Translated from *Uspekhi Khimii*, **44**, 1517-1533 (1975) U.D.C. 678.072:532.13(047.1)

Rheological Properties of Thermosetting Compositions

M.S.Akutin, G.V.Vinogradov, B.V.Yarlykov, N.V.Afanas'ev, and I.K.Sanin

The current state of research on the plastic properties of compositions based on reactive oligomers is assessed. Methods used to study their properties during deformation are examined. The influence of external factors, composition, and specific structural features of the compositions on their residence time in the plastic state and on their deformation characteristics is discussed. Possible lines of investigation on the rheological properties of thermosetting compositions are considered. A list of 135 references is included.

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I. INTRODUCTION

Thermosetting compositions are based on reactive oligomers and fillers, plus any required additives. The distinguishing feature of these materials is their inherent ability, when heated or at a low temperature, to pass into an infusible and insoluble state by the formation of steric bonds (a three-dimensional network) as a result of chemical reactions[1-4]. Thermosetting resins, in contrast to many thermo plastics, are highly resistant to arcing and possess good dielectric properties; they are stable in many corrosive media and exhibit considerable rigidity. Because of this combination of valuable properties thermosetting plastics find diverse applications in the national economy[5].

The character of the reactions which cause the setting of reactive oligomers largely determines the conditions of formation of high polymers, and hence should be taken into account in the choice of technical scheme for the processing of oligomeric substances into a polymeric material. Reactive oligomers can be divided[6] into several groups: (1) those having multiple bonds and cyclic oligomers, able to undergo chain and stepwise polymerisation — "polymerisation oligomers" —including oligoester-acrylates, oligosiloxanes, polymers and copolymers of butadiene and isoprene, etc.; (2) oligomers containing functional groups are able to undergo polycondensation, migration copolymerisation, or polycoordination — "oligomers with functional groups" (phenol-formaldehyde, urea, glyptal, etc.); and (3) oligomers having a chain of π-conjugation which may contain functional groups, including oligovinylenes, oligophenylenes, etc.

In the present Review we shall consider mainly materials of the second type. Actual cross-linked polymers are characterised by various structural inhomogeneities, which explains in particular their diminished strength (in comparison with the calculated value), as well as the ability to flow at high temperatures and pressures possessed by certain irregular polymers with a low density of cross-linking.

Structural inhomogeneity affects not only the mechanical and physical properties of the material but also the kinetics of further cross-linking, which may involve both groups attached to the existing three-dimensional structure and those located at more accessible sites. It may therefore be expected that the same primary reaction, especially at relatively high degrees of conversion, will exhibit different rate constants, representing different kinetic mobilities of the units of the three-dimensional structure.

The properties of polymers may vary within wide limits depending on the structure, chemical nature, and frequency of cross-links[6] Polymers possessing neither solubility nor the capacity of viscous flow are formed only on the attainment of quite high degrees of conversion of the initial multifunctional compounds. The formation of three-dimensional cross-linked polymers is accompanied by a gradual loss of fluidity and concomitant increase in viscosity. It is therefore important to assess the rheological properties of the system in order to elucidate the nature of the processes occurring in reactive oligomers and filled compositions based on them.

Three types of processes — direct extrusion, transfer moulding, and injection moulding with preliminary mastication of the material —are now widely employed for converting thermosetting compositions into finished articles[7].

Many publications on the processing of thermosetting resins usually point out the need to establish high injection pressures[8-10]. Materials based on phenol-formaldehyde oligomers can be processed properly with almost all types of equipment, including moulding machines with worm mastication. The considerable heat resistance of materials based on reactive oligomers enables them to be processed in ordinary extruders[11-14].

The difficulty of processing lies in the near impossibility of drawing a boundary between the end of mastication and the beginning of setting, since irreversible cross-linking begins to develop at the same time as softening of the material[15]. No significant part is played by the particle size of the thermosetting compositions when the material is fed into the channel of the worm. However, the friability of the mass to be processed is significant[9].

Pressure is another important variable in processing. The permissible pressure is lower for materials that tend to undergo mechanical degradation and disintegration at high rates of processing. Thus aminoplasts are processed at only half the rates of deformation used with phenoplasts[16]. The maximum rate of injection can be realised in the processing of phenol-formaldehyde compositions and materials based on melamine-formaldehyde oligomers.

High pressures and rates of injection of thermosetting melts cause intense wear of moulds and gates, but in some

cases this is attributed to inadequate mastication of the material[16]. This is probably responsible also for the vigorous evolution of heat when an attempt is made to increase the capacity of the machine by rotating the worm more rapidly. Few if any data are available on the homogeneity of the melt in the channel of the worm. Estimation of this property from the extruded material emerging from the die is unreliable, since intense mixing may occur during extrusion, as in the processing of elastomers and thermoplasts. It has been suggested[17] that the quality of mastication can be assessed in several cases e.g. from the temperature of the material leaving the masticator.

This optimisation of the processing of thermosetting compositions requires an investigation of the change in their properties on passing from initial to plastic and then to hardened state, i.e. the rate of passing from one state to another, the duration of the plastic state. It is also necessary to study the effects of numerous technical factors—temperature, speed, pressure, degree of filling, and particle size of filler—at all stages of processing.

II. ASSESSMENT OF PLASTIC PROPERTIES OF THERMOSETTING COMPOSITIONS BY RHEOLOGICAL METHODS

The maximum amount of information on the state of the material and the role of various factors in its processing can be obtained by making rheological measurements under conditions approximating to actual moulding.

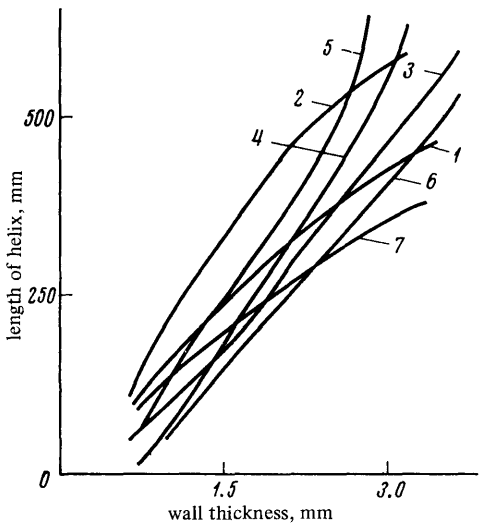


Figure 1. Comparison of fluidities of phenoplasts and various thermoplastics with longitudinal filling of a helical cavity (injection pressure 700 kg cm^{-2}): *1*) Genal 4000 phenoplast; *2*) Genal 4050 phenoplast; *3*) polypropylene; *4*) glass-filled nylon; *5*) polystyrene: *6*) ABS; *7*) Genal 4300 phenoplast.

The standards required for the composition to be processed are increasing because of the great sensitivity of injection moulding to variations in the properties of the material; in particular, the scatter of material characteristics from batch to batch must be as small as possible. It is also desirable to lengthen the time the material remains in a plastic state, and to diminish the viscosity of thermosetting compositions. A single system for assessing the viscosity properties of the latter is lacking, because of the poor reproducibility of measurements made with different designs of apparatus[18].

The principal characteristics which must be used to compare thermosetting compositions are the initial viscosity, the time the material remains in a plastic state, the duration of setting, and the change in fluidity during setting. The initial viscosity and the duration of the transition from plastic to hardened state are often determined at a standard temperature[18]. It is noteworthy that thermosetting compositions in a plastic state approach melts of ordinary thermoplastics in their viscosity characteristics (Fig. 1).[19]

The most diverse methods are used for determining those technical characteristics of thermosetting compositions that may be useful under practical conditions, but systematic accounts of them can be found[20,21]. The first group involves estimating fluidity during extrusion, when the results depend on the conditions of deformation. In the second group of methods the viscosity is determined under conditions approximating to those of injection moulding and extrusion.

Among the numerous methods of the first group the most widely used are the examination of fluidity by compression between two plane-parallel plates[22], the "beaker method"[23,24], extrusion through different channels[25–29] and its *Rossi-Peaks* modification, determination of fluidity during flow into a conical channel[31] or into a mould in the form of an Archimedean screw[24,32,33], etc.[34–36]. All these methods involve obtaining arbitrary characteristics, which does not permit adequate assessment of the fluidity of thermosetting compositions.

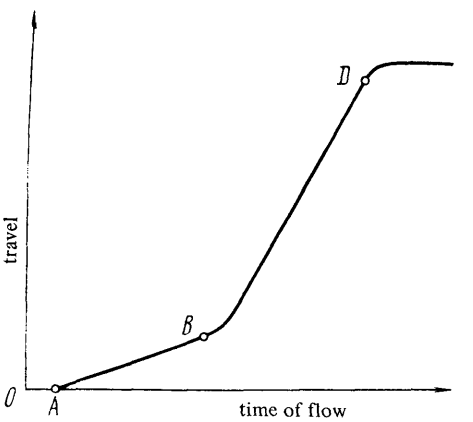


Figure 2. Assessment of viscosity properties of thermosetting compositions by Meysenbug's method (Darmstadt test): *OA*) heating range; *AB*) softening range; *BD*) flow range; *D*) start of setting of composition.

The second group of methods are based mainly on rotary viscosimetry, which enables the experimental conditions (temperature, duration, régime of deformation) to be varied within very wide limits[37–46]. Those most widely used for thermosetting compositions are Meysenbug's method[47,48],

the flow test[49,50], the Kanavets apparatus[51–55], and the Brabender plastograph[49,56–59]. The test results are used to determine the duration of the plastic state, the viscosity properties of the material, the rate of setting, etc.[60]. Figs. 2[20] and 3[61] illustrate typical relations. The methods differ in the mode of deformation, either specifying a constant torque and recording the variation in rate of flow with time, or using a specified constant rate of travel and measuring the resulting torque.

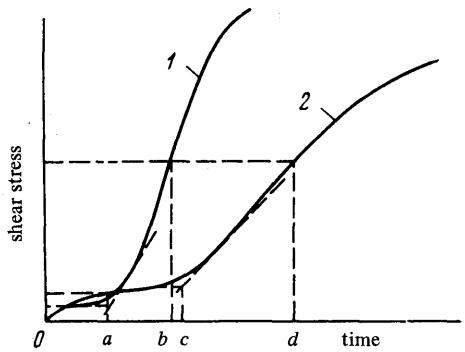


Figure 3. Kinetics of the hardening recorded on a Kanavets plastometer[35] of thermosetting materials of: *1*) Novolak type; *2*) resol type; *Oa*, *Oc*) periods of time in plastic state; *Ob*, *Od*) setting times.

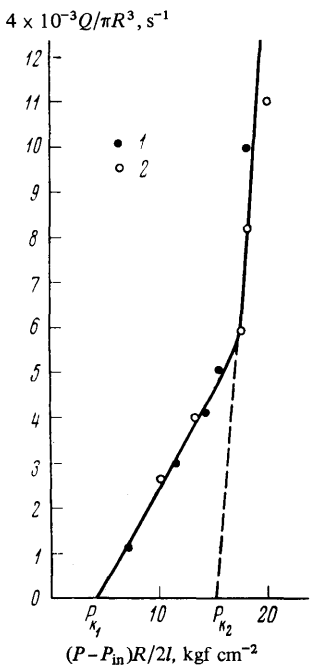


Figure 4. Flow curve of K-18-2 composition: P_{k_1}) lower fluidity limit; P_{k_2}) upper fluidity limit; *R*) radius of gate; *1*) 1 mm; *2*) 1.5 mm; *Q*) bulk flow rate; *l*) length of gate; $P-P_{in}$) pressure drop in channel.

Knowledge of the rheological properties of the compositions under processing conditions is necessary in order to compare the mouldability of different thermosetting materials and describe the flow of the melt in the pouring channels and the mould cavity[62–65]. Capillary and capillary–rotary instruments are also used[66]. Rheological properties were determined[62] by extruding the material through gates of different diameters, the main result being the discovery of two fluidity limits for a composition (Fig. 4). The flow curves were described analytically by means of Bingham's law. Capillary viscosimetry yielded[67,68] flow curves for a composition analogous to the Soviet material K-18-2 at shear stresses not exceeding 5 kg cm^{-2}, below the lower fluidity limit P_{k_1} (Fig. 4). The flow curve was satisfactorily described[67] by a power relation of the type

$$\tau = k \cdot \left(\frac{4Q}{\pi R^3}\right)^{\frac{1}{n_1}},$$

where τ is the shear stress, Q the space velocity, and R the radius of the capillary, while the constants were k = = 1.0 (kg cm^{-2})^{n_1} s and n_1 = 2.07. However, both here and in other work[37,68,69] capillary flow curves were obtained only at one temperature. Hence the results do not permit calculation of the activation energy of deformation, which would have permitted a fuller comparison of the technical properties of the compositions.

Use of a PPR-1 rotary instrument to examine the rheological properties of K-18-2 composition with deformation at a constant rate of shear revealed a limiting shear strength, which rose with increase in the intensity of deformation[70]. However, no limiting stresses like the Bingham fluidity limit were detected[70], in contrast to earlier statements[62,66]. A limiting shearing strength is typical[71–73] of the breakdown of the three-dimensional structural framework formed by the disperse phase (sawdust). Plastic disperse systems, among which thermosetting melts may be included, exhibit a fall in shear stress with increase in rate of deformation on passing through the limiting shearing strength.

Investigation of the rheological properties of K-18-2 moulding powder on a Brabender plastograph revealed[43] considerable boundary-layer slippage during movement of the mass in the gap between the working members. However, another worker[68] observed no slippage of material in the boundary region.

Thus results of the above work on the viscosity properties of thermosetting materials by capillary and rotary viscosimetry have occasionally been contradictory.

Dynamic methods are currently in widespread use for investigating the most diverse materials. Information obtained in this way enables us not only to determine the temperature of transition from one state to another but also to record the development of particular processes with time. The use of dynamic methods also avoids breakdown of the structure, like that occurring during deformation in rotary and capillary viscosimeters.

Despite the promise of the dynamic method, very few results have been obtained on thermosetting compositions, although the first attempts have been made to determine the duration of the plastic state of the binder at various temperatures. Thus the setting of phenolic oligomers and unsaturated oligoesters has been investigated[74] by means of a torsional pendulum, and a similar determination has been made[75] of the viscoelastic properties of the binder. Somewhat apart from these investigations are experiments on the viscoelastic properties of oil-filled phenolic oligomers near their glass point[76]. By varying the oil content

from 0 to 50% the temperature dependence of the mechanical loss angle tan δ was obtained for four frequencies. The results indicated the relation

$$T_g = A \cdot \lg \varphi + B$$

between the degree of cross-linking φ and the glass point of the oligomer T_g, where A and B are constants. The molecular mobility of the phenolic oligomer is assumed to be independent of the degree of cross-linking.

III. EFFECTS ACCOMPANYING THE DEFORMATION OF COMPOSITIONS BASED ON REACTIVE OLIGOMERS

Results obtained by the above methods are sometimes used to plot relations between shear stress and rate, (flow curves), as in the investigation of the viscosity properties of thermoplastics and elastomers. However, most workers do not regard this as possible, probably because it is not generally accepted that viscous flow can take place in thermosetting compositions. Indeed, until recently no studies had been made of their viscosity properties at low rates of shear by means of various rotary instruments, nor had the constancy of the flow curves been verified when compositions were extruded through capillaries of different radii.

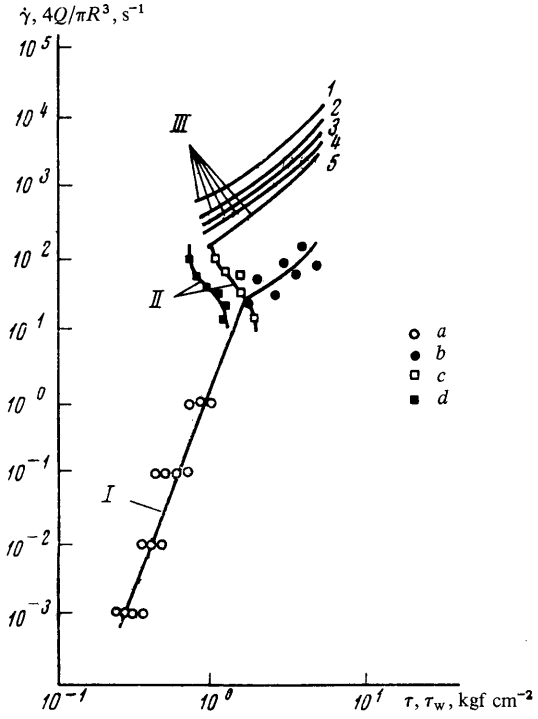


Figure 5. Flow curves of K-18-2 compositions without a hardener at 120°C: I) region of flow (viscosimeter: *a*) REV-1; *b*) capillary); II) pressure dependence of bulk flow rate measured with cylinder–cylinder type of viscosimeter (surfaces of working members: *c*) grooved; *d*) smooth); III) dependence of $4Q/\pi R^3$ on τ_W obtained with capillary viscosimeter [diameters of capillaries (1–5 mm) indicated on curves].

Boundary-layer slippage plays a decisive role[77,78] over wide ranges of shear stress and rate of shear (at rates of deformation of phenoplasts closely similar to those of actual processing conditions). External friction between the material and the wall of the channel may lead to a sharp increase in rate of rotation of the worm. Similar results are obtained in the deformation of thermoplastics[79], for which it has been shown in particular that the rate of slippage is independent of temperature. Region (II) in Fig. 5,[77] in which the shear stress falls with increase in rate, is especially interesting. In the case of raw rubbers this phenomenon was at one time attributed to breakdown of the structure[80,81]. In this case slippage of the material relative to the measuring surfaces is possible[79,82], and the same conclusion was reached by the above workers[77,78].

However, a decrease in stress with increase in rate cannot always be detected in the tests. Thus with elastomers the transition from internal to external friction during extrusion through a capillary takes place at constant stress while the rate increases several dozen times[83]. An analogous phenomenon has been recorded in the investigation of thermosetting compositions, although it was explained by the development of degradation[84].

A characteristic sign of the development of rubberlike elasticity in a polymeric material during extrusion through a capillary is the swelling of the jet of extrudate. Since thermosetting compositions are based on reactive oligomers with different degrees of filling, strongly developed rubberlike elasticity is hardly to be expected. This is supported by results obtained with phenolic compositions[85] which showed that the mould was filled by a molten jet equal in diameter to the gate, this work also indicated that binder and filler may separate, which would impair the homogeneity and the strength characteristics of the final article[85]. This effect was due not only to poor adhesion between binder and filler but also to inadequate homogenisation during mastication. An experiment was therefore undertaken in which the extrudate emerging from the nozzle was divided into four parts, the fluidity of each of which was determined by a standard method. The pouring properties deteriorated along the extrudate, which confirmed the hypothesis that the initial composition had been insufficiently homogeneous.

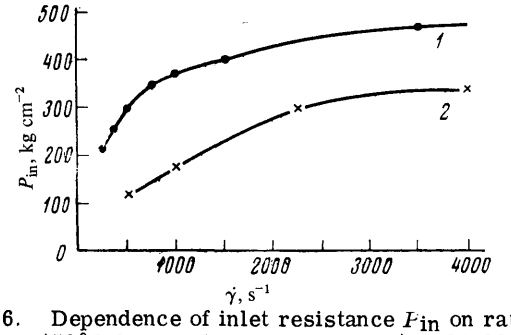


Figure 6. Dependence of inlet resistance P_{in} on rate of shear $\dot{\gamma}$ at 150°C for moulding material: *1*) K-21-22; *2*) K-214-2.

A specific problem in the processing of thermosetting compositions is the need to establish considerable pressures in the dispensing zone, owing to the great pressure losses on entry to the gate. This hypothesis is supported

by the experimental results[63,77,86] plotted in Figs. 6 and 7. Such considerable pressure losses might apparently be due to the development of cross-linking, but the same results are observed in the absence of a hardening agent[77] as in its presence[63,86]. The need to establish high pressures is probably due to the high viscosity and considerable limiting shear strength of thermosetting compositions with finite degrees of filling. The pressure in the dispensing zone can be somewaht lowered if the geometry of the inlet is modified. Thus by changing the inlet angle by 60° we can not only eliminate stagnant zones but also reduce the input losses on the average by 25%.[87]

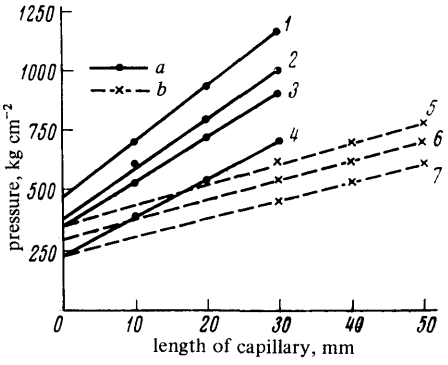


Figure 7. Dependence of pressure on length of capillary for the flow of K-21-22 moulding material at 150°C through an orifice of diameter: *a*) 2 mm; *b*) 4 mm with different rates of shear (s^{-1}): *1*) 3500–3800; *2*) 1400 to 1500; *3*) 950–1000; *4*) 330–360; *5*) 720; *6*) 480; *7*) 200 to 300.

Examination of the fluidity of moulding materials by Meysenbug's method showed[88] that adding up to 1% of a plasticiser considerably improves the reproducibility of estimates of the properties of the compositions. However, the fluidity remains almost unchanged with variation in the plasticiser content from 1% to 3%. The reproducibility of the properties of thermosetting compositions in quite convincing evidence of the favourable effect of the plasticiser[89]. It is interesting that plasticisers that do not react chemically with the oligomer enhance the plasticity of the composition at all stages while hardly affecting the duration of the plastic state[90]. However, if chemical reaction occurs between plasticiser and oligomer, not only a decrease in viscosity but also a longer period in the plastic state is observed.

An attempt was made[62,63] to use the measured coefficients of friction of the test materials to calculate the loss of pressure at the inlet to the nozzle. Thus for K-21-22 material with a rate of shear of 500 s^{-1} the pressure difference at the inlet to the channel found by Bagley's method[91] was 300 kg cm^{-2}, while the pressure loss due to friction of the thermosetting composition was 90 kg cm^{-2}. The difference between these values was then taken in the viscosity calculations to be the pressure loss at the inlet to the die. These workers considered that slippage of material relative to the walls of the capillary was almost completely absent in the deformation of thermosetting compositions at such considerable rates of shear. Their results enabled the input correction P_{in} to be related to the rate of shear $\dot{\gamma}$ by the power formula

$$P_{in} = C \cdot \dot{\gamma}^a,$$

in which C and a are constants depending on the properties of the moulding materials and the temperature[63]. A formally similar relation was obtained[77] with the rate of slippage as variable, when the input correction was unaffected by temperature.

Study of the rheological properties of thermosetting compositions shows that careful reproduction of the test conditions is necessary for the results to be comparable. Plastometers with parallel plates and rotary viscosimeters are therefore becoming ever more widely used. A comparison was made[58] between results obtained with a Brabender plastograph using an extruder as mixer and those obtained with a Kanavets type of rotary viscosimeter. Experiments with a phenol–cresol–formaldehyde oligometer filled with sawdust are noteworthy[58]. With 5 g of material at 100°C and the rotor rotating at 30 rev/min almost complete irreproducibility was found, since the test mass stuck to the mixer paddles and the drag fell sharply. Analogous disintegration of the specimen can occur also in tests with rotary instruments of the cone–plane type, in which hydrostatic pressure is absent. As a consequence, the dependence of rate on torque may acquire the form described by other workers[77,78,80–82].

It is of the greatest interest in investigating the rheological properties of thermosetting compositions to establish flow in a capillary, since conditions then approach those of actual injection moulding. The need for high pressures, the almost complete absence of rubberlike elasticity after emergence from the capillary, and also the rheological results indicate the "rodlike" motion of the compositions[77]. The experimental results show that the rate of discharge is almost entirely determined not by flow but by the rate of boundary-layer slippage v_0. The dependence of stress τ on this rate is then[77]

$$\tau = A_s \cdot v_0^m,$$

where A_S and m are constants. Measurements for technical purposes can be speeded up by using a capillary viscosimeter[93] with automatic recording of the relation between stress and rate of deformation. Deformation conditions accompanying slippage and calculations of the chief parameters (stress and rate of shear, rates of slippage) have been discussed in detail[94–100].

Investigation of the flow at low rates of deformation of compositions based on reactive oligomers has shown[101–106] that the rheological properties of the oligomers—Newtonian liquids—change abruptly when fillers are added to them. At a certain filler content a régime of boundary-layer slippage is established when the compositions undergo deformation in capillary and in rotary viscosimeters.

IV. EFFECT OF TECHNICAL MOULDING CONDITIONS ON PROPERTIES OF THERMOSETTING COMPOSITIONS IN THE PLASTIC STATE

In order to investigate the viscosity properties of thermosetting compositions under conditions as close as possible to actual processing schedules, a Kanavets type of plastometer was fixed to the outlet from the masticator nozzle, enabling the viscosity of the material to be determined at a rate of shear of 0.014 s^{-1}, low enough for the effect of the heat produced by friction to be neglected[107].

Application of relations used[40,61,108] to describe the behaviour of thermosetting materials showed that the temperature in the masticator should not exceed 120°C when standard compositions were processed: otherwise premature setting takes place[109]. Fig. 8 illustrates the temperature dependence of the time during which the material remains in a plastic state[107].

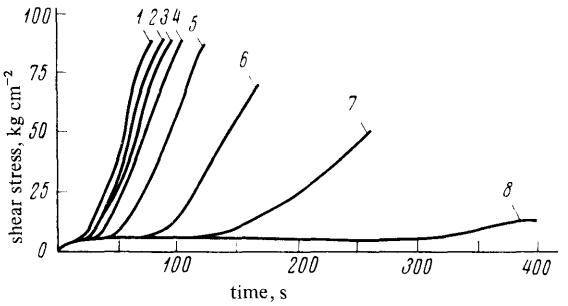


Figure 8. Kinetics of the setting of a phenol–formaldehyde composition at different temperatures (°C): *1*) 190; *2*) 180; *3*) 170; *4*) 160; *5*) 150; *6*) 140; *7*) 130; *8*) 120.

The physicochemical properties of articles made from thermosetting compositions exhibit anisotropy owing to orientation of the filler particles[85,107,110]. Orientation of the oligomer itself during injection moulding probably makes no contribution[85]. At some distance from the gate filler particles are usually oriented perpendicular to the direction of flow; in narrow channels the orientation is parallel. The orientation effect is diminished by under extrusion: i.e. injection takes place into an open mould; parts which initially break off under the influence of pressure, then join with great force[32].

The use of high pressures in the processing of thermosetting compositions naturally raises the question of the effect of pressure on their fluidity and on the duration of the plastic state. Results obtained[31] by the methods of Schwittmann and of Meysenbug were quite reproducible, but were not compared with those obtained by other methods. Work on melamine and phenolic oligomers showing that the duration of the plastic state becomes shorter with increase in pressure[88] is of greater interest. A study of flow during extrusion[64] revealed direct proportionality between rate of flow and pressure up to around 600 kg cm^{-2}, which suggested that Newtonian flow was maintained up to high pressures. However, no more data have appeared on the Newtonian flow of a filled composition, despite the numerous investigations in this field made with various types of viscosimeters[37,43,62,63,66–70,77,78,111–114].

In the "beaker" method it was suggested[64] that pressure, viscosity η, and dimensions of a standard "beaker" were interrelated by the formula

$$\frac{\bar{p}}{\eta\bar{\omega}H} \approx 0{,}5\left(\frac{R}{d}\right)^2,$$

where d is the thickness of the wall of the vessel, H the depth of the specimen, and $\bar{\omega}$ the mean speed of the plunger, while $\bar{p} = \pi R^2 \Delta\bar{p}$, in which $\Delta\bar{p}$ is the mean extrusion pressure.

The fluidity of a composition not only varies on passing from one type of oligomer to another but also is largely dependent on the moisture content of the initial material[115,116]. Usually the latter does not exceed a few percent, since further increase, in spite of the consequent decrease in viscosity, produces a sharp deterioration in physicomechanical properties of the hardened composition.

The particle size of the filler has a noteable effect on the viscosity properties of the thermosetting composition: it was shown for the typical compositions K-18-2, K-21-22, and others that increase in the particle size from 0.1 to 0.5–0.6 mm not only increases the viscosity of the system but also considerably shortens the period in a plastic state[117]. Unfortunately, very few data have been published on the effect of the filler content on the rheological properties of thermosetting materials[101–106].

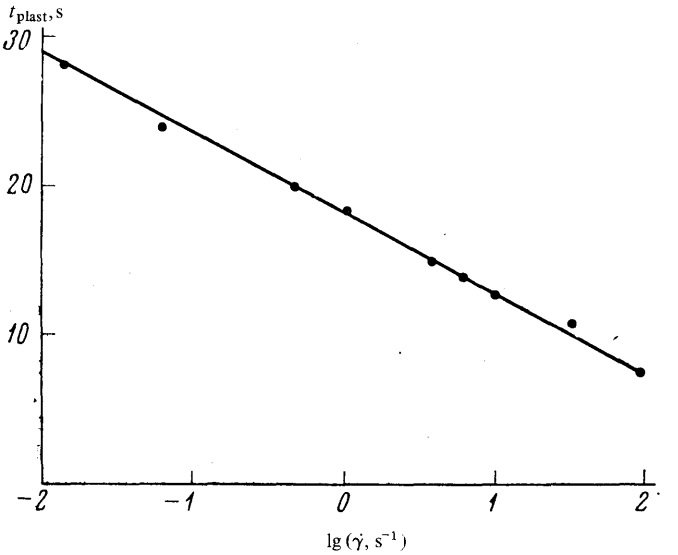


Figure 9. Dependence of length of stay of K-18-2 in plastic state t_{plast} on rate of deformation $\dot{\gamma}$ at 170°C.

This latter omission is aggravated by the impossibility of transferring to thermosetting materials methods of calculating deformation régimes developed for thermoplastics[71,72], because of their specific character. In moulding machines with worm mastication the former materials are processed at very high rates of deformation. Analogous conditions in the processing of thermoplastics may cause the polymer to crystallise[118,119] or to break down[120–122]. Intense deformation also intensifies chemical reactions[78], which is of especial interest for the processing of thermosetting materials. Fig. 9 shows that the time in the plastic state becomes shorter with increase in rate of deformation[41,123]. The role of deformation in the setting of a composition is largely determined by the temperature: e.g. deformation at 120°C may shorten the period in the plastic state by factors of about 4–5, whereas at 170°C by factors of only 2–3 for the same range of shear rates. These conclusions are supported by the results of capillary viscosimetry[37]. The preliminary rolling of thermosetting

compositions also shortens the period the material remains in a plastic state.

The kinetics of setting— the second most important process occurring during the moulding of articles from thermosetting compositions— is mostly assessed by a rheological method[40,61] which has found widespread use both in the Soviet Union and abroad. However, several other methods are known for studying the hardening process, based on the measurement of physicomechanical, electrical, and thermal characteristics of the material, as well as chemical methods. Thus rates of setting have been determined by a thermochemical method[124], from the volume shrinkage[125,126], the variation in molecular weight[127], the variation in dielectric properties[128], chromatographically[129,130], by infrared spectroscopy[131], from the proportion of acetone-insoluble oligomer[132], etc.[111]. The quantity of ammonia evolved has been used[133,134] to study the kinetics of the hardening by hexamethylenediamine of the phenol-formaldehyde oligomer No. 18 and the composition K-18-2 based on it.

Many different theories have been suggested to account for the rheological behaviour of elastomers and thermoplastics during deformation. No mathematical model which would describe the behaviour of thermosetting compositions during deformation is yet available, despite our knowledge of the variation in their properties with various factors and the accumulation of much experimental information. We shall therefore consider only an attempt[135] to describe the flow of a thermosetting material in a cylindrical mould. This started from the pressure dependence of the bulk flow rate Q

$$a_n \frac{d^n Q}{d p^n} + a_{n-1} \frac{d^{n-1} Q}{d p^{n-1}} + \ldots + a_0 Q = Q_0, \qquad (1)$$

and was confined to the simplest cases with $n = 1$ and $n = 2$. The constants $a_1, a_2, \ldots, a_n$ depend on the properties of the material undergoing processing and on the conditions of filling of the mould, while Q_0 is the volume of the casting. With the boundary conditions $p = 0$ when $Q = 0$ and $p \to \infty$ when $dQ/dp = 0$, the relation

$$Q = Q_0 (1 - e^{-\frac{p}{r}}) \qquad (2)$$

was obtained for $n = 1$. The constant r depends on the length l and cross-section S of the die, the duration of flow t_v, and the effective viscosity of the composition η^*:

$$r = r(l, S, t_v, \eta^*).$$

This dependence was written

$$r = (l\sqrt{S})^{\alpha} \frac{\eta^*}{t_v},$$

in which α is constant for the apparatus used. Solving the differential equation (1) for $n = 2$ yields

$$Q = Q_0 + C_1 e^{-\frac{p}{r_1}} + C_2 e^{-\frac{p}{r_2}}, \qquad (3)$$

where r_1 and r_2 depend on the properties of the composition and the conditions of filling of the channel, while C_1 and C_2 are integration constants. The value of r was found from the slope of the plot of $\ln (Q_0 - Q)$ against p. The results[135] indicate that the deformation of polymerisation oligomers is well described by formula (2), and that of polycondensation oligomers by formula (3).

In view of the above results of investigations on the deformation of thermosetting compositions, in which the rate of slippage predominates (under conditions approximating closely to actual processing), it is necessary to set up a mathematical model of the injection moulding of these materials allowing for the "rodlike" character of their motion in channels, and also to develop a rheological model to describe the flow of materials based on reactive oligomers.

REFERENCES

1. A. F. Nikolaev, "Sinteticheskie Polimery i Plasticheskie Massy na ikh Osnove" (Synthetic Polymers and Plastics), Khimiya, Moscow and Leningrad, 1966.
2. V. V. Korshak (Editor), "Tekhnologiya Plasticheskikh Mass" (Technology of Plastics), Khimiya, Moscow, 1972
3. G. S. Petrov and A. N. Levin, "Termoreaktivnye Smoly i Plasticheskie Massy" (Thermosetting Resins and Plastics), Goskhimizdat, Moscow, 1959.
4. I. Sh. Pik and A. N. Levin, "Osnovy Proizvodstva Izdelii iz Plastmass" (Principles of the Manufacture of Articles from Plastics), KOIZ, Moscow, 1954.
5. "Raschet i Konstruirovanie Izdelii iz Reaktoplastov" (Calculation and Design of Articles from Thermosetting Compositions), Izd. MDNTP Dzerzhinskogo, Moscow, 1967
6. A. A. Berlin, T. Ya. Kefeli, and G. V. Korolev, "Poliefirakrilaty" (Polyesteracrylates), Nauka, Moscow, 1967.
7. R. M. Kruzlikov and B. M. Notkin, Plast. Massy, No. 5, 39 (1971).
8. E. W. Vaill, Rev. gén. Caoutchouc. Ed. Plast., 5, 287 (1968).
9. A. Rothenpieler, Kunststoffe – Rundschau, 16, 531 (1969).
10. P. Ehrentraut, Plastverarbeiter, 20, 389 (1969).
11. D. L. Messingen and H. D. Jost, Plast. Technol., 14, 57 (1968).
12. Kautschuk und Gummi, Kunststoffe, 25, 226 (1972).
13. J. Kestler, Mod. Plast., 46, 58 (1969).
14. E. Hartmann and K. Hauenstein, Plastverarbeiter, 21, 624 (1970).
15. H. P. Gilfrich, Kunststoffe Plast., 17, 16 (1970).
16. R. G. Dietz, Kunstst., -Berat., 15, 725, 745 (1970).
17. E. Hartmann and K. Hauenstein, Kunststoffe-Rundschau, 17, 543 (1970).
18. Plaste und Kautschuk, 17, 141 (1970).
19. Plast. Technol., 18, 36 (1972).
20. A. Bachmann and T. Bertz, "Aminoplaste", Leipzig, 2nd edition, 1970.
21. R. Thater, Plaste und Kautschuk, 10, 35 (1963).
22. M. Forrer, British Plastics, 4, 19 (1932).
23. A. Schwittman, Kunststoffe, 34, 1 (1944).
24. P. Fina, Plast. Technol., 12, 27 (1966).
25. G. Menges, P. Ehrentraut, and W. Dalhoff, Gummi, Asbest und Kunststoffe, 19, 943 (1966).
26. M. Krahl, Kunststoffe-Technik, 10, 168 (1940).
27. R. Burns, British Plastics, 12, 214 (1940).
28. P. Ehrentraut, Kunststoffe und Gummi, 4, 152 (1965).
29. D. Nortmann, Plaste und Kautschuk, 6, 365 (1959).
30. G. Penning and L. Meyer, Kunststoffe, 28, 295 (1938).
31. W. Woebocken, T. Basbous, and R. Rasching, Kunststoffe, 57, 974 (1967).
32. H. Wallhäuber, Kunststoffe, 59, 326, 603 (1969).
33. V. N. Grinblat and V. V. Lapshin, Plast. Massy, No. 9, 29 (1966).
34. P. Ehrentraut, Plastverarbeiter, 20, 547 (1969).

35. R. Houwink and N. Heinze, Kunststoffe, 28, 283 (1938).
36. R. Liedmann, Plaste und Kautschuk, 3, 27 (1956).
37. A. S. Perevertov, I. F. Kanavets, An. D. Sokolov, and V. K. Maryashin, Plast. Massy, No. 1, 69 (1969).
38. F. G. Mussatti, and C. W. Macosco, Polymer Eng. Sci., 13, 236 (1973).
39. I. F. Kanavets and L. G. Batalova, Plast. Massy, No. 10, 27 (1962).
40. I. F. Kanavets, "Otverzhdenie Termoreaktivnykh Press-poroshkov i Metod Rascheta Minimal'noi Vyderzhki pri Pressovanii Izdelii iz Fenoplastov" (Hardening of Thermosetting Moulding Powders and Calculation of Minimum Holding in the Moulding of Articles from Phenoplasts), VINITI, Moscow, 1957.
41. N. N. Danilkin, I. F. Kanavets (deceased), and A. S. Perevertov, Plast. Massy, No. 11, 38 (1969).
42. G. Menges, P. Ehrentraut, and W. Dalhoff, Kunststoffe, 57, 957 (1967).
43. V. V. Skachkov and K. A. Salazkin, Trudy MIKhM (Moscow), No. 36, 138 (1970).
44. D. L. Kerr and A. J. Dontje, SPE J., Tech. Papers, 12, (1966).
45. G. Menges and W. Dalhoff, Kunststoffe, 59, 584 (1969).
46. S. N. Varadhachry, SPE J., No. 6 (1967).
47. C. M. Meysenbug, Kunststoffe, 45, 48 (1955); 47, 14 (1957); 49, 130 (1959).
48. R. Thater, Plaste und Kautschuk, 7, 255 (1960).
49. H. Mandler, Plastverarbeiter, 14, 83 (1963); 21, 959 (1970).
50. T. Bertz, C. Neundorf, and G. Köhler, Plaste und Kautschuk, 10, 84 (1963).
51. I. F. Kanavets, L. G. Batalova, and A. G. Romashova, Plast. Massy, No. 1, 63 (1960).
52. K. Ulbricht, Plaste und Kautschuk, 19, 912 (1972).
53. P. Ehrentraut, Kunststoffe, 57, 439 (1967).
54. N. N. Danilkin and I. F. Kanavets, Plast. Massy, No. 5, 71 (1969).
55. A. S. Perevertov, V. N. Tsvetkov, N. V. Shorygina, I. L. Klipinitser, and V. K. Maryashin, Plast. Massy, No. 9, 11 (1972).
56. B. Schreiber, Bericht Z-67-1885, SVUM, Prague, (1967).
57. V. Jelinek, Bericht Z-66-1765/3, SVUM, Prague, (1967).
58. B. Schreiber, Kunststoffe, 59, 362 (1969).
59. A. Rothenpieler and R. Hess, Kunststoffe, 62, 215 (1972).
60. M. S. Akutin and N. V. Afanas'ev, "Teoreticheskie Osnovy Pererabotki Plastmass" (Theoretical Foundations of the Processing of Plastics), Izd. MKhTI Mendeleeva, Moscow, 1974, Part II.
61. I. F. Kanavets, "Opredelenie Tekhnologicheskikh Kharakteristik Termoreaktivnykh Plastikov" (Determination of Technical Characteristics of Thermosetting Plastics), Izd. ITEI Akad. Nauk SSSR, Moscow, 1956.
62. A. D. Sokolov and I. F. Kanavets, Plast. Massy, No. 12, 21 (1963).
63. A. D. Sokolov and I. F. Kanavets, Plast. Massy, No. 3, 18 (1965).
64. L. Ya. Tsipes and B. M. Notkin, Plast. Massy, No. 1, 35 (1969).
65. N. I. Basov, V. A. Lyubartovich, A. I. Leonov, and Yu. V. Kazankov, Teor. Osnovy Khim. Tekhnol., 7, 80 (1973).
66. A. D. Sokolov and I. F. Kanavets, Plast. Massy, No. 6, 23 (1964).
67. G. Meyer, Plaste und Kautschuk, 13, 660 (1966).
68. A. Rothenpieler, Kunststoffe, 59, 747 (1969).
69. V. S. Kim, T. M. Prokhorova, and K. A. Salazkin, Trudy MIKhM (Moscow), No. 36, 63 (1970).
70. N. N. Danilkin and I. F. Kanavets, Plast. Massy, No. 1, 29 (1970).
71. G. V. Vinogradov and K. I. Klimov, Dokl. Akad. Nauk SSSR, 71, 697 (1950).
72. V. P. Pavlov and G. V. Vinogradov, Kolloid, Zhur., 28, 424 (1966).
73. I. M. Belkin, G. V. Vinogradov, and A. I. Leonov, "Rotatsionnye Pribory" (Rotary Instruments), Mashinostroenie, Moscow, 1968.
74. J.K. Gillham and A. F. Lewis, J. Appl. Polymer Sci., 7, 2293 (1963).
75. S. V. Akimov and M. V. Barkova, Plast. Massy, No. 12, 46 (1969).
76. S. Naganuma and Y. Takahashi, Kobunshi Kagaku, 28, 16 (1971).
77. N. I. Basov, V. A. Lyubartovich, V. A. Mironov, E. D. Paskin, A. I. Leonov, and Yu. V Kazankov, Mekhanika Polimerov, 820 (1971).
78. N. I. Bassow, A. I. Leonow, Yu. W. Kasankow, W. A. Ljubartowitsch, and V. A. Mironow, Plaste und Kautschuk, 19, 507 (1972).
79. J. Ishimori, J. Ui, and J. I. Mori, J. Soc. Materials Sci. Japan, 13, 376 (1964).
80. G. M. Bartenev and Z. G. Povarova, Kolloid. Zhur., 28, 171 (1966); Plaste und Kautschuk, 13, 152 (1966).
81. G. M. Bartenev, V. V. Kuznechikova, Z. G. Povarova, and V. A. Kargin, Vysokomol. Soed., 11A, 2172 (1969).
82. G. W. Winogradow, A. Ja. Malkin, B. W. Jarlykov, E. K. Borissenkowa, and N. K. Blinowa, Plaste und Kautschuk, 19, 907 (1972).
83. G. V. Vinogradov, A. Ya. Malkin, Yu. G. Yanovsky, Je. K. Borisenkova, B. V. Yarlykov, and G. V. Bereshnaja, J. Polymer Sci., A-2, 10, 1061 (1972).
84. V. V. Abramov and I. F. Kanavets, Plast. Massy, No. 4, 56 (1967).
85. G. Richter, Plaste und Kautschuk, 16, 840 (1969).
86. G. G. Stankoi, E. B. Trostyanskaya, Yu. N. Kazanskii, V. V. Okorokov, and O. Ya. Mikhasenok, Plast. Massy, No. 9, 49 (1968).
87. V. V. Okorokov, Yu. N. Kazanskii, and G. G. Stankoi, Plast. Massy, No. 8, 27 (1969).
88. H. J. König, Kunststoffe, 59, 305 (1969).
89. I. F. Kanavets, L. G. Batalova, and A. G. Romashova, Kolloid. Zhur., 19, 204 (1957).
90. V. K. Maryashin, I. F. Kanavets (deceased), and A. S. Perevertov, Plast. Massy, No. 2, 20 (1971).
91. E. B. Bagley, J. Appl. Phys., 28, 624 (1957).
92. O. Bartos, J. Polymer Sci., B3, 1025 (1965).
93. V. G. Bortnikov and D. R. Shamgunov, Plast. Massy, No. 8, 27 (1971).
94. W. L. Wilkinson, "Newtonian Liquids" (Translated into Russian), Mir, Moscow, 1964.
95. I. G. Oldroyd, J. Colloid Sci., 4, 333 (1949).
96. Z. D. Jastrzebski, Ind. Eng. Chem. Fundamentals, 6, 445 (1967).
97. G. W. Winogradow and L. I. Iwanowa, Rheol. Acta, 7, 243 (1968).
98. V. Semjonow, Kunststoffe, 56, 163 (1966).
99. R. Berger, Plaste und Kautschuk, 19, 113 (1972).
100. B. A. Toms, J. Colloid Sci., 4, 511 (1949).

101. M. S. Akutin, G. V. Vinogradov, N. V. Afanas'ev, B. V. Yarlykov, and I. K. Sanin, Plast. Massy, No. 10, 39 (1973).
102. N. V. Afanas'ev, M. S. Akutin, and I. K. Sanin, "Tezisy Dokladov XVIII Konferentsii po VMS" (Abstracts of Papers at the Eighteenth Conference on Macromolecular Compounds), Nauka, Moscow, 1973, p.231.
103. M. S. Akutin, I. K. Sanin, and N. V. Afanas'ev, Trudy MKhTI Mendeleeva, No. 74, 144 (1973).
104. N. V. Afanas'ev, M. S. Akutin, I. K. Sanin, and N. P. Stvolova, Trudy NKhTI Mendeleeva, No. 80, 144 (1974).
105. N. V. Afanas'ev, B. V. Yalykov, M. S. Akutin, and I. K. Sanin, Trudy NKhTI Mendeleeva, No. 80, 154 (1974).
106. N. V. Afanas'ev, M. S. Akutin, B. V. Yarlykov, I. K. Sanin, L. V. Ryzhova, and T. I. Kamenskaya, Plast. Massy, No. 3, 36 (1975).
107. G. Menges and W. Dolhoff, Plastverarbeiter, 20, 19 (1969).
108. I. F. Kanavets, Dokl. Akad. Nauk SSSR, 95, 1271 (1954).
109. E. L. Kalinchev and Zh. P. Terent'eva, Plast. Massy, No. 11, 31 (1972).
110. K. A. Salazkin and V. V. Skachkov, "Trudy Konferentsii po Kompozitsionnym Materialam" (Proceedings of a Conference on Composition Materials), Gomel, 1972.
111. K. R. Hoffman, SPE J., 25, 31 (1969).
112. R. Hughes, SPE J., 26, 26 (1970).
113. W. G. Frizelle and J. S. Norfleet, SPE J., 27, 44 (1971).
114. R. Hughes, Mod. Plast., 46, 104 (1970).
115. K. Hauenstein, Kunstst. Plast., 18, 56, 101 (1971).
116. H. J. Röder, Plaste und Kautschuk, 9, 456 (1962).
117. A. S. Perevertov, An. D. Sokolov, I. F. Kanavets (deceased), N. N. Danilkin, V. I. Sviridov, and A. P. Batashov, Plast. Massy, No. 6, 30 (1970).
118. M. R. Mackley and A. Keller, Polymer, 14, 16 (1973).
119. R. S. Porter and J. H. Southern, Amer. Chem. Soc. Polymer Prepr., 11, 266 (1970).
120. C. R. Desper, J. Appl. Phys., 41, 4284 (1970).
121. K. P. Goetze and R. S. Porter, J. Polymer Sci., C. 35, 189 (1971).
122. J. L. den Otter, Rheol. Acta., 10, 200 (1971).
123. A. D. Sokolov and I. F. Kanavets, Plast. Massy, No. 2, 54 (1967).
124. G. L. Slonimskii, V. A. Kargin, and L. I. Golubenkova, Dokl. Akad. Nauk SSSR, 93, 311 (1953).
125. L. I. Sedov and L. I. Zotov, Plast. Massy, No. 7, 59 (1966).
126. L. A. Igonin, N. A. Krasulina, and V. A. Kargin, Kolloid. Zhur., 18, 34 (1956).
127. C. John and G. H. Char, Modern Plastics, 36, 117 (1961).
128. J. O. Salver, J. Polymer Sci., A3, 1911 (1965).
129. V. P. Pshenitsyna, A. L. Peshekhonova, G. L. Grishina, and A. N. Shabadash, Plast. Massy, No. 2, 34 (1968).
130. A. L. Peshekhonova, V. P. Pshenitsyna, G. A. Grishina, and I. I. Krotkova, Plast. Massy, No. 2, 20 (1969).
131. L. A. Igonin, E. G. Gintsberg, N. A. Krasulina, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 111, 1252 (1956).
132. L. Ya. Tsipes, T. E. Alekseeva, and I. S. Yudicheva, TEI Proizvodstvo i Pererabotka Plastmass, No. 7 (1968).
133. N. I. Basov, Yu. V. Kazankov, A. I. Leonov, V. A. Lyubartovich, and V. A. Mironov, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 1578 (1969).
134. N. I. Basov, V. A. Lyubartovich, V. A. Mironov, A. I. Leonov, and Yu. V. Kazankov, Mekhanika Polimerov, 619 (1971).
135. G. J. P. Dujardin, Kunststoffe, 61, 177 (1971).

Department of Plastics Processing and Application Technology, Mendeleev Moscow Institute of Chemical Technology

Polymer Rheology Laboratory, Institute of Petroleum-chemical Synthesis, USSR Academy of Sciences