on material history, which determines the state of crystallizable components. Fig. 6.2.5 shows results of viscosity measurements for a model sample (containing 25% wax) cooled at different rates. At a starting temperature (48°C), material is a homogeneous liquid whereas during cooling a gelation of wax components takes place and viscosity increases. The gelation temperature (viscosity attains some limiting high value) depends on rate of cooling. This also depends on wax content.

Measurement of gelation temperature helps to estimate the wax content but also data similar to that presented in Fig. 6.2.5 can be used for design of a pipeline for crude oil transportation.

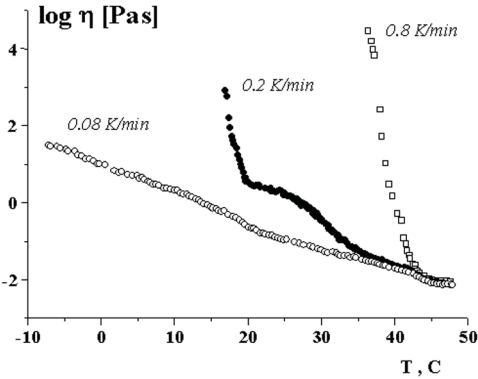


Figure 6.2.5. Influence of cooling rate (given on curves) on viscosity of a crude oil with 25% wax. Measurements were carried out at constant shear stress 7.4 Pa. [Adapted, with permission, from P. Singh, H.S. Fogler, N. Nagarajan, *J. Rheol.*, **43**, 1437 (1999)].

Similar to many other structured systems, thixotropic effect is often observed for waxy crude oils. Viscous properties of crude oil can be described by the Casson model (see Eq. 3.3.8), but upward and downward flow curves are different and, consequently, preliminary deformation results in a decreased yield stress.⁶

No general equations or recommendations for construction of a rheological model can be given for crude oils because of their variety. However, it is possible to obtain parameters required for engineering calculations.

Oil is a raw material used in production of numerous commercial products.

This contributes to a large number of standardized methods used to control their quality. These methods usually measure parameters of material performance, which cannot be recalculated into absolute characteristics of rheological behavior.

A list of main standard methods is presented below.

- Seconds Saybolt Universal SSU
- Kinematic Viscosity, centistokes
- Kinematic Viscosity, ft/sec.
- Saybolt Furol, SSF
- Redwood 1 Standard
- Redwood 2 Admiralty
- Engler
- Barbey
- Parlin Cup
- Ford Cup
- Mac Michael
- Zahn Cup
- Demmier Cup
- Stormer Load
- Pratt and Lambert.

Light engine oils are usually treated as Newtonian liquids, though some viscoelastic effects can be observed at high rates of deformation. Therefore, they are characterized primarily by their viscous properties at low and high temperatures.⁷ According to Standard SAE⁸ J300, engine oils are marked as xWy, where the first index x is a low temperature viscosity parameter (which is measured at -18°C). The lower the index, the lower the low temperature limit of practical application of oil.⁹ The last index y is kinematic viscosity (in mm^2/s) measured at 100°C . The letter W means that an oil can be used in winter time.

The real performance of lubricating mineral oils is more complex, especially in low temperature applications. Wax and paraffin crystallization in crude oils is also important for lubricating materials. Viscosity of mineral oils used as a base for lubricants depends on the rate of cooling and crystallization of wax.¹⁰ This results in appearance of yield stress at low temperatures. Certainly, this effect is very crucial for engine start up in winter time,

and rheology is the method of choice for estimation lubricant quality.

Various *greases* are also oil-based products. The principal advantage of greases is absence of fluidity in a stationary state, i.e., at low shear stress. From rheological point of view, it means that these materials have yield point and they are most likely obtained by addition of solid components to oil. These additives form an inner structure characterized by a certain strength (and that is “yield stress”). Yield stress causes grease not to flow out of a bearing. Greases are viscoplastic materials and yielding is their important designed function.

The rheological behavior of viscoplastic materials was discussed in section 3.2.2. The main peculiarities of their flow properties are shown in Fig. 3.5.5 and discussed in reference to this figure. Low shear stress domain is not very important because viscosity in this part of a flow curve, η_0 , is so high that behavior resembles a solid. Yield stress and viscosity, η_∞ , in the high shear rate range are important characteristics of greases. The difference between η_0 and η_∞ is substantial (Fig. 3.5.5 contains only a schematic diagram and it is not meant to give quantitative information on a scale of difference between η_0 and η_∞ values). Low values of η_∞ provide low friction in bearing. The level of yielding is important for starting an engine. Structure of greases is thixotropic and its strength increases with time. This is especially important for winter applications. The engineering properties of greases are mainly determined by their rheological characteristics.

Bitumens (also known as *asphalts*) consist another group of oil-based products. They are viscoplastic materials of high viscosity. Frequently, their elasticity (or viscoelasticity) is also important in their applications. Bitumens (natural or synthetic) are resin-like mixtures of higher hydrocarbons and their derivatives. Bitumens or asphalts, which are liquid binders, can be mixed with mineral fillers, such as sand, gravel and other modifying components to form paving or roofing compounds and other construction products. They are composite materials with dispersed particles.

Behavior of these products in real applications depends on numerous factors. For

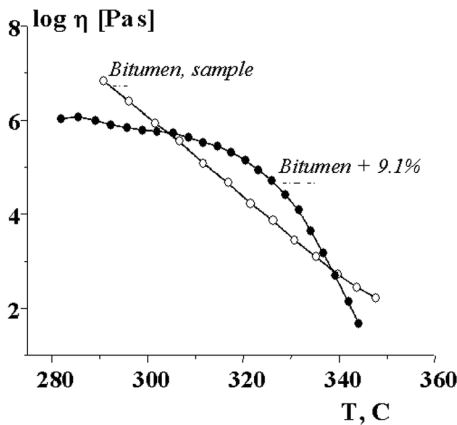


Figure 6.2.6. Example illustrating bitumen modification by addition of polymer (SBS – block copolymer of butadiene and styrene). [Adapted, with permission, from F. Martinez-Boza, P. Partal, F.J. Navarro, C. Galegos, *Rheol. Acta*, **40**, 135 (2001)].

example, in pavement applications, the amount and type of aggregate, and temperature properties of bitumen (especially low temperature properties), play a dominant role in temperate climatic conditions. Geographic location of pavement also plays an essential role as well as many other factors. Rheological properties of compositions used in road construction are frequently modified to address local requirements. One example of such modification is shown in Fig. 6.2.6. Here, the effect of addition of a block copolymer changes the relationship between viscosity and temperature. It is not immediately evident which one of these two materials is “better” or what else should be done in order “to improve” material. The answer depends on the requirements of the application. How-

ever, rheology gives a chance to compare materials of different compositions and suggests avenues to required modification of properties.

Viscous properties of asphalts are important for technological processes. Maintenance of characteristics of pavements or other compounded products depends on their viscoelastic properties and mechanical strength; the latter is most likely related to viscoelasticity of material.

In real practice, measurements of viscoelastic properties can be carried out in a limited experimental frequency (or time) window, whereas such materials as asphalts are used in a wide temperature range and therefore relaxation times are changing by many decimal orders. As discussed in section 2.7, estimation of relaxation characteristics of material in a wide time range can be solved by applying the time-temperature superposition principle. It was proven that this method may also be applied to asphalts¹¹ to estimate their relaxation properties and to calculate their strength and lifetime at different stresses.

In many other cases, it is possible to estimate quality of asphalt based on the correlation between their structure and rheological properties, on one hand, and rheological properties and performance characteristics in product applications, on the other hand. Rheological measurements are also applied as standard methods in quality control and the results of these measurements are the necessary parameters for material characterization.

The following are the applications of rheological methods in oil industry:

- measurement of rheological properties of oils and oil-based products to develop reliable engineering criteria for pipeline design
- estimation of temperature boundaries for transportation of crude oils and applicability of oil-based composite materials
- classification and grading of petroleum products for different applications
- development of new oil-based products on the basis of correlation between applied properties of these products and their rheological characteristics.

6.2.3 FOOD PRODUCTS

Dough was one of the first objects of rheological studies, which demonstrated that dough is a viscoplastic material.¹² Dough testing in bread production is probably the most successful application of modern, sophisticated, rheological studies in control of product development and intermediate quality testing.¹³

Numerous food products were examined by rheological methods. The main problem in testing food products is their inhomogeneity. It is relatively easy to test such products as mayonnaise or cream but very difficult to experiment with a variety of products which have variable composition. Specific to food industry, rheological methods are widely used for product quality testing.

A list of some standard methods of testing food products is given below.¹⁴

Continuous Puree Consistometer
Denture Tenderometer
MIT Denture Tenderometer
General Foods Texturometer
Brabender Farinograph
Mixograph
Extensiograph
Alveograph
Chopin Alveograph
Cone Penetrometer

Bloom Gelometer
 F.I.R.A. Gel Tester
 Bostwick Consistometer
 FMS and Adams Consistometer
 Werner-Bratzler Shear
 Zhan Viscometer
 Kramer Shear Cell
 Brookfield Disks and T-bars
 Stephens Texture Analyzer
 Simple Compression

Difficulties in applications of standard rheological experimental methods for food products lead to attempts to invent new approaches for characterizing these materials. Squeezing flow between two parallel plates was considered a useful method for measuring rheological properties of “semi-liquid” food products, such as tomato paste, low fat mayonnaise and mustard.¹⁵

Analysis of rheological properties of numerous food products showed that they are mainly characterized using the following features:

- non-Newtonian flow properties
- yield stress
- thixotropy

while elasticity and viscoelastic properties, though they exist, are not very important.

It is also worth adding that the region of non-linear viscoelastic behavior of these products is reached at low deformation.

This is explained by the weakness of physical structure existing in these materials, which is easily broken by small stresses. It was found experimentally that shear stress must be as low as 0.2 Pa (for *yogurt*) in order to carry measurements in a linear viscoelastic range.¹⁶

A typical example of viscous properties of some liquid-like food products is presented in Fig. 6.2.7 for *tomato puree* and *mayonnaise*.¹⁷ The following characteristic features of rheological behavior of these products (as well as some others) are seen in this figure: the rapid change from upper to lower branches of a flow curve is large but flow at low shear stresses occurs and flow at maximum viscosity in this stress range is of practical importance.

The measured level of yield stress is several hundred Pa, which is typical for paste-like food products. Yielding does not happen rapidly but viscosity is constant for some shear stress range. This type of rheo-

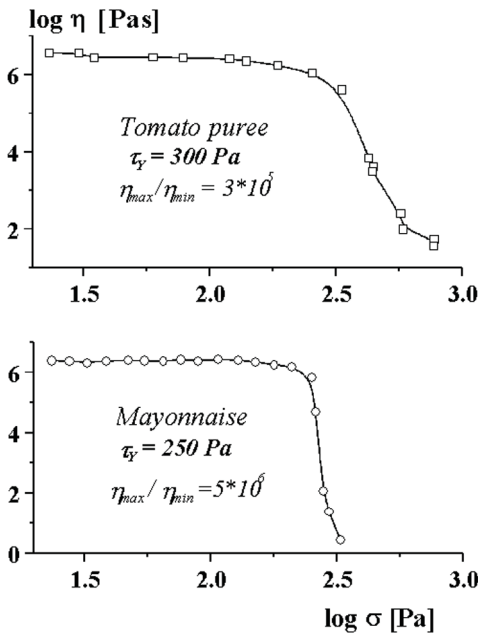


Figure 6.2.7. Flow curves of food products. Original experimental data obtained by C. Gallegos. [Adapted, with permission, from H.A. Barnes, *J. Non-Newt. Fluid Mech.*, **81**, 133 (1999)].

logical behavior was observed for many food materials including some unusual products, such as “*black cumin*”.¹⁸

Properties of *chocolate* mass¹⁹ are characterized by its rheological parameters. The recommended method²⁰ of measuring rheological properties of chocolate mass is based on the Casson equation and viscous properties are measured in the shear rate range from 5 to 60 s⁻¹. Typical values of rheological parameters (entering the Casson equation) are:

for milk chocolate:	$\sigma_Y = 0\text{--}20 \text{ Pa},$	$\eta_p = 0.5\text{--}2.5 \text{ Pa}\cdot\text{s}$
for chocolate bar grades:	$\sigma_Y = 10\text{--}200 \text{ Pa},$	$\eta_p = 1\text{--}20 \text{ Pa}\cdot\text{s}.$

The full range of the above mentioned rheological effects was observed in testing *peanut butter*.²¹ This is a suspension with micron-size particles. The yield stress in the range of 24–370 Pa (depending on composition) was measured. Its value correlated with stabilizing of a suspension structure. Strong non-linear effects in periodic oscillations were evident even at very low stress level. Time-dependent effects and non-Newtonian flow behavior were also observed in product testing.

Yield stress determines quality and/or composition of product. Sour cream is a good example. The yield stress depends on the amount of fat and it can be used as a quantitative measure of sour cream quality under standardized test conditions.

Qualitative description of steady-state (excluding time-dependent behavior) properties is based on the Hershel-Bulkley equation or similar ones (see Eq. 3.3.9). If the clearly pronounced yield stress is absent, it is possible to describe flow properties of food products by other equations. For example, flow curves measured for aqueous dispersions of *spray-dried egg yolk* were successfully fitted into the Carreau-type equation with adding a limiting value of the minimum Newtonian viscosity at high shear rates (see Eq. 3.3.3).²²

Many food products consist of polymeric substances. General approaches developed for polymer materials are also applied to food, as was demonstrated, for example, for *soy flour*.²³

6.2.4 COSMETICS AND PHARMACEUTICALS

There is a great variety of cosmetic and pharmaceutical materials such as body lotions, face creams, toothpastes, liquid soaps, and so on. The difference between “creams” and “pastes” is not essential, and from a rheological point of view, it is more quantitative than qualitative. Many materials are emulsions, i.e., dispersions of liquid droplets in another continuous liquid phase. There is frequently some amount of solid component dispersed in a continuous liquid phase.

Two main classes of emulsions are distinguished: oil droplets dispersed in a water phase (*O/W emulsion*) or a water phase dispersed in a continuous oil phase (*W/O emulsion*). Emulsions with more complex structure also exist. Disperse phase is stabilized with emulsifier covering the surface of droplets.

Pharmaceutical emulsions, like many other emulsions, are liquids and can flow at any stress. Disperse phase creates some “structure” appearing due to inter-particle interactions of a different nature. This structure contributes to a stress domain where viscosity drops rapidly. This stress region resembles yielding. At higher stresses, these systems are typical non-Newtonian liquids.

Two main rheological characteristics are most important in pharmaceuticals:

- non-Newtonian flow properties
- yield stress.

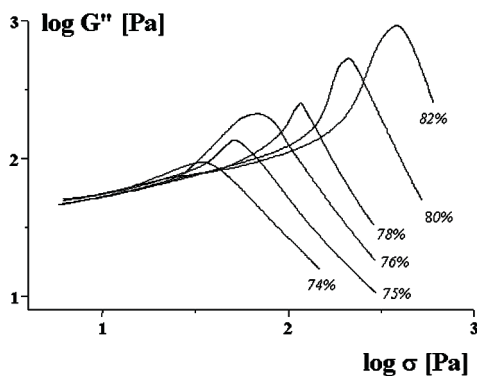


Figure 6.2.8. Loss modulus as a function of stress amplitude in testing highly concentrated W/O cosmetic emulsion. Concentrations of a disperse phase are shown at the curves. Curves are drawn instead of points in original publication. [Adapted, with permission, from A. Ponton, P. Clément, J.R. Grossiord, *J. Rheol.*, **45**, 521 (2001)].

The selection of a target value for these parameters is determined by human experience and goals of application. Many cosmetics are viscoplastic materials (“pastes”) and yield stress is important because the material is expected to remain on the skin for a long time. The level of the yield stress depends on the application. The yield stress of body lotion is very low, about several Pa. The optimal level of σ_Y for body lotion is about 10 Pa, and for soft creams, σ_Y may reach 100 Pa. Thixotropic behavior is also important in some applications, and thixotropic effects are caused by an inner structure of some pharmaceuticals (e.g., see Fig. 3.5.7). This is a weak structure and it can be measured at low stresses.

Elasticity is not essential for application of these materials, although viscoelastic properties and frequency dependence of elastic modulus are measured. These systems are strongly non-linear because inter-particle forces are weak and elastic in nature. Therefore, even at small deformation, amplitude the loss modulus becomes strain-dependent.

“Super-concentrated” cosmetic materials of the W/O type with concentration of disperse phase exceeding 74 vol.% form an unusual group of emulsions.²⁴ The disperse droplets are not spheres but polyhedrons. Such emulsions are viscoelastic liquids. The limit of linearity corresponds to very low stresses (see Fig. 6.2.8). Dependencies of this kind are typical for cosmetic emulsions²⁵ and the maximum of the loss modulus is treated as yield stress. Its value is low but the existence of yield stress in pharmaceuticals in many cases is crucially important for application,²⁶ because creams should remain on a body surface without flowing.

Nature of components, concentration of a disperse phase, and intimate details of the structure of an emulsion are the most important influences of rheological properties of pharmaceutical products and cosmetics. Measured rheological parameters by themselves do not express quality and application characteristics of material. They only become valuable when compared with organoleptic features of materials, which cannot be expressed by objectivity of measurement but must be compared with consumer acceptance of a product. Rheology helps to quantify these observations.

6.2.5 BIOLOGICAL FLUIDS

The central concept in measurement of rheological properties of biological fluids is to establish the norm for a healthy individual and to compare the results of measurements for any person with such norm. But norms may differ for various individuals in a broad range, and measures of this kind should be used with extreme caution in these applications.²⁷

Blood is undoubtedly the most important biological fluid and its rheology is interesting from both theoretical and applied points of view. Other biological fluids such as synovial fluid and sweat are also interesting subjects for rheological analysis.

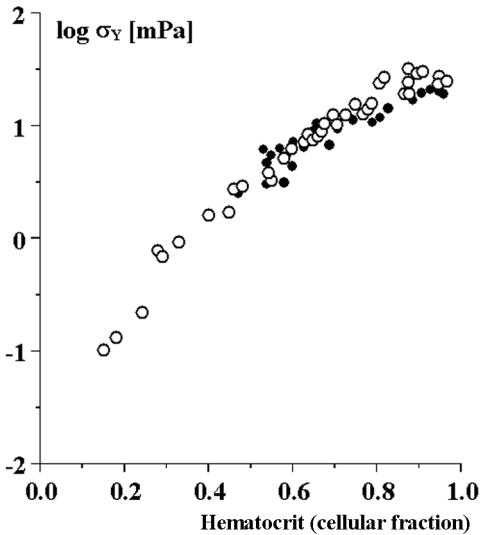


Figure 6.2.9. Yield stress as a function of the content of hematocrit (content of red blood cells). Open labels – original data; black labels – literature data. [Adapted, with permission, from C. Picart, J.-M. Piau, H. Gallard, P. Carpentier, *J. Rheol.*, **42**, 1 (1998)].

“Blood is a juice of very special kind”²⁷ – this statement is true in many aspects. By its structure, blood is a multi-component system (suspension) consisting of elastic deformable particles (mainly red blood cells) dispersed in Newtonian liquid (plasma). Blood viscosity (at different velocities of flow), rate of coagulation (accompanied by evolution of rheological properties), and influence of medicinal preparations are directly related to the health state of an individual. The main problem in characterization of properties of blood is absence of a “norm”. Measurements are useful to compare properties of blood of the same person to study their evolution but are difficult to generalize and compare with the health status of an individual.

Another problem in estimation of blood properties is its instability, caused by temperature and chemical reactions in the presence of air oxygen. These reasons

require special measures to assure that the rheological characteristics are free of artifacts. It is doubtful whether blood shows a real yield stress. If it has, it may indicate that blood was exposed for too long to a low shear stress and it is objectionable from a biological point of view. Sometimes blood is treated as a “percolating physical gel” to determine conventional “yield stress” as its characteristic property.²⁸ As discussed in section 3.3.3, the determination of yield stress depends on the method of approximation. If a method is selected for the whole range of samples, their properties can be compared unambiguously. This is shown in Fig. 6.2.9, where stress at shear rate equal 10^{-3} s^{-1} was “taken as a realistic approximation of the yield stress of blood”. Experiments were carried out in a Couette-type viscometer and deformations of red cells due to wall effects were absent. It is not a real, physically meaningful yield stress but a convenient measure of rheological properties of blood. A good correlation between “yield stress” and the content of red cells was observed. The fitting curve for all points is well described by the cubic dependence:

$$\sigma_Y = A\varphi^3 \quad [6.2.2]$$

where φ is the content of red blood cells and A is an empirical constant.

The yield stress data appear to be different for three donor blood samples, though the variability of data was not very large.²⁸ The authors of the publication emphasize that the results are strongly dependent on the details of the experiment. In particular, the measurements made with smooth or roughened capillary surface lead to very different conclusions. Variation of method used for estimating yield stress can give quite different numerical values of this parameter. In development of rheological methods for studies of

blood properties, especially in clinical practice, it is very important to standardize conditions of measurement and use the same procedure for treating experimental data.

Application of rheological analysis was found useful for other biological materials, such as bones, tissues, arteries, etc.

6.2.6 CONCENTRATED SUSPENSIONS

These materials include a variety of compositions. Concentrated dispersions in low viscosity liquids, such as suspensions of minerals, sand or stones in water, drilling compositions, slurries, slush, mud, coal suspensions, coating colors, paints, and so on, are interesting objects of rheological investigations. The following rheological properties of concentrated suspensions are typical:

- non-Newtonian flow including possible thickening at high concentrations and high shear rates
- yielding; the yield stress is a strong function of concentration
- critical concentration threshold corresponding to structure formation; at concentrations above this limit such effects as jamming, wall slip, and so on, take place
- thixotropy.

The attention here is drawn to the “structure” formed by solid particles.

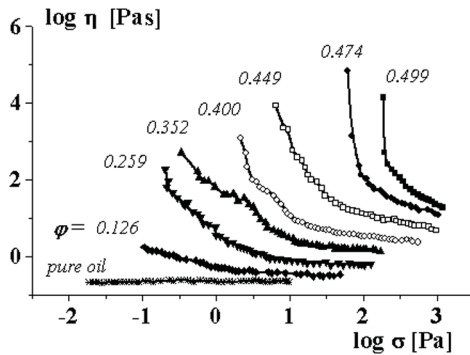


Figure 6.2.10. Effect of concentration on flow curves of PMMA spherical particles (diameter 5 μm) in silicon oil. [Adapted, with permission, from L. Heymann, S. Peukert, N. Aksel, *Rheol. Acta*, **46**, 307 (2002)].

Contrary to the data in Fig. 3.2.3, the low shear stress domain, corresponding to very high constant values of viscosity, was not reached in Fig. 6.2.10, even though high shear rate constant values of viscosity are present in Fig. 6.2.10. But it is likely that such a domain exists at low shear stresses for all suspensions, regardless of concentrations.

Viscoelasticity of material is generally not as important because structure is formed by hard solid particles. The structure can be modified by the viscoelastic matrix. Inter-particle interactions have negligible influence on viscoelastic properties of material. Solid filler suppresses elasticity of the matrix.

The domination of a particular rheological effect depends on numerous factors, primarily on solid phase concentration and inter-particle interactions which can be modified by different methods.

Yield stress, σ_Y , caused by a structure formed by solid components, does not depend on viscosity of the matrix. This is shown for model materials in Fig. 3.2.5 and it applies to

A typical example demonstrating evolution of viscous properties in transition from dilute to concentrated suspensions is shown in Fig. 6.2.10. Addition of solid particles leads to appearance and gradual broadening of a non-Newtonian region in a flow curve, which eventually results in rapid yielding. Experimental data was obtained for numerous suspensions, though the boundary of concentration domains, corresponding to flow-to-yielding transition, depends on the nature of dispersed particles and their surface treatment.

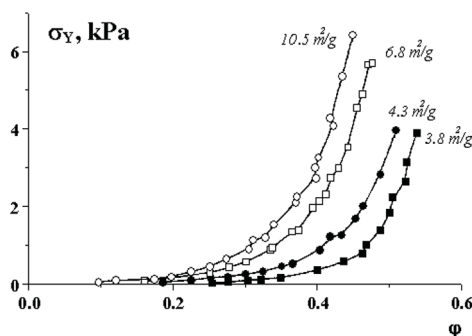


Figure 6.2.11. Yield stress in Al_2O_3 slurries as a function of volume fraction. Curves correspond to different sizes of particles presented by their surface area (shown on curves). [Adapted, with permission, from Z. Zhou, M.J. Solomon, P.J. Scales, D.V. Boger, *J. Rheol.*, **43**, 651 (1999)].

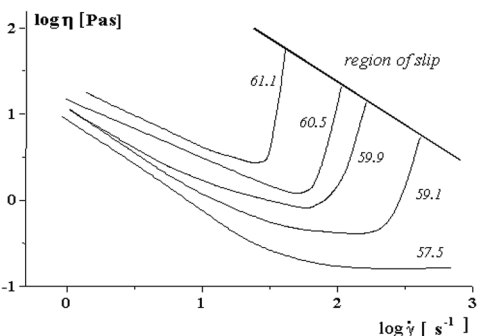


Figure 6.2.12. Flow characteristics of slurry consisting of $1\ \mu\text{m}$ particles of silica in water at $\text{pH} = 8.1$ with $0.10\ \text{M}$ added NaCl . Volume concentration (in%) of the solid phase is shown on curves. Points obtained in the original publication are omitted. [Adapted, with permission, from G.V. Franks, Z. Zhou, N.J. Duin, D.V. Boger, *J. Rheol.*, **44**, 759 (2000)].

the majority of concentrated suspensions. At the same time, a matrix can influence the inter-particle interaction determining the strength of a solid-like structure formed by filler. The values of σ_Y depend on solid phase concentration and the nature of solid particles, and their surface treatment.

The yield stress in concentrated suspensions in a low viscosity matrix depends on the concentration of solid particles. Fig. 3.2.4 and Fig. 6.2.11 demonstrate it very clearly. The role of particle sizes (surface area) is also evident from this experimental data. The concentration and particle size dependencies of yield stress, σ_Y , for experimental data of this figure can be represented by the generalized fitting function:

$$\sigma_Y d_s^2 = k \varphi^n \quad [6.2.3]$$

where d_s is average diameter of particles, k and n are fitting parameters. It was found that for the concentration range $\varphi < 0.42$, the exponent $n = 4.2$ (at higher concentration n rapidly increases). The analogous dependence of yield stress on concentration was observed for numerous suspensions, for example, for clay dispersions.²⁹ In fact, the exponential dependence $\sigma_Y(\varphi)$ discussed in section 3.3.3 may be approximated by two power-law functions with changing power-law index values.

It is reasonable to think that there is some threshold concentration in suspensions corresponding to the formation of solid-like structure. The exact value of concentration corresponding to this threshold depends on the composition of the system.

Formation of such solid-like structure leads to rapid increase of yield stress and to changes in rheological behavior of material. A typical example is shown in Fig. 6.2.12.³⁰ First of all, a very strong influence of concentration in a narrow range of its change is pertinent. Thickening effect is observed at concentration above some threshold. The most popular interpretation of this effect is related to formation of clusters.³¹ This effect of volumetric dilatancy is similar to attempts to force dry sand through a tube at high applied force. Shear thickening can be attributed to increased inter-particle interaction.

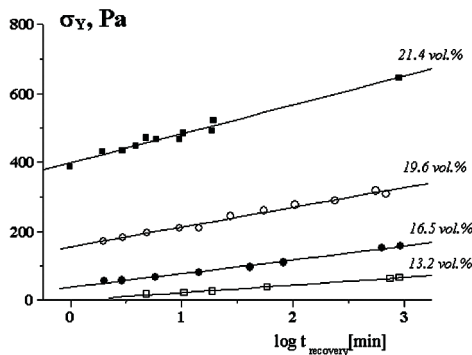


Figure 6.2.13. Thixotropy of concentrated suspensions: recovery of yield stress as function of rest time for Na-montmorillonite-based suspension. Concentration is shown on graph. [Adapted, with permission, from R.G. de Kretser, D. V. Boger, *Rheol. Acta*, **40**, 582 (2001)].

suspensions as bentonite-in-water suspensions.³⁴ Sometimes, thixotropy (structure formation and destruction) can be observed as an unusual effect of periodic oscillation of apparent viscosity.³⁵

Thixotropy is mainly understood as reversible changes of viscosity (due to deformation and rest). In section 3.5.1 it was shown that strength of material is also time-dependent. For concentrated suspensions, it results in time dependence of yield stress for materials which were initially destroyed by deformation. This effect is illustrated in Fig. 6.2.13.

Thixotropic effects are typical of concentrated suspensions of different types, though not widely investigated. Their quantitative description is important for some technological processes, in particular for mixing and transportation.

As was mentioned in Section 3.3.4.3, concentration dependence of rheological properties of concentrated emulsions is similar (in many aspects) to behavior of suspensions. For example Fig. 3.2.9 discussed in Section 3.3.4.3 clearly demonstrates that the shape of flow curves changes in a rather narrow concentration range and this change is similar to evolution of viscous properties of concentrated suspensions (see, for example, Fig. 6.2.10). At high concentrations (Fig. 3.2.9), flow curves can be treated as those of solid-like substance with very high viscosity at low shear stresses exhibiting the yield stress.

6.2.7 ELECTRO- AND MAGNETO-RHEOLOGICAL MATERIALS

Electro- and magneto-rheological materials (ER and MR materials, respectively) are a special type of concentrated dispersions of solid particles in a viscous medium.³⁶ Their solid phase can be formed from inorganic materials. But, it can also be formed from hydrated starch particles³⁷ or any other particles, which have induced dipole or dipole-dipole interaction creating a continuous structure. These suspensions consist of micron-level particles dispersed in a continuous phase. An inter-particle interaction in ER and MR liquids depends on concentration of particles as well as on permittivity (for ER) and permeability (for MR) materials.

Shear thickening at high shear rates is typical of many widely-used technological materials, for example, surfactant-stabilized concentrated kaolin-in-water suspensions.³²

From an applied point of view, existence of a critical concentration at which strong shear thickening and transition from flow to slip becomes dominant, preventing steady transportation of a suspension, is the most important finding.

Structure formation is a reversible process³³ and from a rheological point of view it leads to thixotropy of material. The existence of thixotropy and, as its manifestation, viscosity bifurcation, was demonstrated for such popular concentrated

A structure formed after applying an electrical or magnetic field has some strength due to interaction of these dispersed particles. Therefore, such a composition placed in an electrical or magnetic field loses fluidity at stresses lower than the strength of structure and becomes a viscoplastic medium with yield stress corresponding to the strength of particle structure. Application of field results in drastic changes of rheological properties.

This effect can be used in numerous practical applications, such as construction of switching devices, electrical valves, breaks, clutch dampers, and so on.

The rheological behavior of electro-sensitive suspensions can be described by equation used for viscoplastic medium, for example, the Bingham type, but with coefficients depending on the strength, E , of an electrical field:³⁸

$$\sigma(\dot{\gamma}, E) = \sigma_Y(E) + \eta \dot{\gamma} \quad [6.2.4]$$

Rheological properties of ER and MR materials can be changed from a purely viscous liquid to a viscoplastic medium. According to Eq. 6.2.4, the following characteristics are important for ER liquids: viscosity, η , in the absence of a field, and the dependence of the yield stress on E . In magneto-rheological materials the yield stress depends on magnetic flux density, B , instead of E .

For practical applications, the characteristic time of switching, t_{sw} , i.e., time of formation and disappearance of solid-like structure, is an important factor. For systems of practical interest this time must be in the range of 1-10 ms.

Structure formation on switching on an electrical field leads to yield stress and/or increase in apparent viscosity. Material subjected to stresses below σ_Y is solid-like and this transition is of practical interest for applied science.

The transition to solid-like behavior can be demonstrated by measuring the elastic modulus under a superimposed electrical field. A typical example is shown in Fig. 6.2.14 for diatomite suspension in transformer oil. Increase of elastic modulus attains several decimal orders of magnitude.

The peculiarities of rheological behavior of electro-rheological liquids depend on concentration of the solid phase, though the strength of the structure (i.e., yield stress) is also sensitive to particle size distribution.³⁹ Analogous effect of particle size distribution on rheological properties is a characteristic feature of various emulsions and suspensions.

An example illustrating magneto-rheological effect is shown in Fig. 6.2.15, where the dependence of yield stress on magnetic flux density, B , is shown. In an original study,⁴⁰ this dependence was measured for 10% suspension of carbonyl iron in silicone oil and in 6 different greases. Silicone oil was a Newtonian liquid and greases were viscoplastic materials with σ_Y values in the

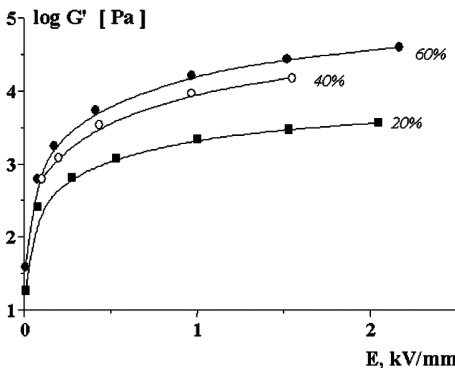


Figure 6.2.14. Electro-rheological effect: influence of electrical field on storage modulus of diatomite suspensions at frequency of 0.16 Hz, amplitude of shear deformation of 0.027. Concentrations are shown at the curves. [Adapted, with permission, from E.V. Korobko, V.E. Dreval, Z.P. Shulman, V.G. Kulichikhin, *Rheol. Acta*, **33**, 117 (1994)].

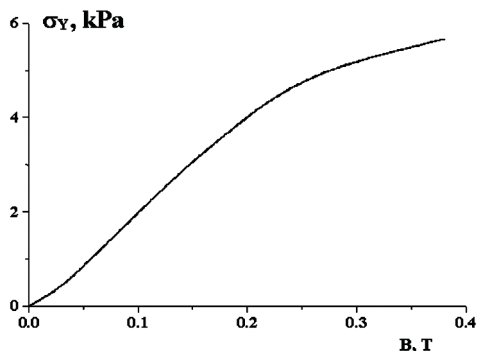


Figure 6.2.15. Magneto-rheological effect: dependence of yield stress on applied magnetic flux density for carbonyl iron suspension in different media. A line is an averaged curve drawn for the same particles dispersed in 7 different media. [Adapted, with permission, from P.J. Rankin, A.T. Horvath, D.J. Klingenberg, *Rheol. Acta*, **38**, 471 (1999)].

range of 1–37 Pa. The dependencies $\sigma_Y(B)$ for all these systems are within a narrow range, and the line in Fig. 6.2.15 is an averaged curve. The magnetic field produces a structure with a strength several orders of magnitude higher than initial yield stress and in practice this strength does not depend on viscosity of the matrix.

Properties of ER materials can be characterized by a dimensionless group (known as the *Mason number*, Mn) equal to a ratio of viscous to polarization forces.⁴¹ Polarization forces are proportional to the square of electrical field strength and electrical parameters of the system. However, experimentally observed $\sigma_Y(B)$ dependence is usually described by a power-law equation with an exponent close to 1.5.⁴²

Transition from viscous to viscoplastic behavior takes place at some critical value of the Mason number, which depends on the concentration of the interacting particles. Linear dependence of σ_Y on concentration of filler is a good approximation of real performance of some ER materials,⁴³ though more complicated concentration dependencies of σ_Y can be observed, as was shown in section 6.2.6.

Electro-rheological effect can also play a role in mixtures of two immiscible liquids, e.g., polymer blend, including a liquid crystal polymer component.⁴⁴ However, due to high viscosity of the polymer system, transient switch-time in such systems increases up to several seconds, and viscosity jump is not sufficiently rapid as compared with suspensions of solid particles.

6.2.8 CONCLUDING REMARKS

The following is the summary of the concepts discussed so far in this chapter.

Rheological measurements provide a set of parameters characterizing properties of material under test. It is supposed that these parameters are related to molecular structure and composition of industrial materials. Establishing a correlation between rheological parameters and structure factors is the central research problem. The results of rheological measurements by themselves are not a direct indication of quality and application properties of a product. The latter must be based on practical experience and expert evaluation.

First, there is a triangle: “*rheological properties*” – “*molecular structure and composition content*” – “*quality and application*”. Any side of this triangle is the subject of studies and only the complex results of these studies form a basis for application of rheological methods in material control and characterization.

Rheology operates with different measures of resistance to deformation, primarily determined by viscosity and modulus, though these characteristics are being understood in a more complex sense than when they were initially introduced in basic theories. There is a difficult and in many cases impossible to solve task of carrying out rigorous measurements based on a modern complicated continuum or molecular theories. Such measure-

ments can be a goal of advanced academic investigations, which are not directly ready for technological applications. As an alternative to this rigorous approach, a great number of conventional industrial methods of material characterization, related to rheology, have been proposed and are used in practice of testing various real materials.

Second, the principal direction of application of rheology in material characterization is *standardization* of proposed experimental methods, including the design of the apparatus used and the testing procedure. The benefit of standardization depends on correctness of the method selection for a specific field of application and its sensitivity to factors which are assumed by experts as determining product quality.

The choice of the most sensitive rheological parameter depends on the goals of testing. The traditional subject of rheology is flow of materials. Then, the dominant share of experimental methods is related to viscosity measured under different conditions. Many real (either technological or biological) materials are viscoplastic, and their rheological properties in the low shear stress range can be useful for assessment of their quality. In other cases, time-dependent behavior, primarily thixotropic properties of material, can play an essential role in application.

Third, it is not enough to limit oneself to apparent viscosity as an applied measure of rheological properties of real materials but it is necessary to deal with a wider choice of material characteristics. Among them, the yield stress is very important for many materials and its reliable measurements are promising for practical applications.

6.3 RHEOKINETICS (CHEMORHEOLOGY) AND RHEOKINETIC LIQUIDS

6.3.1. FORMULATION OF PROBLEM

Rheological methods are used in practice to control chemical reactions in oligomeric and polymeric systems, physical transformations, and quality of products at different stages of process. This branch of rheology is called *rheokinetics*, or sometimes the terms *chemorheology* and *kinetorheology* are also used.⁴⁵

Its importance for polymeric materials (though not only these) is explained by high sensitivity of rheological properties, primarily viscosity and elastic modulus, to the length of the macromolecular chain, its structure, and/or concentration of polymer in solution. This is contrary to reactions of low-molecular compounds, where rheological properties of reactive media are only slightly affected during the course of reaction.

In rheokinetic measurements two different cases can be distinguished:

- linear polymerization, where the increase of a linear chain is a dominating process
- curing, where chemical reactions lead to formation of a three-dimensional network.

In the first case, viscosity increases gradually (if reaction takes place in a liquid phase). In the second case, when continuous network formation begins, viscosity becomes unlimitedly high and material loses its ability to flow. The third case of interest for rheology is related to chemical (or physical) transformation of polymeric materials without changes of chain length or its branching.

6.3.2. LINEAR POLYMERIZATION

Rheokinetics of linear polymerization depends on the process chemistry and/or the chain growth mechanism. Three main reactions can be realized and modeled, such as: ionic polymerization, radical polymerization, and polycondensation.

According to the simplest model of *ionic polymerization*, the growth of chains happens on the active centers; both molecular mass, MM, of a newly-formed polymer and its concentration change.

The model of *free-radical polymerization* is based on the supposition that MM of the forming polymer is constant and polymerization proceeds by increase of its content in a reactive medium.

Polycondensation is a process of polymer formation by reaction of growing chain ends; concentration of polymer in reactive medium is constant but its molecular weight increases.

Then, viscosity dependence on concentration of polymer in a reactive medium (solution) and its MM is supposed to obey the standard rules discussed in section 3.3. Based on these simplest arguments, rheokinetic dependencies of viscosity, η , on the degree of conversion, β , for the three model schemes of polymer formation in solution can be obtained as follows:

for ionic polymerization:

$$\eta = K_1 \beta^{a+b} \quad [6.3.1]$$

for free-radical polymerization:

$$\eta = K_2 \beta^b \quad [6.3.2]$$

for polycondensation:

$$\eta = K_3 (1 - \beta)^{-1} \quad [6.3.3]$$

where K_1 , K_2 , and K_3 are constants, and the exponents a and b are the same as in the dependencies of viscosity on MM. As the first approximation, it can be assumed that for high MM compounds $a \approx 3.5$ and for concentrated solutions $b \approx 5$.

The types of $\eta(\beta)$ dependencies are different for various chemical processes. In addition, it is necessary to determine the kinetics of polymerization, i.e., the equation describing the time dependence of the degree of conversion, $\beta(t)$. Such equations are known for polymerization processes of different types.⁴⁶ Then, it is possible to calculate time dependence of viscosity for polymerization processes of any type.

Fig. 6.3.1 is an illustration of the time dependencies of viscosity and the degree of conversion measured simultaneously.⁴⁷ Strong influence of temperature on rheokinetics of polymerization is pertinent. In fact, temperature influences rheokinetics in two ways. First, viscosity depends on temperature. Second, kinetics of chemical reaction is highly sensitive to temperature. Direct estimations show that the second factor always dominates.

Calculation of time dependence of viscosity based on pure chemical and kinetic arguments is illustrated in Fig. 6.3.2 for free radical polymerization of methylmethacrylate. Dotted (calculated) lines were found based on laboratory studies of kinetics of polymerization and from independent data on viscous properties of

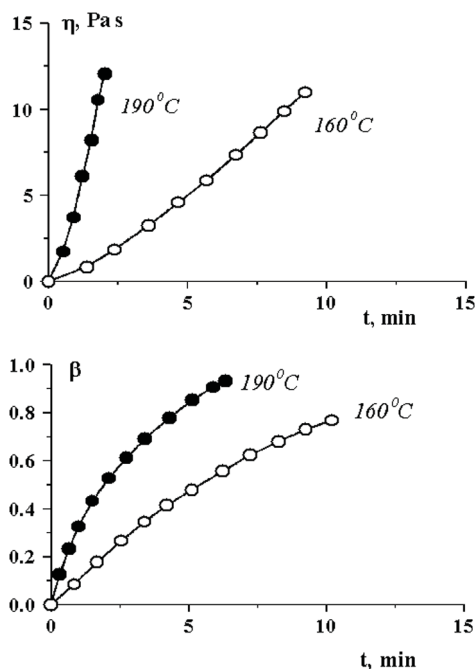


Figure 6.3.1. Rheokinetics of ionic polymerization of dodecalactam. Evolution of the degree of conversion, β , and viscosity, η , at two temperatures. [Adapted, with permission, from A.Ya. Malkin, S.G. Kulichikhin, S.L. Ivanova, M.A. Korchaghina, *Vysokomol. Soedin.* (Polymers – in Russian), **22A**, 165 (1980)].

polymethylmethacrylate solutions. It is seen that the model of rheokinetic calculations gives realistic results.

Numerous experimental data confirm that the simplest rheokinetic schemes of linear polymerization work satisfactorily when and if chemical processes take place in a homogeneous phase. However, in real technological practice, newly formed polymers can be insoluble (in contrast to their monomers) in a reactive medium, and, at a certain degree of conversion, phase transformation occurs. Rheokinetic data clearly demonstrate this effect, as shown in Fig. 6.3.3. The polymerization proceeds in a mixed solvent and “quality” of solvent is improved for a newly formed polymer by increasing the cyclohexane fraction in rela-

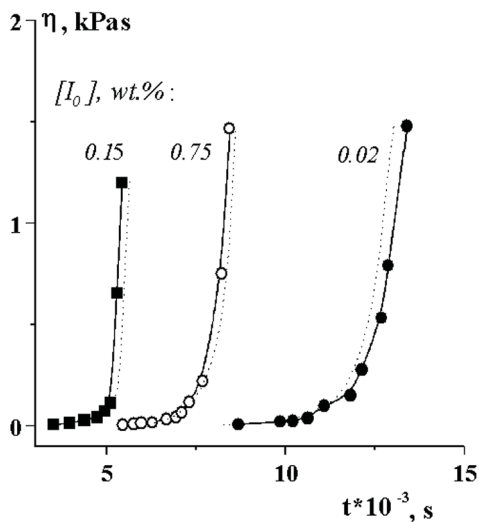


Figure 6.3.2. Comparison of experimental data (solid lines) and calculated viscosity profiles (dotted lines) in polymerization of methylmethacrylate at different content of initiator (its concentrations, $[I_0]$, are shown on curves). [Adapted, with permission, from A.Ya. Malkin, S.G. Kulichikhin, D.N. Emel'yanov, I.E. Smetanina, N.V. Ryabokon, *Polymer*, **28**, 778 (1984)].

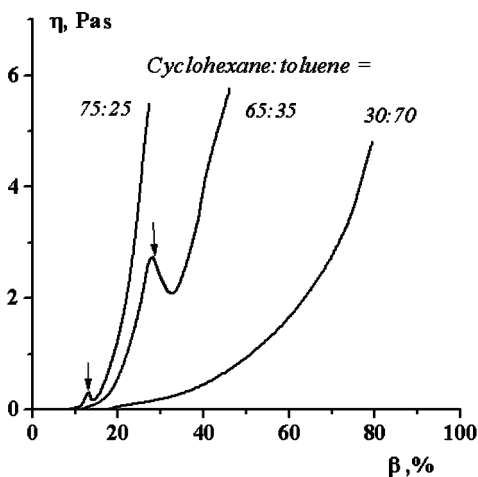


Figure 6.3.3. Polymerization of 50% solution of methylmethacrylate in a mixed solvent (ratios of solvents are shown on curves) – phase separation in the process of polymerization. Arrows show phase transitions. [Adapted, with permission, from A.Ya. Malkin, S.G. Kulichikhin, D.N. Emel'yanov, I.E. Smetanina, N.V. Ryabokon, *Polymer*, **25**, 778 (1984)].

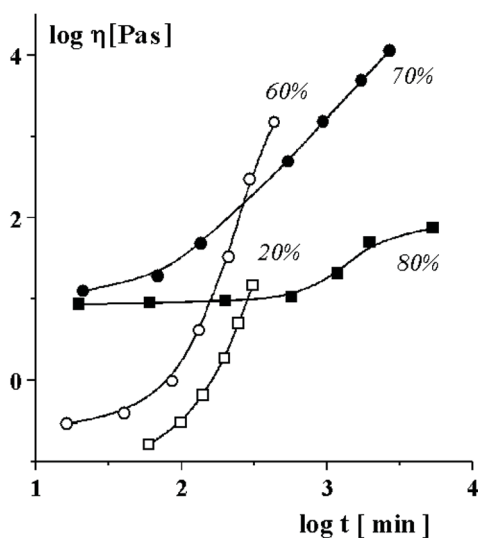


Figure 6.3.4. Evolution of viscosity in the process of synthesis of polysulfone from reactive monomers. $T=150^{\circ}\text{C}$. Concentrations of reactants are shown on curves. [Adapted, with permission, from A.Kh. Bulai, V.N. Klyuchnikov, Ya. G. Urman, I.Ya. Slonim, K.M. Bolotina, V.A. Kozhina, M.M. Gol'der, S.G. Kulichikhin, V.P. Begishev, A.Ya. Malkin, *Polymer*, **28**, 1047 (1987)].

tion to toluene (movement from the right curve to the left curve). Polymerization in “good” solvent proceeds in a homogeneous system and the smooth rheokinetic curve is observed (right curve in this figure). If the concentration of “bad” solvent is higher, the phase separation occurs at earlier stages of the process.

The effects of phase separation in polymerization processes, regardless of cause, is always manifested by a maximum on the rheokinetic curve.

Rheokinetic measurements are, by necessity, accompanied by shearing reactive medium. Then, it is natural to ask whether deformation influences the kinetics of chemical process. Experiments have proven that the answer is “no” if reaction takes place in a homogeneous system. However, the answer is the opposite if the system is heterogeneous. In this case, shearing is equivalent to mixing and averaging the content and properties throughout a reactive vessel, which influences the rate of reaction. However, the role of shearing can

be even more impressive, if and when deformations shift the conditions of phase separation. This phenomenon has already been mentioned in section 3.5.3, and Figs. 3.5.14 and 3.5.15 are very clear demonstrations of the shear-induced rheokinetic effects.

Rheokinetic measurements also demonstrate the transition to diffusion-controlled stage of reaction in linear polymerization, even if this transition is not accompanied by phase transition. This is shown in Fig. 6.3.4 for polycondensation synthesis of polysulfone. According to the general principles of chemical kinetics, the increase in concentration of reactants in solution causes acceleration of reaction. This concept is valid and corresponds to transition from 20 to 60% concentration. However, further increase of reactant concentration leads to a reverse effect – suppression of polymerization, which is clearly seen from rheokinetic data. This effect is definitely related to the diffusion-controlled limitation of chemical reaction. Rheological measurements are useful instruments in demonstrating this phenomenon.

As a summary of the present section, the following applications of results of rheokinetic analysis of linear polymerization can be mentioned:

- calculation of viscosity change during technological process with application to design of equipment (power of mixer motors, output of pumps, and so on); evolution of rheological properties of reactive medium also influences the flow lines and efficiency of mixing⁴⁸

- monitoring and control of the technological process with feedback to regulating parameters
- study of mechanisms of polymerization and estimation of their kinetic factors; this is achieved by comparison of theoretical predictions coming from different models with experimental data; a particular case of this line of investigation is based on using the Toms effect as a rheokinetic method.⁴⁹

6.3.3 OLIGOMER CURING

Evolution of two main parameters – viscosity and modulus of elasticity – in the process of oligomer curing is schematically shown in Fig. 6.3.5. Both factors are important in technological applications. The following general characteristics of rheokinetic analysis of the oligomer curing process, based on experimental data obtained for numerous oligomeric systems, can be formulated:

- viscosity grows unlimitedly when approaching a “critical” point (of time or degree of conversion); this point is called a *gel-point*, t^* ; gelation occurs at a certain degree of transformation, β^*
- noticeable values of the elastic modulus appear before the gel-point, though the main part of its growth takes place after the gel-point; however no special points can be marked on the $G(t)$ dependence and the value of modulus at β^* depends on the mechanism of three-dimensional network formation (more exactly, on functionality of reactants)
- modulus reaches its constant limiting value at the end of curing process
- loss tangent passes through a maximum at the gel-point, so it is a point of relaxation transition.

Let us discuss behavior of different rheological characteristics of curing in more detail.

6.3.3.1 Viscosity change and a gel-point

The rate of viscosity growth is very important for technological applications at the stage of article formation. Viscosity should not be too high during wetting of reinforcing filler or forming a part's shape. However, increase in viscosity is expected to be rapid after completion of these technological operations in

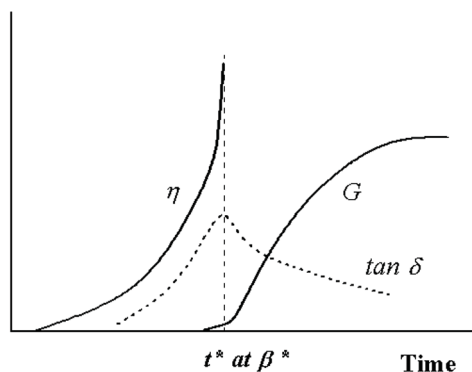


Figure 6.3.5. Evolution of main rheological parameters during oligomer curing.

order to shorten the overall process. It is necessary to know the technological time, i.e., time required to reach gel point, when the oligomer being cured is still in a liquid form.

Two matters are important for technology – estimation of the gel-time, t^* and formulation of the kinetic equation for viscosity evolution in time.

Gel-time is a limiting time at which $\eta \rightarrow \infty$. It is usually found by extrapolation procedure. One viscometric method of its determination is shown in Fig. 6.3.6. Constructing dependence of reciprocal viscos-

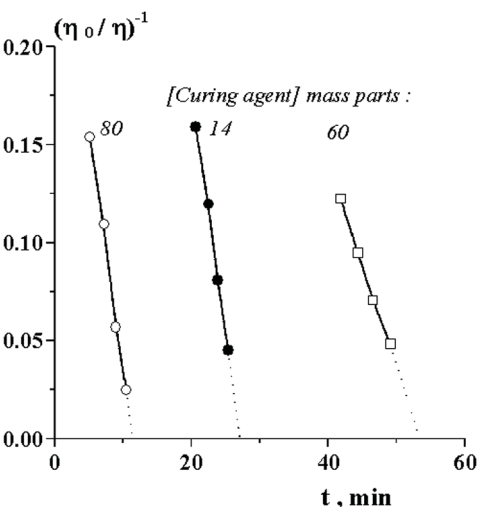


Figure 6.3.6. Finding a gel-time by extrapolation in coordinates $\eta^{-1} - t$ for an epoxy resin with different content of curing agent (shown on curves). [Adapted, with permission, from A.Ya. Malkin, S.G. Kulichikhin, M.L. Kerber, I.Yu. Gorbunova, E.A. Murashova, *Polym. Eng. Sci.*, **37**, 1322 (1997)].

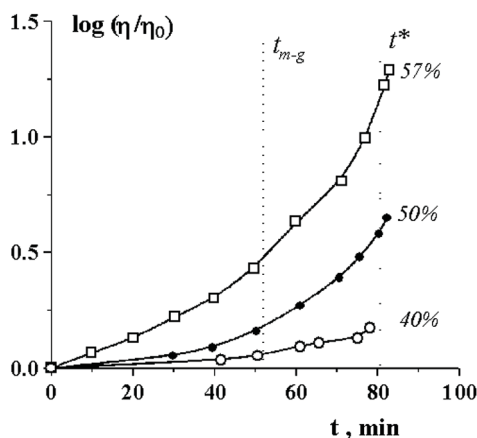


Figure 6.3.7. Viscosity evolution on curing melamine-formaldehyde resin in water solutions. Concentrations are shown at the curves. $T = 80^{\circ}\text{C}$. Dotted line t_{m-g} – time of micro-segregation as observed by an optical method. Dashed line t^* – gelation of system as a whole. [Adapted, with permission, from A.Ya. Malkin, S. G. Kulichikhin, *Adv. Polymer Sci.*, **101**, 217 (1991)].

ity (or ratio η_0/η , as in Fig. 6.3.6, where η_0 is viscosity of the initial uncured system) versus time and extrapolating this dependence to $\eta^{-1} = 0$, it is easy to find t^* . This method is satisfactory in many cases.

There are two limiting cases:

- macro-curing in which a three-dimensional network is formed throughout the whole volume of the sample
- micro-gelation in which curing proceeds in separate particles dispersed in solvent.

Fig. 6.3.7 shows how micro-gelation (marked by a dotted line t_{m-g}) takes place before the loss of fluidity of material (marked by a dashed line t^*) occurs. Micro-gelation, or micro-phase segregation, is observed by an optical method as intensive increase of optical density of material because of formation of insoluble cured micro-particles of colloidal size. This is the limiting case of heterogeneous curing. In fact, curing of real oligomeric products is more or less heterogeneous and statistically homogeneous curing is a limiting ideal case only.

Quantitative description of viscosity growth, which is necessary for practical calculations in modeling technological processes, can be based on various concepts.

Very rapid increase in viscosity suggests the use of exponential formulas of various types. A number of $\eta(t)$ relationships can be described by the simplest exponential equation:

$$\eta = \eta_0 e^{t/t_c} \quad [6.3.4]$$

where η_0 is the initial value of viscosity (at $t = 0$), and t_c is some characteristic time constant (not to be confused with t^*).

This equation does not fully fit experimental data, because it does not predict unlimited growth of viscosity on approach of the gel-point. However, it describes a wide range of viscosity values. Generally, it is assumed that this equation can be applied up to viscosity $\sim 10^3$ Pa*s. This limit corresponds to a high viscosity level that is close to the limit of fluidity of most materials. For these reasons, it gives an acceptable technological estimation of conditions of gelation.

A rigorous approach to $\eta(t)$ dependence is based on a scaling concept.⁵⁰ The following equation is expected to be valid only close to a gel-point:

$$\eta = \eta_0(1 - t/t^*)^{-s} \quad [6.3.5]$$

where s is the “scaling factor”. It equals 0.7 ± 0.07 .

Numerous experimental data show that an equation of an analogous type can describe $\eta(t)$ dependence even in a wider time domain, but the value of exponent s is not equal to the theoretical value but may change in a wide range, depending on chemical composition of the curing system, temperature, and so on. Therefore, s is not a constant for various real systems, which means that the scaling concept is not valid in many practically important situations. This experimental fact can also be treated as indirect proof of heterogeneity of curing real oligomeric materials.

Another empirical equation for $\eta(t)$ dependence can be proposed:

$$\eta = \eta_0 \exp\left(1 - \frac{t}{t^*}\right)^{-a} \quad [6.3.6]$$

This equation contains a limited number of fitting parameters and correctly predicts important features of $\eta(t)$ dependence: existence of gel-point (approach to $\eta \rightarrow \infty$) and rapid growth of viscosity during curing.

Finally, it is worth mentioning that rheokinetics of chemical processes of curing does not always coincide with results of kinetic study made by chemical and/or other physical methods. Different methods emphasize different transformations and that is why even the form of kinetic equations obtained can be very different, depending on the method applied.⁵¹

6.3.3.2 Curing at high shear rates

Shearing may influence the rate of chemical reaction in several ways. *First*, shearing is a mixing. In this sense, shearing promotes contacts of reactive groups and *accelerates* a reaction. *Second*, shearing can be a kinetic factor by itself (see section 3.5 and Fig. 3.5.16). The kinetic effect of shearing can be observed in multi-phase systems only, but no direct evidence of this effect in curing processes is known. *Third*, deformation at high shear rates leads to intensive *heat dissipation* and thus to non-isothermal effects. Increase in temperature accelerates reaction and thus shortens oligomer processing.

Let the induction period, when oligomer can be treated as low-viscosity liquid, be t_0 at low shear rates (in isothermal conditions). At high shear rates, due to heat dissipation the induction period becomes shorter and equals t_n . Dimensionless value $\tilde{T} = t_n/t_0 < 1$.

Model calculations show⁵² that \tilde{T} is a unique function of the dimensionless shear rate, Γ , which is expressed as

$$\Gamma = \frac{E\sigma_0\dot{\gamma}t_0}{c\rho RT_0^2} \quad [6.3.7]$$

where E is the activation energy of viscous flow, σ_0 is the shear stress, at which the isothermal induction period t_0 is measured, $\dot{\gamma}$ is the shear rate at which the induction period of curing is measured, c is the heat capacity, ρ is density, R is the universal gas constant, and T_0 is the initial temperature at which t_0 is measured.

The final equation expressing this dependence is

$$\tilde{T} = \frac{1}{\Gamma} \ln(1 + \Gamma) \quad [6.3.8]$$

Experimental data obtained for various oligomeric systems, having different chemical mechanism of curing, and at different initial temperatures, T_0 , confirm that this equation completely describes experimental data (one example is shown in Fig. 6.3.8). The effect of shortening the induction period can be as high as a hundred times.

Comparison of experimental and theoretical results shows that a non-isothermal effect is responsible for shortening the induction period at high deformation rates and, therefore, deformation rate plays a minor (if any) role in kinetics. However, it would be

premature to make this conclusion about a direct kinetic role of shearing if curing leads to phase segregation, as in the case of melamine-formaldehyde oligomers (Fig. 6.3.7).

In technological practice, high shear rates are common. That is why the results of measurement of the induction period performed at low shear rates should be used cautiously for estimating of lifetimes of oligomeric compositions used in real technology.

6.3.3.3 Curing after gel-point

Monitoring the process of curing after gel-point is possible on the basis of elastic modulus measurements.

The general understanding of the curing process is based on two basic concepts: formation of the three-dimensional network of chemical bonds at a certain degree of transformation (conversion), β^* , and possible transition to glassy state at curing temperature. This transition occurs at some degree of conversion because network den-

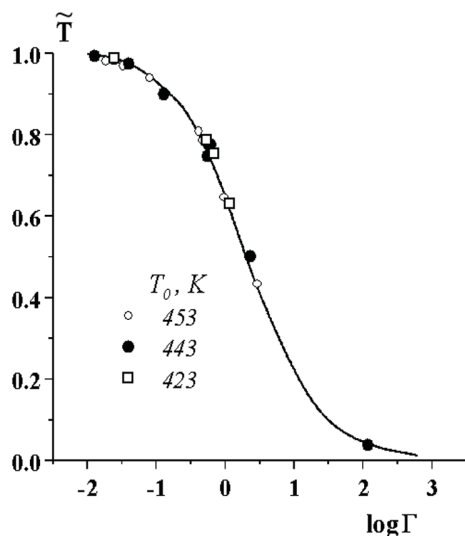


Figure 6.3.8. Curing at high shear rates – dependence of the dimensionless induction period on dimensionless shear rate. Experimental data are presented for a silicon-organic oligomer at different initial temperatures, T_0 . Solid line is calculated in accordance with Eq. 6.3.8. [Adapted, with permission, from A.Ya. Malkin, G.I. Shuvalova, *Vysokomol. Soedin.* (Polymers – in Russian), **27B**, 865 (1985)].

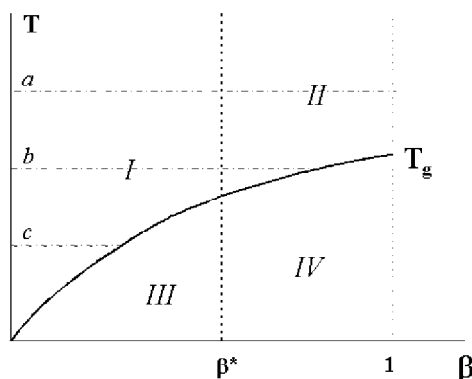


Figure 6.3.9. Dependence of the glass transition temperature on the degree of conversion.

liquid (it can flow); in domain II, material is elastomer (cured rubber); in domain III, material is vitrified liquid; and in domain IV, material becomes a glassy polymer (a polymeric glass).

This scheme permits us to propose the primary analysis of process of isothermal curing at different temperatures. Three temperatures, designated a, b, and c in Fig. 6.3.9 mark different stages and behaviors as discussed below.

If curing proceeds at a temperature corresponding to line a, initially the liquid oligomeric system changes to the rubbery state after crossing line β^* . Process of curing continues to the end – to the complete consumption of reactive groups. Then the final value of $\beta=1$. Moving along line a, one maximum corresponding to passing through line β^* can be observed on the $\tan\delta$ -vs.-time dependence.

If curing takes place at a temperature corresponding to line b, a liquid system also passes to the rubbery state at $\beta = \beta^*$ and the process continues in a rubbery state to line T_g corresponding to the glass transition temperature. After this point, the chemical reactions stop because of freezing molecular motions, though in this case, when $\beta < 1$ two maxima on the $\tan\delta$ -vs.-time dependence (corresponding to transition through β^* and glass transition temperature) are observed.

If curing proceeds at a temperature corresponding to line c, glass transition takes place before β^* , i.e., when material is still in a liquid state. Glass transition also manifests itself as $\tan\delta$ -vs.-time dependence passes through a maximum.

Kinetic factor is not reflected in the scheme in Fig. 6.3.9 at all, in spite of the fact that it is one of the determining factors in rheokinetic studies, as becomes evident from the so-called T-T-T (Transformation-Time-Temperature) diagram in Fig. 6.3.10.⁵³ Curing is impossible above the line T_d , because of intensive thermal degradation at high temperatures. Curing is also impossible below the line T_g because chemical reactions are frozen at low temperatures. There is a domain between the lines T_d and T_g (shaded zone in Fig. 6.3.10) in which curing is realized. The S-shape form of curve T_g is caused by the competition between rate of curing and distance of processing temperature from the glass transition temperature.

sity must be sufficiently high to restrict molecular mobility (at a given temperature). The transition to glassy state occurs at isothermal conditions (in contrast to a trivial understanding of the glass transition as a phenomenon taking place on cooling).

The sequence of physical events which can happen on curing is presented in Fig. 6.3.9. The solid line is a dependence of the glass transition temperature, T_g , on the degree of transformation, β . The vertical dotted line, β^* , corresponds to the gel-transition. Four domains of different states of material are recognized and designated by Roman numbers: in domain I, material is

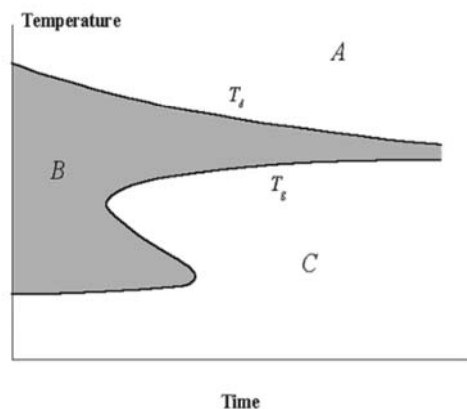


Figure 6.3.10. T-T diagram of curing. T_d – line of thermal degradation; T_g – line of the glass transition. A – domain of thermal degradation; B (shadowed zone) – domain of curing; C – domain of solid state. [Adapted, by permission, from J.K. Gillham, *Polym. Eng. Sci.*, **19**, 676 (1979)].

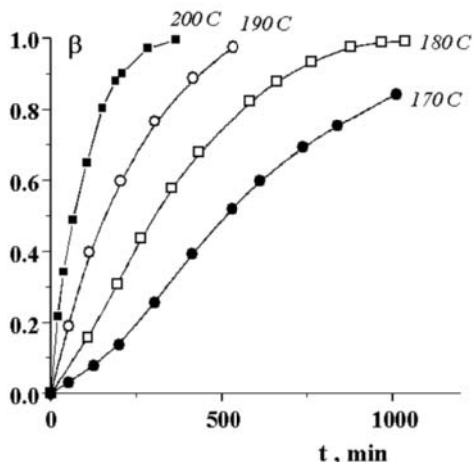


Figure 6.3.11. Kinetics of curing of an epoxy silicone organic oligomer at different temperatures. [Adapted, by permission, from S.G. Kulichikhin, P.A. Astakhov, Yu.P. Chernov, V.A. Kozhina, L.I. Golubenkoba, A.Ya. Malkin, *Vysokomol. Soedin. (Polymers – in Russian)*, **28A**, 2115 (1986)].

Diagrams such as those presented in Fig. 6.3.10 can be constructed for different curing systems, and they are the basis for selection of technological parameters of curing.

Rheokinetic curves for the $G'(t)$ dependence are different for various ranges of the T-T-T diagram. If curing takes place along line a, as in Fig. 6.3.9, the final equivalent state of material is reached at various temperatures, and this state is characterized by the limiting (or equilibrium) value of modulus, G'_∞ , which in practice does not depend on temperature or frequency. Then, it is reasonable to determine the degree of transformation, β , in the following way:

$$\beta(t) = \frac{G'(t) - G'_0}{G'_\infty - G'_0} \quad [6.3.9]$$

where $G'(t)$ are current values of elastic modulus and G'_0 is its initial value. In fact, in all cases $G'_0 \ll G'_\infty$ and therefore the following equation is valid:

$$\beta(t) = \frac{G'(t)}{G'_\infty} \quad [6.3.10]$$

An example illustrating experimental results of curing of oligomer from liquid through rubbery state is shown in Fig. 6.3.11. The curve for the lowest temperature also reaches the limiting value $\beta = 1$, though this part of the curve is not shown in this figure because it corresponds to time as long as 10^4 min.

Incomplete curing is shown in Fig. 6.3.12. In this case, the limiting values of elastic modulus are different at various temperatures because they relate to different degrees of transformations. Eq. 6.3.10 can be used in this case too, if G'_∞ is treated as the limiting

value of modulus at the highest temperature, which is supposed to be above the glass transition line. The form of all curves is analogous to those shown in Fig. 6.3.12, but the ordinate axis are limited to 1. Practical application of results of curing analysis and comparison of different materials and conditions of curing are based on fitting equations for rheokinetic curves. A general equation for kinetics, obtained by treatment of the results of calorimetric studies of curing, can be written in the following form:⁵⁴

$$\dot{\beta} = (k_1 + k_2\beta^m)(1 - \beta)^n \quad [6.3.11]$$

or

$$\dot{\beta} = k_0(1 - \beta)^n(1 + C\beta^m) \quad [6.3.12]$$

where k_0 , k_1 , k_2 , m , n , and C are empirical parameters.

The particular cases of these equations are of interest. If $C = 0$, it means that the kinetics of curing is described by the standard n^{th} -order equation (for example, $n = 1$ corresponds to the first-order kinetics, $n = 2$ to the second-order kinetics, and so on). If $C > 0$, it shows that the kinetic equation reflects the effect of self-acceleration.

The same equations were applied to the kinetics of curing, and many constants are necessary for fitting experimental data. For complete curing curves, as in Fig. 6.3.11, the kinetic equation of self-acceleration type can be written as:

$$\dot{\beta} = k_0(1 - \beta)^n(1 + C\beta) \quad [6.3.13]$$

and practically all experimental data can be described using $n = 1$ or $n = 2$. In this case, the constant k_0 is the initial rate of curing process, and C reflects the effect of acceleration, regardless of the chemical mechanism of this phenomenon.

Incomplete curing, as in Fig. 6.3.12, requires introduction of a special term into the kinetic equation which reflects this effect. A convenient rheokinetic equation for incomplete curing can be written as

$$\dot{\beta} = k_0(1 - \beta)^n(1 + C\beta)(1 - \zeta\beta) \quad [6.3.14]$$

where $n = 1$ or 2 . The new factor ζ reflects the effect of limited curing. At $t \rightarrow \infty$, the limiting degree of curing $\beta_{\text{lim}} = \zeta^{-1}$ is reached.

Though standard frequency of 1 Hz is mainly used for rheokinetic monitoring of curing reactions by measuring G' as a function of time, the measurements can be carried out at different frequencies as well. It is difficult to compare results obtained at different frequencies, because the sample is changing during measurements. This methodological problem can be solved by the mechanical Fourier transform spectroscopy (MFTS) method, when several frequencies are superimposed and the output signal is analyzed by using the Fourier series.⁵⁵ This shows that measuring at different frequencies gives non-identical results. Evolution of different relaxation modes during oligomer curing may also be examined.

Rheokinetic studies of curing processes (in different versions of instruments) are widely applied in the technology of oligomers for the following purposes:

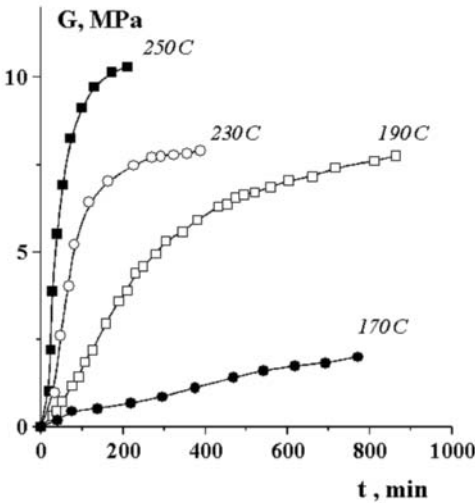


Figure 6.3.12. Kinetics of curing of phenylmethylsiloxane oligomer at different temperatures. [Adapted, by permission, from S.G. Kulichikhin, G.I. Shuvalova, V.A. Kozhina, Yu.P. Chernov, A.Ya. Malkin. *Vysokomol. Soedin.* (in Russian), **28**, 497 (1986)].

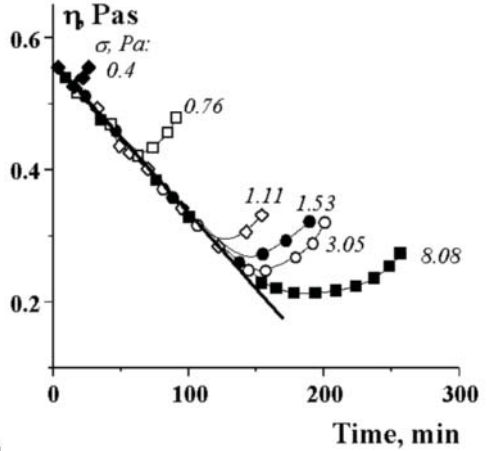


Figure 6.3.13. Viscosity evolution in conversion of polyvinylacetate to polyvinylalcohol in homogeneous (decreasing thick solid line) and heterogeneous (increasing parts of curves) domains. The influence of shear stress on transition to the heterophase system is shown. The reaction takes place in 20% solution in ethanol at 20°C. [Adapted, with permission, from A.Ya. Malkin, S.G. Kulichikhin, V.A. Kozhina, Z.D. Abenova, *Vysokomol. Soedin.* (Polymers – in Russian), **28B**, 408 (1986)].

- selection of the optimal technological regimes (time-temperature evolution) for compositions of practical interest
- estimation and control of product quality
- qualitative comparison of different materials
- solving boundary problems in modeling different technological processes.

6.3.4 INTERMOLECULAR TRANSFORMATIONS

6.3.4.1 Polymeric reaction

Polymer-polymer transformations (chemical reactions occurring in side groups of a macromolecular chain) is a natural part of chemical technology. Transformations of such kind are easily detected with rheokinetic methods because changes in chain structure lead to changes of its rigidity (flexibility) and, thus, of rheological properties of material. Rheological measurements permit detection of phase transitions caused by chemical transformations. Shearing influences the phase state of the system and thus the kinetics of transformations.

Both situations – polymer-polymer transformations in a homogeneous state and influence of shear stress on this transformation due to transition to the heterogeneous state – are presented in Fig. 6.3.13, showing results of rheokinetic studies of polyvinylacetate conversion to polyvinylalcohol induced by sulfuric acid. The descending (linear) branch of dependence corresponds to a homophase reaction and viscosity decrease accompanies polymer-polymer reactions. Superposition of shearing leads to phase transition and the reaction reaches a heterogeneous domain.

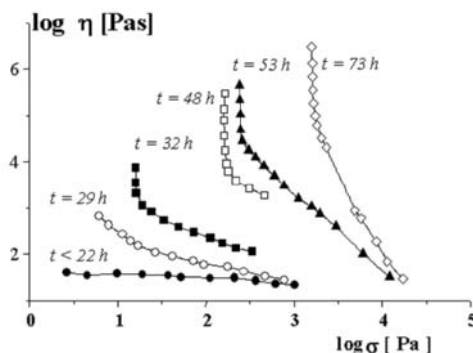


Figure 6.3.14. Solution-to-gel transition: evolution of rheological properties as a result of gelation process of a 12% solution of polysulfone in dimethylacetamide with 6% of water at $T = 22^\circ\text{C}$. [Adapted, with permission, from A.Ya. Malkin, L.P. Braverman, E.P. Plotnikova, V.G. Kulichikhin, *Vysokomol. Soedin.* (Polymers – in Russian), **18A**, 2596 (1976)].

Rheokinetic study is a convenient and sensitive method of monitoring chemical reactions of polymer chains.⁵⁶

6.3.4.2 Physical transformations

Changes in material state can be caused by slow physical processes (“aging”), such as crystallization and formation of intermolecular physical bonds. Any of these processes are reflected in changes of rheological properties of material. Rheological measurements are useful instruments of monitoring the state of material and estimating its technological quality. There are numerous materials for which these processes are of practical importance. Fig. 6.3.14 shows a characteristic example. Aging causes transition from fluid, through viscoplastic media (with a clearly expressed yield point), to a rubbery gel-like material.

6.4 SOLUTION OF DYNAMIC PROBLEMS

6.4.1 GENERAL FORMULATION

The previous parts of the book were devoted to description of material properties “at a point”, i.e., establishing relationships between local stresses and deformation rates related to a point. The central problem in measuring these properties (Chapter 5) was the transition from measured macro-values (forces, torques, velocities) to the relationships between local tensors related to dynamic and kinematic values. For solving any applied problems of movement of a rheologically-complex medium, the inverse problem must be solved – this is a transition from rheological properties measured in the laboratory to prediction of material behavior in a real technological practice.⁵⁷

The general formulation of this problem is: rheological properties of material are known (measured) – how then to find the relationship between forces and velocities for an arbitrary geometry of deformation (flow)? The answer to this question is represented by the scheme in Fig. 6.4.1.

The first line in this scheme is evident: it is relationships between stresses and deformations (and deformation rates) measured in different simple schemes of flow. Methods of measurements were discussed in Chapter 5 and numerous results of such measurements were presented in different parts of the book, mainly as dependencies of the shear stress on shear rates, as well as the elongational stress on uniaxial deformation rate.

The left side of the second line in Fig. 6.4.1 is the fitting of experimental data by a suitable empirical or theoretically-based equation. Experimental data are usually obtained in one-dimensional flow conditions in order to simplify their treatment. Then it is necessary to choose a method of their generalization for three-dimensional, 3D, deformations because flow in a real processing environment takes place in 3D space. This general equation is called a *rheological equation of state* or *constitutive equation* (or a *rheological*

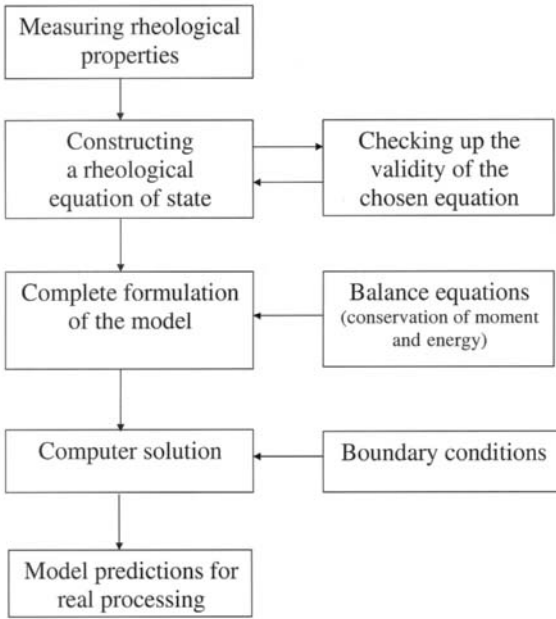


Figure 6.4.1. General scheme illustrating the method of solving applied dynamic problems.

(as discussed in Chapter 1). The principal point is that the methods of such presentations are ambiguous and it is possible to do it in different manner. This leads to different rheological equations of state for the same initial experimental data. Consequently, the predictions of different rheological equations of state might appear different for a new dynamic or kinematic situation. The right side of the second line shows that it is necessary to confirm that at least in some new experimental situations a generalized rheological equation of state gives reliable predictions of material behavior.

There are several general rules (or principles) which must be fulfilled in formulation of a rheological equation of state:⁵⁸

- *Principle of coordinate invariance* requires that formulation of the rheological equation of state does not depend on choice of a coordinate system while inertial systems are used. This requirement is realized by formulation of any relationship between stress and deformation tensors *via* their invariants.
- *Principle of determinism* means that the stress state of material points can depend on prehistory of its deformation but does not “feel” or forecast what will happen in the future. In fact, this principle is cast into the theory of viscoelasticity where previous history of material is expressed *via* integrals with fading memory.
- *Principle of local action* supposes that only the closest neighboring points can influence the stress state at some chosen points. This principle denies the possibility of a long-distance action, though in some cases long-distance forces can exist but they are not of mechanical origin.

model) and initial experimental data enter this equation as a particular case.

Therefore, a crucial step is listed on the right side of the second line. This is the checking of a chosen rheological equation of state for conditions quite different than the initial experimental scheme used for measuring stress vs. deformation rate relationship.

For example, initial data are shear stress vs. shear rate. These data are fitted by one of the equations discussed in section 3.3. Can one use this equation for prediction of material behavior in uniaxial extension? To answer this question it is necessary to write the fitting equation in 3D form using ideas of continuum mechanics in order to receive an invariant presentation of experimental data

- *Principle of material objectivity* expresses the idea that behavior of material must be written in such a way that it would be independent of any motion of an observer, and in particular, of movement and rotation of a rigid body as a whole.⁵⁹ Based on this principle it is necessary to use some complicated laws to coordinate transformation and objective tensors of deformations such as the Rivlin-Eriksen and the White-Metzner tensors mentioned in section 1.3.1.

Solution of boundary problems, which is the final goal of modeling any technological process, begins with complete formulation of a system of equations describing this process. The central step here is a complete formulation of the model (left side of the third line in Fig. 6.4.1). This is based on combining a rheological equation of state with balance (or conservation) equations (the right side of the third line in Fig. 6.4.1). The latter are the general laws of nature. Three of them are of interest for the problem under discussion.

Conservation of momentum

This are equations formulating the conditions of equilibrium of all forces acting at a point. They were written in section 1.1.6 as a system of Eqs. 1.1.18 and in a simplified form as Eqs. 1.1.19. They can be written in different coordinate systems, for example, in cylindrical coordinates (see Eqs. 1.1.20). The equations for conservation of momentum are written in components of stress tensor, which are 6 unknown variable values.

Conservation of mass

This equation expresses the concept of constancy of mass. If we consider the flux of mass entering an elementary unit volume (i.e., at a point) and leaving the same volume and assuming that media is incompressible, then mass of material inside this volume must be constant. This concept leads to the following balance equation:

$$\frac{\partial v_1}{\partial x_1} + \frac{\partial v_2}{\partial x_2} + \frac{\partial v_3}{\partial x_3} = 0 \quad [6.4.1]$$

where the notation of velocity components, v_i , and axes, x_i , is related to the Cartesian coordinate system.

Conservation of energy

This is also a fundamental law of nature expressing the following concept: changes of energy inside some volume of space can happen, due to heat flux into this volume and heat dissipation inside this volume as a result of viscous flow (which is dissipative by its nature). In some cases, it is necessary to take into account the heat of phase transitions or reactions taking place in this volume. Sources of energy other than heat flux are usually not taken into consideration in formulating dynamic problems. Heat flux is possible due to existence of temperature gradients. That is why the equation of conservation of energy is formulated for temperature, T .

Balance of heat fluxes in relation to a unit space volume leads to the following equation written in the Cartesian coordinate system:

$$\frac{\partial T}{\partial t} + v_1 \frac{\partial T}{\partial x_1} + v_2 \frac{\partial T}{\partial x_2} + v_3 \frac{\partial T}{\partial x_3} = a \left(\frac{\partial^2 T}{\partial x_1^2} + \frac{\partial^2 T}{\partial x_2^2} + \frac{\partial^2 T}{\partial x_3^2} \right) + \frac{W}{\rho c_p} \quad [6.4.2]$$

where v_i are the components of velocity vector, a is the thermal diffusivity, ρ is density and c_p is the thermal capacity. The coefficients a , c_p , and ρ as well as viscosity are (potentially temperature-dependent) properties of matter.

The value, W , entering this equation is an intensity of energy dissipation. This value is the work required to sustain flow. For a viscous fluid, it is expressed as the product of stresses and deformation rates:

$$W = \sum_{i,j} \sigma_{ij} D_{ij} \quad [6.4.3]$$

where D_{ij} are components of the deformation rate tensor and σ_{ij} are components of stress tensor. It is evident that W is an invariant value (in respect to the choice of a coordinate system).

Based on the above concepts, it is possible to formulate a flow model for material under discussion. Two main possibilities exist: to consider flow of a time-independent or a time-dependent media. Then, it is possible to move to the fourth line of the scheme in Fig. 6.4.1.

Solution of a system of equations describing movement of a medium with known rheological properties is possible if boundary conditions are formulated. In fact, just these conditions specify peculiarities of flow in any arbitrary geometry, either through channels of a certain form or around solid bodies. Equations describing flow of rheologically complex liquids are very complex and only the simplest cases can be treated as analytical functions. At present, there are no principal difficulties in solving any correctly formulated boundary problem using modern computer techniques and developed computational methods. That is why the fourth line in the scheme of Fig. 6.4.1 supposes that only technical difficulties can appear in modeling any real technological (processing) situation.

The solution of any concrete boundary problem gives quantitative model predictions of material behavior in a real processing operation. And this is the bottom line in Fig. 6.4.1, which is the final goal of application of rheological methods for engineering design and operation.

It means that starting from rheological experiments it is possible to forecast all technological parameters of a process, such as dependence of output on force, stress and temperature fields, and so on, up to discussing (based on the obtained numerical solution) the influence of variation of initial technological factors (composition, initial temperature, etc.) and boundaries of stability of real technological process.

Measuring rheological properties of different materials is a basis for engineering rheology, which is used for designing technological equipment and predicting processing characteristics of various real materials.

Engineering practice encounters two main types of flow: flow through tubes under applied pressure ("*pumping*") and flow caused by movement of a solid boundary surface ("*drag*" flow). The latter case can be caused by flow produced by rotation of screw, calibrating rolls, brush spreading paint, rotor inside a mixer, and so on.

6.4.2 FLOW THROUGH TUBES

This is an important engineering problem, which models many real situations in transportation of rheologically complex liquids. The prime goal of calculations consists in establishing a relationship between pressure gradient in a tube (or pipe) and output. This

scheme is a good approximation of some other more complex situations encountered in processing equipment.

The simplest case is flow through a tube of a circular cross-section.

The output, Q , vs. pressure, p , dependence is calculated based on the analytical presentation of a flow curve.

Some of the most important cases are considered below.

In the simplest case of flow of Newtonian liquid with viscosity, η , the $Q(p)$ dependence is expressed by Poiseuille's well-known law:

$$Q = \frac{\pi R^4 p}{8\eta L} \quad [6.4.4]$$

where R and L are the capillary radius and length, respectively.

The Q vs. p dependence for a power-law type non-Newtonian liquid (see Eq. 3.3.4)⁶⁰ is expressed as

$$Q = \frac{\pi K R^{m+3}}{m+3} \left(\frac{p}{2L} \right)^m \quad [6.4.5]$$

This equation can be rewritten as

$$Q = K_f p^m \quad [6.4.5a]$$

The last equation shows that for power-law liquid, Q is proportional to p^m , where m is the same exponent as in rheological law and K_f is a form- or geometrical-factor. Then it is possible to think that for channels with an arbitrary cross-section this relationship is also correct with its own value of a geometrical (front) factor depending on the form of a cross-section of channel.

The Q vs. p dependence in flow of a viscoplastic Bingham-type medium (see Eq. 3.3.9) through a cylindrical channel is expressed by the Buckingham-Reiner equation (see solution of Problem 3-9):

$$Q = \frac{\pi R^4 p}{8\eta_p L} \left[1 - \frac{8L\sigma_Y}{3pR} + \frac{1}{3} \left(\frac{2L\sigma_Y}{pR} \right)^4 \right] \quad [6.4.6]$$

where the rheological constants η_p and σ_Y are the same as in Eq. 3.3.7.

This equation can also be presented in the following equivalent form:

$$Q = \frac{\pi R^3 \sigma_R}{4\eta_p} \left[1 - \frac{4}{3} \left(\frac{\sigma_Y}{\sigma_R} \right) + \frac{1}{3} \left(\frac{\sigma_Y}{\sigma_R} \right)^4 \right] \quad [6.4.6a]$$

Transport characteristics for practically important case of flow of the Hershel-Bulkley viscoplastic medium is written as:

$$Q = \frac{n\pi R^3}{K^{1/n} \sigma_R^3} (\sigma_R - \sigma_Y)^{(1+n)/n} \left[\frac{(\sigma_R - \sigma_Y)^2}{1+3n} + \frac{2\sigma_Y(\sigma_R - \sigma_Y)}{1+2n} + \frac{\sigma_Y^2}{1+n} \right] \quad [6.4.7]$$

where σ_R is the shear stress at wall which is expressed in usual manner as $\sigma_R = pR/2L$ and σ_y , K and n are rheological constants, as in Eq. 3.3.9.

The above-written relationships are useful engineering equations for designing transport pipe systems, as well as channels in technological (processing) equipment.

However, there are the following limitations in applying these equations:

- they are written for steady flow in long tubes; therefore they are not correct for designing dies (for example, for channels with length-to-diameter ratio of order of 1), especially in flow of viscoelastic liquids; in the latter case the dominant role in resistance belongs to an elastic response
- time effects of thixotropic or rheokinetic nature might be important in the flow of some materials; these effects are not taken into consideration in formulation of the above-written equations.

These situations must be treated using more complicated equations constructed for special time-dependent materials.

Solution of dynamic problems of flow through a channel of an arbitrary cross-section is achieved by introducing the form-factor characterizing the geometrical form of cross-section. For Newtonian liquid, the basic linear relationship is given by Eq. 5.2.13 which is written as

$$Q = \frac{K}{\eta} p \quad [6.4.8]$$

Analytical method of finding constant K consists of rigorous solution of the dynamic problem of flow through a channel with arbitrary cross-section. The channel can be rectangular, elliptic, or have any other cross-section. For channels with complicated geometry, the solution is found by numerical methods.

Examples – form-factors for different cross-sections

Some important examples of the following geometries will be discussed:

- Flow through an elliptic channel with semi-axis a and b
- Flow through a flat channel. In this case, a channel is formed by two parallel flat plates; the gap, $2h$, between them is much smaller than their width $b \gg h$
- Flow through a circular channel formed by two co-axial cylinders along their axis; the radius of the outer cylinder is R_o and of the inner cylinder is R_i .
- Flow through a channel with a cross-section having a form of equilateral triangle with the length of a side a .

In all mentioned cases, the values of the form-factor can be calculated analytically. These values are listed below.

Cross-section	Form-factor, K
Round	$K = \frac{\pi R^4}{8L}$
Elliptic	$K = \frac{\pi}{4L} \frac{a^3 b^3}{a^2 + b^2}$
Flat	$K = \frac{2bh^3}{3L}$
Annular	$K = \frac{\pi}{8L} \left[(R_o^4 - R_i^4) - \frac{(R_o^2 - R_i^2)^2}{\ln R_o/R_i} \right]$

$$\text{Equilateral triangle} \quad K = \frac{\sqrt{3} a^4}{32\pi L}$$

Modern computer technique permits calculation of form-factor for channels with any arbitrary cross-section. An experimental approach for finding the form-factor is based in measuring Q–P pair of values for liquid of known viscosity. Then the form-factor is found using Eq. 6.4.8.

Tube flow of non-Newtonian liquid is more complex because there is no unique analytical solution for Q(p) dependence analogous to linear dependence for Newtonian liquid and analytical equations for this dependence cannot be presented using a single geometrical factor. However, there is a general solution for calculating the tube characteristic of any non-Newtonian liquid, for which a flow curve has been measured. This is known as the *Rabinowitch-Weissenberg equation* (see Chapter 5, Eq. 5.2.15). This equation can be written as

$$Q = \frac{\pi R^3}{\sigma_R^3} \int_0^{\sigma_R} \sigma^2 f(\sigma) d\sigma \quad [6.4.9]$$

where $\sigma_R = pR/2L$ is the shear stress at a wall, and it is also normalized pressure, and $f(\sigma)$ is the flow curve, i.e., dependence of shear rate and shear stress measured in a laboratory test. If $f(\sigma)$ has been measured, Q(p) dependence can be easily calculated from Eq. 6.4.9.

Function $f(\sigma)$ can be expressed by several appropriate equations. The choice of fitting method to describe function $f(\sigma)$ is an important problem in engineering rheology. An experimenter usually tries to fit experimental points as accurate as possible, sometimes using multi-constant equations for this purpose. However, it is not necessary in any case. As an example, Fig. 6.4.2a presents experimental points obtained for super-concentrated water-in-oil emulsion.⁶¹ These points can be successfully fitted using the Cross-type equation:

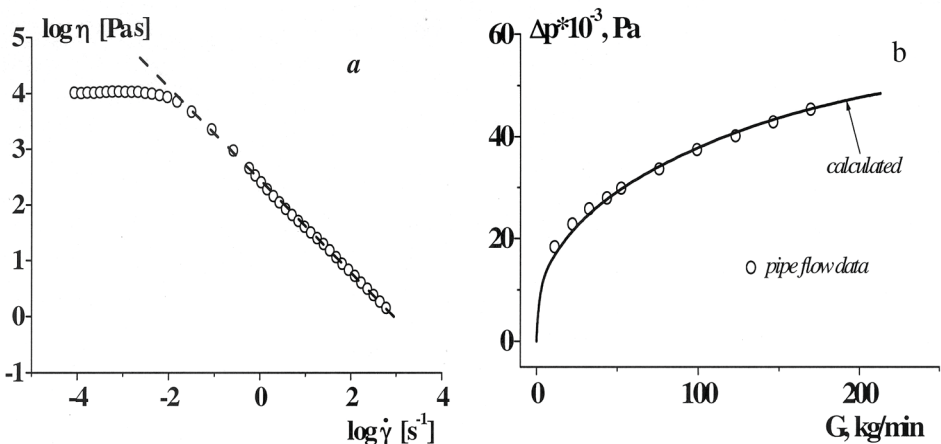


Figure 6.4.2. Flow curve of emulsion (a) and transport characteristic of a tube (b) calculated using power-law approximation of the flow curve. Average diameter of dispersed particles is 8.2 μm . 30°C. [Adapted, with permission, from A.Ya. Malkin, I. Masalova, D. Pavlovski P. Slatter, *Appl. Rheol.*, (2004)].

$$\eta = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^n} \quad [6.4.10]$$

which is a simplified form of the Cross equation, Eq. 3.3.1.

The flow curve in Fig. 6.4.2a comprises the clearly expressed domain of Newtonian flow at low shear stresses and therefore equations with yield stress are not appropriate for this flow curve.

Eq. 6.4.10 can be used for predicting Q-vs.-p dependence for tube flow and undoubtedly this approach gives good results. The high-shear-rate part of the flow curve can be described by a power-law equation, Eq. 3.3.4, as well as the Hershel-Bulkley equation, Eq. 3.3.9. The straight line in Fig. 6.4.2a gives power-law approximation. This type of fitting does not express properly a low stress domain. Fig. 6.4.2b presents Q-vs.-p predictions based on power law approximation calculated from Eq. 6.4.5. Points in this figure are experimental data. Power-law type approximation gives accurate predictions (maximum error does not exceed 2.3%). Similar results were obtained when the Hershel-Bulkley approximation was used.

This result, as well as some other results obtained for different materials,⁶² is explained by the fact that flow rates in real industrial transportation processes are high and high-shear-rate domain of flow curves determines the total output. It is true in numerous cases because industrial engineers are interested in increasing transportation rates. However, many cases can also be pointed out in which behavior of liquid in low-shear-rate domain controls process, e.g., deformation of greases in bearings. In such cases, freedom in the choice of fitting equation becomes invalid.

The choice of analytical approximation of laboratory measured rheological properties should be made based on goals of applications, though in many cases there is no need for “exact” fitting of points obtained in rheological experiment.

In discussion of engineering problems of tube transportation, it is necessary to take into account the following limitations of the above written equations:

- these equations are correct for steady flow through a long channel
- instabilities of various types may appear at high enough flow rates
- normal stresses in shear flow lead to circular fluxes in cross-sections of non-round channels. These fluxes do not give a large input into total energy consumption but can influence mixing processes and quality of final products.

6.4.3 FLOW IN TECHNOLOGICAL EQUIPMENT

These are primarily *drag flows*, i.e., flows caused by movement of solid boundary surfaces in technological equipment.

6.4.3.1 Pumping screw

The complete theory of pumping screw machines (*extruders*) is not a subject of this book.⁶³ Here, only basic concepts related to rheology of pumping materials are discussed.

The general engineering problem in designing a pumping screw extruder consists of establishing the relationship between the speed of screw rotation, power consumption, and output for equipment of known size, temperature regime of processing, and measured properties of material. Rheological properties of material are essential and necessary parts of analysis.

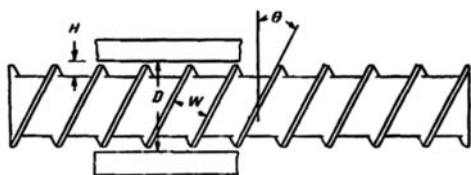


Figure 6.4.3. Screw. Geometrical parameters: D – diameter of barrel; W – distance between the neighboring flights; H – depth of channel; θ – helix angle (flight inclination).

A pumping screw is often used in different technological processes. In particular, various extrusion machines are widely used in polymer technology and transportation devices.

Schematic diagram of a screw is shown in Fig. 6.4.3. Flow takes place in a narrow space between the body of the screw and a cylindrical barrel. Let us imagine that this channel is not cylindrical but transformed into a flat rectangular channel with a width, W , (equal to distance between neighboring flights of screw) and height, H , (distance between a body of screw and a barrel). This operation is correct if it is possible to neglect the curvature of channel, which is acceptable if $H \ll D$. The most important point is the source of liquid flow in a channel. This is relative movement of the upper side (“roof”) of the channel, assuming that the channel is stationary. The velocity of movement has two components – along the channel V_z and in transverse direction due to inclination of the flight with an angle, θ . The velocity component, V_z , provides the output while the transverse component leads to circulation of liquid inside the channel and it is responsible for the mixing effect.

Dynamics of flow in the channel of a screw pump is described by balance equations and a rheological equation of state of liquid. Pumping screw extruders are usually used for plastic processing, and in this case the theory⁶⁴ is based on a power-type viscosity law.

A more complete theory of flow in a pumping screw extruder includes the following important additional details.

Flow in a channel creates a longitudinal pressure gradient; so the pressure gradient exists between neighboring sides of flight. Therefore, a back (leakage) flow in a gap between a flight and a barrel emerges and the negative input of this back flow into total output can be essential. The gap is narrow and non-Newtonian effects in flow through these gaps are pronounced.

Typically, flowing liquid is highly viscous, therefore it is necessary to take into account a dissipative effect. Temperature of barrel is different than that of liquid. It means that it is necessary to consider the process as non-isothermal with thermal exchange between walls of the channel and the flowing liquid.

The complete theory of processes in a *plasticating extruder* must also consider that material enters the channel in a solid form and movement of solid particles and their melting are inherent components of the technological process.

Pumping of plastic melts proceeds, not into empty space but into a die, which forms the shape of the article (profiles of various types – films, tubes, sheets, and so on). The die plays a role of hydrodynamic resistance; therefore, pressure at the end of the screw exits, and under this pressure the back-flow occurs. As a result, a real flow consists of superposition of two fluxes – drag flow produced by the screw and backpressure flow.

This is the most important feature of pumping extruders. Due to superposition of two fluxes the total output, Q , can be (at the first approximation) written as

$$Q = AN - Bp^m \quad [6.4.11]$$

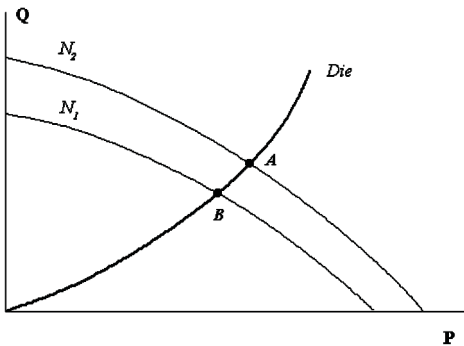


Figure 6.4.4. Performance characteristics of an extruder with a die.

N_2 , express Eq. 6.4.11 for two speeds of rotation ($N_1 < N_2$) and the curve “Die” expresses Eq. 6.4.5a. Points designated as A and B are two pairs of real values of output and pressure (operating points) at two different speeds of screw rotation.

Curves are obtained from measuring rheological (and other physical) characteristics of material. Solution of the problem, including all factors listed above and a full set of balance equations, is very complicated, though it can be realized using modern computation techniques. In fact, there is available standard software which permits calculation of necessary parameters of an extruder based on its characteristics as well as rheological and other physical properties of material used in technological process.

Screw extruders are also used as primary transportation machines, especially for concentrated suspensions (clay suspensions, mud, and so on). For this field of application – in contrast to polymer technology – a rheological equation of state must include yield stress. A power-law type equation is not suitable. However, in this case non-isothermal effects and die pressure might be immaterial. But a complete theory of screw pumping is expected to take into consideration the effect of jamming at high concentrations and high rates of rotation, as was described in section 6.2.6.

Screw extruders can be used as mixing devices. In this case, the main factor is the transverse flow in channel cross-sections and relative movement of layers of different materials. Rheological properties of both components play a dominating role in the mixing process and in formulation of process theory.

The extrusion process includes an important final stage: melt leaves a calibrating die and appears in a free space. The crucial point here is a change of shape of an extruded profile due to elastic forces stored during flow inside calibrating channels of the die. This is a *swelling effect*, which was discussed in section 3.4.4. It is rather simple to measure die swell after flow through a channel with a round cross-section. In real technological practice the extruded profiles are very often asymmetrical. Even if the profile is axisymmetric but not round, for example, in producing square cross-section profiles, there is no guarantee that the profile of the item is the same (square) as the cross-section of the die. The final profile is distorted in comparison with the profile of the die. In particular, it is very difficult to maintain sharp corners of the profile.

where A and B are constants, N is the rotational speed of the screw and m is an exponent in a power-law equation describing rheological properties of liquid.

The real performance characteristics of an extruder in pumping polymer melts reflects two dependencies: performance characteristics of the screw as presented, for example, by Eq. 6.4.11, and resistance of die, as expressed, for example, by Eq. 6.4.5a. Combination of these dependencies results in real performance of an extruder (operating point). This concept is illustrated in Fig. 6.4.4 in which two curves, N_1 and

Calculation of profile evolution after leaving a forming (calibrating) die is a purely rheological problem.

There are two main mechanisms of die swell under isothermal conditions:

- velocity profile rearrangement observed for any liquid; this is a kinematic effect and its value is close to 1.12-1.13 for axisymmetric flow
- elastic unconstrained recovery; its value can be large and this effect is directly related to stored elastic energy in the flow of viscoelastic materials, as was discussed in Chapter 4 for rubbery solids; this mechanism dominates polymer solutions and melts.

The majority of theoretical models of flow in extruder channels are based on nonlinear flow curve only and do not take into account viscoelastic effects. It is incorrect in calculations related to die swell because viscoelasticity and rubber elasticity are main causes of this effect. Therefore, the rheological model becomes very complicated, determination of its constants requires more advanced experimental approach, and practical calculations can be carried out only by computational techniques.⁶⁵ The progress in this field is limited and it is restricted to model calculations of simple geometrical forms.

6.4.3.2 Calendering and related processes

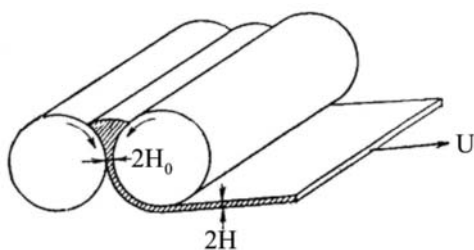


Figure 6.4.5. Calendering.

Schematic diagram of calendering is shown in Fig. 6.4.5. Drag is achieved by rotation of two rollers, frequently with different speeds. Rollers pull material into a gap. Material deforms and flows. The main technological result is a decrease in thickness of a sheet, though some other effects also take place, especially if the speed of rollers rotation is different:

- intensive shearing in a narrow gap is accompanied by a significant heat release; rollers can also be heated up to a higher temperature to increase temperature of material (*heating device*)
- calendered material is composed of many components; intensive shearing in a narrow gap provides good *mixing* of components; flow in an entrance zone is two-directional, which improves mixing
- stresses in the calendering process can be so high that they may cause rupture of molecular chains (*mechano-chemical effect*); roller mills are used to regulate rheological properties of material.

The central goal in the analysis of calendering is search for relationships between speed of roller rotation, output, power of drive that rotates rollers, and forces acting in the transverse direction and causing separation of rollers.

Theoretical analysis of the process is based on analysis of conservation (balance) equations and rheological properties of material.⁶⁶ The analysis of process involves dimensional arguments that are valid for any rheological model. The characteristic longitudinal length, L , (along x -axis in Fig. 6.4.6) is much higher than the characteristic length h in the y -direction, i.e., $h/L \ll 1$. In this approximation, the momentum balance equation can be written as

$$-\frac{\partial p}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} = 0 \quad [6.4.12]$$

Pressure p is assumed to be independent of y and it is a function of x , only: $p = p(x)$.

As a result, the following equation for stress distribution is valid for flow between rollers in the calendaring process

$$\sigma_{xy} = y \frac{dp}{dx} + C(x) \quad [6.4.13]$$

where $C(x)$ is some function of x determined from boundary conditions (on the roller surfaces).

The condition of mass conservation is also valid for any medium and it is formalized by equation

$$\int_{y_2}^{y_1} u(x) dy = Q = \text{const} \quad [6.4.14]$$

where y_1 and y_2 are coordinates corresponding to the roller surfaces, and u is velocity in the x -direction.

Rheology becomes of interest when Eq. 6.4.13 is used because rheological equation of state relates stresses and velocities. In the simplest case of Newtonian liquid with viscosity, η , the following relationship for velocity distribution is obtained:

$$u(y) = U_2 + (U_2 - U_1) \frac{y}{h} - \frac{1}{2\eta} \frac{dp}{dx} (h - y)y \quad [6.4.15]$$

where h is the distance between rollers (depending on x -coordinate).

Pressure distribution, $p(x)$, is found from the condition of constant output, which is calculated from Eq. 6.4.14 and is written as

$$Q = \frac{U_1 + U_2}{2} h - \frac{h^3}{12\eta} \frac{dp}{dx} \quad [6.4.16]$$

The force pushing rollers apart is calculated as the integral of pressure along the whole surface of rollers. The driving torque for rotating rollers is an integral of shear stresses acting at their surfaces.

A qualitative example illustrating evolution of velocity distribution and pressure along the path of material in a gap

between rollers is shown in Fig. 6.4.6. It shows characteristic features of process:

- forward and backward flux in any cross-section
- rapid development of pressure along the material path with its maximum at some cross-section.

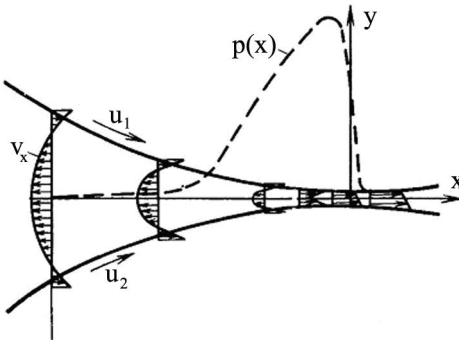


Figure 6.4.6. Velocity and pressure distribution in calendaring. U_1 and U_2 – circumferential velocities of rollers; V_x – velocity in the x -direction, p – pressure.

Extension of the calendering theory to flow of non-Newtonian liquids is made according to the same scheme as for Newtonian liquid, i.e., based on a balance equation with the introduction of an appropriate rheological law. In this case, calculations become more complicated and require application of numerical methods. Elasticity of rolled material is not involved in discussion, though this rheological property plays an important role. Also mixing in calendering does not have definitive solution.

6.4.3.3 Extension-based technologies

There is a group of technological processes in polymer processing based on the application of stretching. The process creates orientation of macromolecules and as a result increases the strength of material.

Fiber spinning is a typical example. It has the following peculiarities:

- deformation (flow and elastic strains) is primarily extensional and shear stresses are neglected
- fiber is strongly inhomogeneous along its length due to die swell at an outlet from die (spinneret) and due to decrease of cross-section of fiber caused by stretching
- flow is non-isothermal due to cooling of fiber until complete solidification (crystallization) of polymer; temperature is inhomogeneous along the radius of fiber due to slow heat exchange through polymer
- tendency to increase speed of spinning leads, in some cases, to various surface instabilities.

All these peculiarities make theoretical analysis of the fiber spinning process difficult and not directly related to a simple model discussed in section 3.7.⁶⁷

Schematic diagram of fiber spinning is shown in Fig. 6.4.7.

Some basic qualitative relationships related to fiber spinning are as follows. The stretching force is constant along the length of fiber and depends on normal stress, σ_E , according to the equation

$$F = \pi \sigma_E R^2 = \text{const} \quad [6.4.17]$$

Volume output, Q , is also constant along the length:

$$Q = \pi R^2 V = \text{const} \quad [6.4.18]$$

where V is the longitudinal velocity that is dependent on radius, R , changing along the length of stretching.

If material being stretched is Newtonian liquid and the Trouton law is valid, then the gradient of elongational velocity, dV/dx , is expressed as

$$\frac{dV}{dx} = \frac{FV}{3\eta Q} \quad [6.4.19]$$

At the starting point, at $x = 0$, $V = V_0$, and then the velocity profile along fiber is expressed as

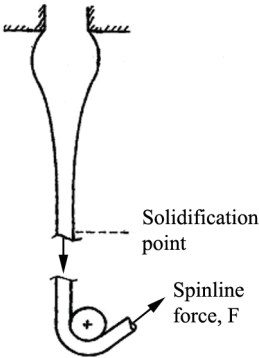


Figure 6.4.7. Schematic representation of the fiber spinning.

$$V = V_0 \exp\left(\frac{xF}{3\eta Q}\right) \quad [6.4.20]$$

The process of stretching is characterized by the value of *draw ratio*, DR, which equals V/V_0 , causing drawing along the length, L. Then, one can write

$$\frac{V}{V_0} = \exp\left(\frac{x}{L} \ln DR\right) \text{ and } \frac{R}{R_0} = \exp\left(-\frac{x}{2L} \ln DR\right) \quad [6.4.21]$$

The above relationships provide some parameters determining performance characteristics of the fiber spinning process. The Trouton law approximation is not good for real technological processes of fiber spinning. It is not reasonable to use any other flow curve equations, as is sometimes done. Rheological properties are modelled by calculation of drawing force as a function of the kinematics of spinning. The complete theory must take into account the transient character of deformations. It is necessary to use a rheological model for viscoelastic medium.

High rates of deformation in extension and importance of orientation effects (as a technological goal of spinning) suggest that deformations in spinning processes are elastic (rubbery). It means that the rheological behavior of material in spinning corresponds to zone III in Fig. 3.3.7, and it is preferable to search for a rheological equation of state from equations discussed in Chapter 4. The time factor can be excluded from rheological equation of state and material can be treated as rubbery but not as a viscoelastic medium.

Rheological approach has to be combined with kinetics of crystallization that proceeds under non-isothermal conditions. Crystalline phase influences constants of rheological equation of state and spinning process continues up to the line of crystallization (solidification) shown in Fig. 6.4.7. After that, material solidifies and its deformation is negligible in comparison with stretching along the distance from a die outlet to the solidification point.

The above physical description of the spinning process seems reasonable, though hitherto a model based on these rheological and kinetics arguments has not been developed.

In discussing the rheology of the fiber spinning process it is also necessary to remember about possible instability effects in high speed stretching (see section 3.5.7).

There are some other technological processes which are based primarily on extension of polymer materials in a rubbery state; that is:

- formation of blown films
- vacuum and/or pressure thermoforming of plates, trays, cups and analogous parts from sheets
- blowing of PET bottles from preform above the glass transition temperature of the polymer.

Technology of these processes is based on the same physical phenomena as fiber spinning, i.e., rheology of extension and kinetics of crystallization (or solidification for glassy materials).⁶⁸ However, in contrast to fiber spinning, bi-axial extension takes place. One invariant of rheological equations of state of rubbery material (as discussed in Chapter 4) supplemented with kinetics of phase transition can be a base for an engineering calculation model for these technological processes.

6.4.3.4 Molding technologies

Molding processes are the major periodic manufacturing operations in the polymer industry. An enormous amount of plastic, rubber, and thermoset parts, ranging from automobile bumpers to personal computers, refrigerator housings to bottles and tires, are produced by molding processes. The automotive, appliance, computer, beverage, tire, and other industries are associated with molding.

Rheology plays a very important role in molding processes. In particular, the shear rate and temperature dependence of viscosity determines the resistance to flow of polymer melts in dies and molds. As flow rate or output of process increases, higher shear rates and accordingly higher shear stresses are developed and higher forces and pressures are required to shape polymer products. The sensitivity of viscosity to variations in shear rate, characterized by the shear thinning effect, determines pressure increase during the mold filling process. This means that polymer melts exhibiting a lower power-law index and, therefore, more shear thinning, and show less increase in pressure with increase of flow rate during processing. Therefore, they will have lower energy consumption. On the other hand, polymer melts exhibiting higher temperature sensitivity of viscosity, i.e., higher activation energy of viscous flow, would cause a faster increase in pressures and forces required to carry out molding processes, which take place under fast cooling rates. Viscosity, and its shear rate and temperature dependence, determine whether a mold is fully filled or not.

Viscoelasticity of polymer melts has a significant influence on polymer molding and the performance of shaped products, especially with respect to a level of frozen-in molecular orientation introduced in them during cavity filling and packing stages and subsequent relaxation processes occurring upon the cooling stage of the molding cycle. In particular, polymer melts exhibiting a higher relaxation time would lead to a higher level of a frozen-in molecular orientation and residual flow stresses in final products. This strongly affects the performance characteristics of final products. Due to these effects, product properties become highly anisotropic. Depending on the type of products made, the molecular orientation effect may be beneficial or detrimental for product performance. For example, in the case of molding optical products, a higher level of molecular orientation introduces higher anisotropy of refractive index, leading to deterioration of their optical quality. In particular, this effect of the frozen-in orientation is well known in the case of injection molding of optical products, such as compact disks, CD, and DVD substrates, and various lenses. A high level of frozen-in birefringence or retardation causes distortion of laser light propagation through CD and DVD media, leading to a poor quality of reproduction of the sound of music and optical pictures. Therefore, very stringent specifications are established concerning the level of residual optical retardation in these molded products. It should also be noted that this optical retardation is strongly affected by process parameters during molding, as well as relaxation characteristics, such as the relaxation times and their distribution, and optical constants of polymer melts, such as the stress-optical and strain-optical coefficients.⁶⁹

Plastics molding is an industry of enormous volume and scope. There are many variations of molding technology.⁷⁰ These processes include compression, injection, injection-compression, co-injection, transfer, resin transfer, blow, rotational molding and thermo-

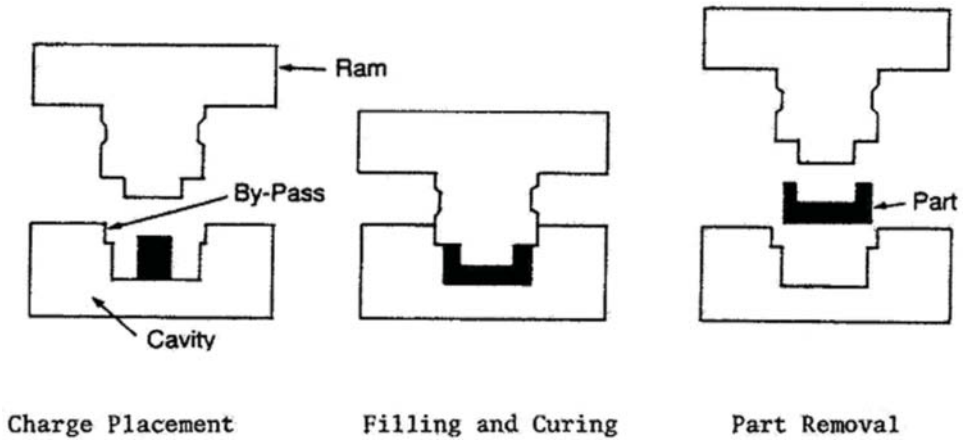


Figure 6.4.8. Schematic representation of the compression molding process.

forming. Here we briefly describe some of these processes with the aim of indicating rheological relevance to the calculation of flow kinematics and dynamics.

6.4.3.5 Compression molding

It is one of the oldest techniques of manufacturing rubber, thermoset and plastic products. Compression molding dates back to the origin of the rubber industry. For many years, this has been a standard technique for molding, but recently it has been replaced to some extent by injection molding. By comparison, injection molding offers advantages in material handling and ease of automation. However, compression molding retains a distinct advantage when processing fiber-reinforced polymers. Moderate flow during compression molding helps to avoid high stresses and strains; therefore, reinforcing fibers are not damaged by flow during mold filling. Thus, a high concentration of reinforcing fibers and long fibers can be incorporated into composite materials.

Compression molding involves pressing (squeezing) of deformable material charge between two halves of a heated mold to fill and cure material in mold, and subsequent part removal (Fig. 6.4.8). In manufacturing thermoset products, transformation of flowable material into a solid product under elevated mold temperature takes place. Compression molding temperatures range from 140 to 200°C. Mold pressures can vary from 20 to 700 bars and curing times can vary from 1 min for thin parts to over 1 hour for very thick rubber parts. Recently, development of thermoplastic matrix composites, to produce strong, lightweight structures, has increased interest in compression molding. In thermoplastic matrix composite molding, temperatures as high as 350°C are utilized.

Compression molding is carried out using compression molding presses. Two types of presses are used – down-stroking and up-stroking. Molds usually operate using a clamping ram or cylinder with clamping capacities ranging from a few tons to several thousand tons. In addition to the clamping capacity, two other characteristics of a press are: the daylight characterizing maximum platen separation, associated with stroke and the platen size ranging from a few centimeters to several meters. The temperature of platens is controlled by a built-in heating or cooling elements or by separate heaters.

There are five stages of compression molding process:

- material preparation
- prefill heating
- mold filling
- in-mold curing
- part removal.

Material preparation includes compounding resin with fillers, fibers and other ingredients or impregnating a reinforcing cloth or fibers with resin. This stage controls the rheology of material and the bonding between fibers and resin. The prefill heating stage is carried out to speed up the molding process. This stage can occur outside or inside the mold before the mold is closed and flow begins. Mold filling starts with material flow and ends when the mold is full. The effect of flow is critical for the quality and performance of the molded product. It controls orientation of fibers, which has a direct effect on the mechanical properties of the part. In processes involving lamination of the long fiber-reinforced composites, there is little flow since the initial charges almost completely conform to the mold. In the case of a thermoset matrix, some curing may occur during the mold-filling stage. The in-mold-curing stage follows mold filling. In this stage, the part is cured in the mold while the final stage of cure may be completed during post-cure heating after part removal. In-mold curing converts the polymer from a liquid to a solid having rigidity sufficient for removal from the mold. Part removal and cool-down are the final stages. This stage plays an important roll in warpage of the part and residual stress development, which arise due to difference in thermal expansion in different portions of the part. Temperature distribution and rate of cooling affect these residual stresses.

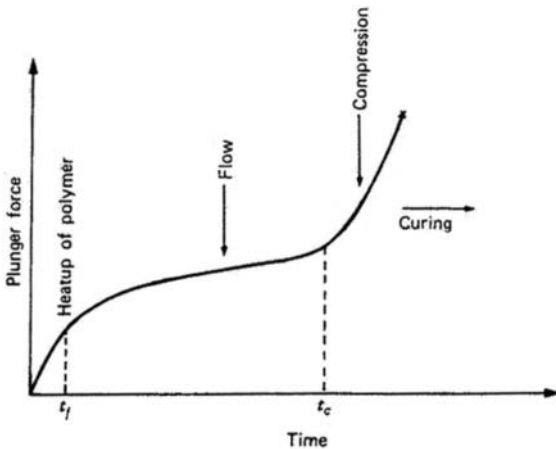


Figure 6.4.9. Schematic representation of the plunger force during compression molding at a constant mold closing speed.

Fig. 6.4.9 shows a typical curve of variation of plunger force required for mold closing as a function of time at a constant closing rate during molding of polymers not containing fibers. In the first region, at time $t < t_f$, corresponding to softening of material, the force increases rapidly as pre-form is squeezed and heated. At t_f , polymer in the molten state is forced to flow into the cavity and fill it. Filling is completed at t_c , corresponding to the initiation of curing. At this stage, compression of polymer melt occurs to compensate for the volume contraction due to curing.

To illustrate how the flow process can be described during compression molding, an idealized case of squeezing flow of a strip or disk blank is considered below. A *preform* in the form of a strip or disk is placed between parallel plates or disks.

Let us assume that in the case of a strip, fluid is confined between two sides in the width direction and the upper plate is moving toward the lower plate at a constant velocity, $\dot{h} = dh/dt$, such that fluid is squeezed and forced to flow to fill the mold in the length direction. The fluid is Newtonian and flow is laminar. The fluid adheres to the surface of the plates. The force required to fill the strip mold is

$$F = \frac{8\eta l^3 B \dot{h}}{h^3} \quad [6.4.22]$$

where η is fluid viscosity, l is the filling length, B is the width of mold, and h is the current separation of plates. This equation can be used to determine force as a function of the closing velocity. If the squeezing process takes place under the force, F , being constant, then Eq. 6.4.22 is converted to a nonlinear ordinary differential equation for an unknown function of $h(t)$.

Let us assume that fluid in the form of a disk is confined between two parallel disks. The upper disk is moving under a constant velocity of $\dot{h} = dh/dt$ such that fluid is squeezed to fill the disk mold. The force required to fill the disk mold is

$$F = \frac{3\pi\eta R^4 \dot{h}}{8h^3} \quad [6.4.23]$$

where R is a radius of the parallel disks.

This equation is known in literature as the *Stefan equation*, indicating how much force is required to fill a disk cavity. If the process of filling a disk mold takes place under a constant force, F , then Eq. 6.4.23 is transferred to a nonlinear differential equation for an unknown function of $h(t)$.

6.4.3.6 Injection molding

It is one of the most widely employed molding processes. Injection molding is used for the processing of thermoplastics, elastomers, thermosets, ceramics, and metals to articles of various complexities. The advantages of injection molding are high production rate, large volume manufacturing with little or no finishing operations, minimum scrap, and good dimensional tolerances.

Injection molding of thermoplastics includes automatic feeding of pellets into a hopper, melting, melt plasticizing, and feeding melt into an injection barrel at a temperature above the glass transition temperature, T_g , for amorphous polymers or melting point, T_m , for semi-crystalline polymers. The melt is then injected through a delivery system consisting of nozzle, sprue, runner system, and gate or gates into a mold having a temperature below T_g or T_m . The melt solidifies in the mold. Then, the mold is opened and the molded product is ejected.

Injection molding of elastomers includes automatic feeding of a preheated or plasticated rubber stock into an injection barrel at a temperature below the vulcanization temperature. Then, rubber is injected through a delivery system into a mold. The mold temperature is kept high enough to initiate vulcanization and subsequently vulcanize rubber inside the mold. After rubber has been vulcanized, the mold is opened and the molded part is ejected.

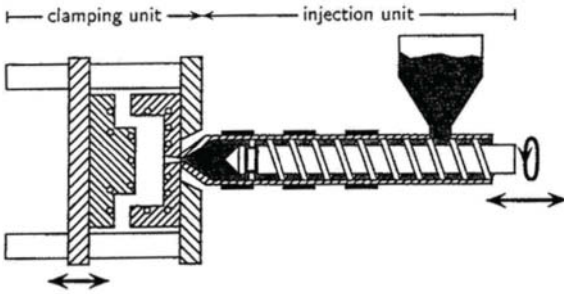


Figure 6.4.10. Schematic representation of the injection molding machine.

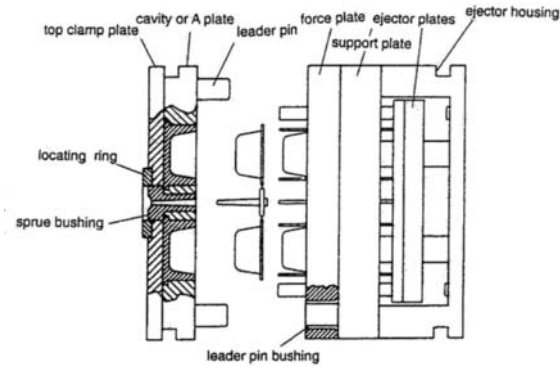


Figure 6.4.11. Schematic representation of a cold-runner, two-plate injection mold.

Injection molding of thermosets and reactive fluids, which are able to form infusible crosslinked structures by irreversible chemical reactions, is also carried out using a hot mold. Reaction injection molding is characterized by in-mold polymerization from monomeric or oligomeric liquid components by fast polymerization reaction. Thermosets are solid or highly viscous materials at ambient temperature. They are frequently highly filled.

An injection molding machine consists of a clamping unit containing mold and an injection unit for feeding, melting and metering thermoplastic material (Fig. 6.4.10). The most widely-used injection units utilize rotating screws to plasticize material. Rotation of the screw causes the plasticized material to accumulate in front of the screw, which is pushed back. The material is injected by forward motion of the

screw acting as a plunger, which pushes melt into the mold. The mold serves two functions: it imparts shape to the melt and cools the injection-molded part. The mold consists of cavities and cores and a base in which they are located (Fig. 6.4.11). The mold contains one or more cavities with stationary and moving mold halves. In many cases, molds may have multiple cavities. The latter is dictated by process economics.

The connection between runner and cavity is called a gate. In mold-making, the gate design is important. The size and the location of the gate are critical. The gate should allow the melt to fill the cavity and deliver additional melt to prevent shrinkage caused by cooling. The material in the gate should freeze at an appropriate time during the molding cycle. Premature freezing will cause an undesirable phenomenon called underpacking, leading to excessive shrinkage and sink marks. The mold also requires a cooling and/or heating system and venting to remove air during the cavity filling and rapid and uniform cooling. Venting is usually achieved by arranging small gaps in the parting line, which permit air to escape quickly. In some cases, forced removal of air is carried out by using vacuum venting. Mold cooling or heating is achieved by placing a number of channels in both halves of the mold through which cooling or heating liquid flows to remove heat from the melt or to add heat to the melt. Mold heating is also done by placing electric cartridge heaters in mold halves.

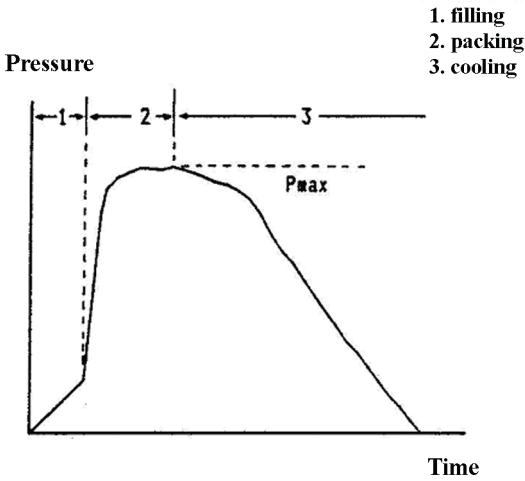


Figure 6.4.12. Schematic representation of the pressure-time curve during filing, packing and cooling stages of injection molding.

The injection molding cycle can be divided into three stages. These include cavity filling, packing (holding), and cooling. The three stages of the molding cycle can be easily seen from Fig. 6.4.12, indicating schematically the pressure variation with time. In the filling stage, the pressure rises as the melt propagates into the cavity. This stage is followed by the packing stage where a rapid increase (typically within 0.1 s) of pressure to its maximum is observed. Then, the cooling stage takes place at which pressure slowly decays.

Molding variables such as injection speed, melt and mold temperatures, packing or holding pressure, and length of the packing stage have a strong influence on pressure development and properties of moldings. Frozen-in molecular orientation, residual stresses, polymer degradation, shrinkage, warpage, and weld line strength are influenced by process variables. In injection molding of semi-crystalline polymers, the molding variables strongly affect crystallinity and microstructure development in moldings, which influence their performance characteristics.

A simple isothermal analysis of mold-filling process in cavities of simple geometries such as tubular and strip mold cavity is outlined below.

Consider a straight tubular mold of radius, R , and length, L . Melt is Newtonian fluid that is injected at a constant pressure or constant rate into the mold. The melt progresses along the mold until it reaches its end. We need to calculate the melt front position and the instantaneous flow rate when a constant pressure is imposed at the mold entrance or pressure as a function of time when a constant velocity is imposed during the molding process. The fluid is incompressible and isothermal under fully-developed flow. If constant pressure is imposed at the entrance of the tubular cavity, the penetration depth is

$$z(t) = \frac{R\sqrt{p_0 t}}{2\sqrt{\eta}} \quad [6.4.24]$$

where t is the filling time. It is seen that the penetration depth $z(t)$ is proportional to the radius R .

When a constant velocity is imposed during cavity filling process, the pressure required to fill mold is

$$p(t) = \frac{8\eta Q^2}{\pi^2 R^6} t \quad [6.4.25]$$

Pressure required to fill a tubular mold cavity is reciprocally proportional to its radius to the power of six.

For filling a strip cavity of thickness, h , under a constant injection pressure, p_0 , the penetration depth is

$$z(t) = \frac{h}{2} \sqrt{\frac{p_0 t}{3\eta}} \quad [6.4.26]$$

The penetration depth $z(t)$ is linearly proportional to the value of h .

For filling a strip cavity at a constant flow rate, the pressure variation with the filling time is

$$p(t) = \frac{12\eta Q^2}{B^2 h^4} t \quad [6.4.27]$$

The pressure varies linearly with the filling time and strongly depends on width, B , and the cavity thickness, h , being reciprocally proportional to the width to the power of two and to the thickness to the power of four.

The process of calculation of filling patterns occurring in real molding processes is more complicated than simple geometries and flow of Newtonian fluid under isothermal conditions discussed here. Molding processes are more complicated because of two- and three-dimensional flow of non-Newtonian viscoelastic fluid under non-isothermal conditions with solidification, crystallization, crosslinking occurring during processes. Various software is proposed for calculation of flow in molding processes based on rheological properties of materials and designs of machines and molds.

Movement of material during mold filling can be so intensive that high deformations result in liquid-to-solid-like transition (see section 3.6.3). This problem is treated sometimes from the point of view of the stability of the stream. The theoretical analysis includes constitutive equations.⁷¹

6.4.3.7 Injection-compression molding

The injection-compression molding technique has been developed to utilize advantages of both molding techniques. This technique utilizes the conventional injection molding machine and a compression attachment. At first, polymer melt is injected in order to partially fill the mold, which is partially open. Then, the compression stage is introduced which leads to the final closing the mold by squeezing flow of melt. This compression stage is introduced to replace the packing stage of conventional injection molding. Since the pressure developed during the compression stage is significantly lower than that in the packing stage of conventional injection molding, injection-compression molding introduces lower residual stresses, lower molecular orientation and birefringence, less and more even shrinkage, and better dimensional tolerances. At the same time, this process maintains high output, good process control, and automation inherent to conventional injection molding. The process is especially useful for molding thin parts that require high quality and accuracy. However, the process requires careful timing of injection clamp position and force. Injection-compression molding is presently employed in making optical disks (DVD and CD) where requirements for dimensional tolerances and the optical retardation are very stringent. In production of the optical disks, this process is called

coining. In comparison with injection molding, there are few little experimental and theoretical studies in the literature on injection-compression molding.

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QUESTIONS FOR CHAPTER 6

QUESTION 6–1

Compare sensitivity of different rheological methods to variation of molecular mass.

QUESTION 6–2

Explain why MFI of polymer used for film extrusion must be higher than in tube extrusion (see Fig. 6.2.3).

QUESTION 6–3

Is it possible to vary elasticity of melt without changing the average molecular mass of polymer?

QUESTION 6–4

Explain the advantage of synthetic lubricants in comparison with mineral oil based lubricants.

QUESTION 6–5

Derive Eq. 6.4.5. As an intermediate result, obtain an equation for a radial velocity distribution.

QUESTION 6–6

How does velocity profile during flow in a tube change during transfer from Newtonian to a power-law type liquid? Make a comparison by analyzing the ratio of maximum to average velocity.

QUESTION 6–7

Prove Eq. 6.4.6 for the Bingham liquid. Explain the necessary conditions required for movement of the Bingham viscoplastic media through a tube.

QUESTION 6–8

Eq. 6.4.5a is convenient for solving engineering problems of flow of non-Newtonian liquids through channels with non-circular cross-sections. Can a similar equation be formulated for viscoplastic liquids? Explain your answer.

QUESTION 6–9

Why does elasticity appear before gelation during polymer curing, i.e., formation of a three-dimensional chemical network?

QUESTION 6–10

Describe what happens if an end of the pumping screw of an extruder is blocked? What pressure will be developed?

Answers can be found in a special section entitled Answers.