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## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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**To cite this Article** Faitelson, L. A.(1980) 'Rheological Properties of Filled Polymer Melts', International Journal of Polymeric Materials, 8: 2, 207 – 223

**To link to this Article:** DOI: 10.1080/00914038008077948

**URL:** <http://dx.doi.org/10.1080/00914038008077948>

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# Rheological Properties of Filled Polymer Melts †

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*(Received June 6 1979)*

Basic rheological considerations are applied to filled polymer systems. Filler particle size, phase interface, and network formation are among the variables considered.

## INTRODUCTION

At present, composites enabling solid bodies to be produced with high macroscopic strength on the basis of components available in modern technology are used as principal engineering materials. Worldwide production rates for polymer-based composites greatly exceed those for polymer substances. A feature of composite materials is the possibility of designing not only constructions and goods, but also materials as such. One approach finding extensive use is to create dispersion-strengthened substances whose particles bound crack propagation in polymer materials; a second method implies the use of fibers which are distributed in a more pliable matrix and are arranged principally along main stresses. In the latter case, breaks in individual fibers cause no material destruction, since stresses are transmitted to other fibers via the matrix.

With regard to a rigid component in the composite, it is necessary to distinguish between reinforced and filled products. In the former, strain and strength are predetermined mainly by reinforcement, i.e. by oriented layers of fibers or filaments, fabric or voluminous yarn, while the matrix holds the reinforcement together and enables the load to be distributed between reinforcement elements; in the latter case, the above properties are controlled by the matrix. Various disperse particles, short fibers, monocrystals are used for fillers.

The matrix serves as a principal bearing component in filled composites,

† Presented at the 10th All-Union Symposium on Polymer Rheology held June 20–24, 1978, in Perm (USSR).

its properties vary within boundary layers at the particle surface, and the interaction between these layers, in addition to the effects of rigid inclusions, affects mechanical properties of a composite. The present review discusses filled polymer systems and their resistance in a fluid matrix state, i.e. under the conditions close to the processing situation. Such compositions make it possible to produce a wide range of substances maintaining technological production advantages of thermoplasts, i.e. extrusionability, injection moldability, and processibility by other modern and highly efficient techniques. Data of the effect of fillers on mechanical properties of the matrix in a flow state are applicable to any amorphous polymers, if temperature  $T$  exceeds glass transition temperature  $T_g$ .

Filling can modify physico-mechanical, thermophysical, dielectrical and other properties of the matrix in a desired way, but at the same time it makes processing more complicated due to a considerable increase in viscosity with higher concentration of a solid filler. Therefore, designing a product implies a search for a trade-off between improving performance characteristics and deteriorating processibility, i.e. accounting for processing economy. The effect of polymer filling on the composite performance properties and design methods is well documented in the literature, whereas mechanical behaviour of filled systems when the polymer matrix is in a flow state has been given much less investigative attention.

Filled polymers represent heterogenous systems. Linear dimensions of filler particles, however, are, in most cases, much smaller than those of the design elements of thus produced goods, and than those of operating ducts in the processing equipment; in other words, the macroscopic flow scale substantially exceeds average separation of adjacent filler particles. Therefore, filled polymer melts and solutions may be considered as some originally macrohomogenous isotropic continuous media; their behaviour can be described by the known methods of continuum mechanics.

Theoretical prediction of the effective rheological properties of filled polymer systems therefore depends on finding the relationship between macroscopic flow variables and rheological functions of each component, taking into account the average hydrodynamic pattern on each filler particle level. The solution of this problem goes back as far as Einstein's contribution dealing with the effect of rigid spherical particles in extremely low concentrations on low molecular-weight fluid viscosities, i.e. the situation with no hydrodynamic interaction. Gudyir has found a similarity between the mathematical description of the linearized viscous flow and the linear elasticity of an incompressible solid body.<sup>1</sup> Smallwood has derived an expression for a diluted dispersion of rigid spherical particles in the elastic matrix. Thus, it has been stated<sup>2</sup> that  $\eta_K/\eta_M = G_K/G_M$ , where  $\eta_K$ ,  $\eta_M$  are viscosities, and  $G_K$ ,  $G_M$  are shear moduli for the composite and the matrix,

respectively and  $G_M \ll G_K$ . Shear rate  $\dot{\gamma}$  in the Newtonian media is replaced by shear strain in Hook bodies. Assumption is also made of a full matrix adhesion to filler particles. When filler concentration increases, hydrodynamic interaction cannot be ignored, and the problem of calculating effective characteristics becomes enormously complicated. The lack of any common approach to describing various flow events for such compositions explains the great number of ratios suggested for viscosity to be determined as a function of filler concentration<sup>3</sup>.

If there is a solution for a composite with an elastic matrix, i.e. an expression for the effective modulus, then using the correspondence principles<sup>4</sup> makes it possible to find effective viscoelastic characteristics as well as viscosity of a composite with the Newtonian matrix. Elastic and conjugated viscoelastic substances should have the same model representation. The correspondence principle is based on the application of integral transformation techniques leading to sophisticated inversion problems. Excluded here is, for example, the case of an incompressible viscoelastic matrix containing rigid isometric particles. For such compositions, the following equalities should be satisfied<sup>5</sup>

$$\eta_K/\eta_M = G_{eK}/G_{eM} = H_K/H_M = f(C)$$

where  $H_K = H_K(\theta)$ ;  $H_M = H_M(\theta)$  are relaxation time  $\theta$  spectra for the composite and the matrix; and  $f(C)$  is the function only of the volume concentration of filler particles. This is a case of utmost interest. A flow, however, is a much more complicated process as compared with elastic straining, since a flow may be characterized by superimposing hydrodynamic aggregation phenomena, orientation effects, i.e. the effects related to the time history of particles, imported by their adjacent counterparts.

If the shape of rigid filler particles deviates from that of a sphere, then at low concentration the Newtonian matrix should reveal a relationship between shear viscosity and shear rate, and the appearance of normal stress differences; viscoelastic properties.<sup>6</sup> In this case, size distribution of particles is of substantial importance. Such effects are qualitatively determined in the Newtonian matrix, if spherical particles are elastically deformable, but viscoelastic properties of such systems are more sophisticated.<sup>7</sup>

As filler particle sizes decrease, the probability of their uniform distribution within the matrix diminishes, and there arises a marked tendency towards aggregation and agglomeration, and a more or less developed secondary filler structure can be formed even at low concentrations. Despite extensive discussion of the structuralized system flow mechanism in the literature, there is no satisfactory model quantitatively coupling interaction forces with rheologic functions of the medium.

Particular consideration should be given to the importance of phenomena taking place on the phase interface of polymers. As distinct from low mole-

cular-weight fluids whose adsorptional layers on the solid surface are several angströms thick, thickness of boundary layers in high molecular-weight fluids may reach several microns.<sup>8</sup> The mechanical properties of boundary layers differ substantially from these of the rest of the matrix, which fact has been proved by various independent investigative methods. A reservation should, however, be made in that boundary layers are not uniform in their mechanical properties, and here the matter in question is their effective thickness characterizing the system behaviour under experimental conditions.

If the widespread hypothesis of fluctuation networks in polymer melts is to be accepted,<sup>9</sup> then filler particles cause an increasing number of such entanglements.<sup>10</sup> The participation of the same macromolecules in boundary layers of several adjacent particles, starting from a certain filler concentration, leads to a secondary quasicrosslinked structure.<sup>11</sup> It is the boundary layer to solid particle volume ratio that should be the basis for evaluating the filler activity in a given matrix. High degrees of filling cause increased unsoundness including porosity, and environmental resistance of the product drops considerably.<sup>12</sup> Therefore, the filling degree is restricted by limit values in the above sense, and of interest are only lower concentrations which will be treated below.

When processed under conventional flow conditions, polymer melts and concentrated solutions as distinct from low molecular-weight fluids reveal, in addition to nonlinear viscous resistance, an ability to accumulate enormous recoverable strains which cause a number of mechanical behaviour peculiarities.<sup>13</sup> When using such a medium as the matrix, it is necessary to account for the effect of filler particles on the totality of viscous and viscoelastic properties. Most experimental studies, however, dealt only with the effect on viscous properties,<sup>14-16</sup> which is inadequate for predetermination of the product structure transformations in the course of a mechanical processing and the features imparted by a high elasticity of the matrix. Only in a few papers was an attempt made to estimate elastic properties by an indirect factor, namely the extrudate swelling after leaving a circular nozzle (extrudate to nozzle diameter ratio  $D/D_0$ ). Some papers presented the results of determining filler effects on the first normal stress difference,<sup>17-19</sup> elastic recovery following steady-state shear flow interruption, and complex shear modulus constituents at periodic deformations. However, the effect of rigid disperse particle concentrations in the matrix on the above characteristics of shear flow and periodic linear deformation is presented only in.<sup>11, 20-22</sup> Note that periodic shear acting on filled polymers drastically reduces the linearity limit by strain amplitude, a fact which greatly complicated the measurement technique. In some cases, all the measurements performed were concerning only periodic deformation in nonlinear region, and it was suggested that, in highly filled polymers, there was no linear straining region. But methodologic-

ally correct experiments have shown this zone to be clearly outlined even at 70 volume percent filling.<sup>23</sup> At this concentration and frequency of 25 Hz the upper linearity limit of deformation is reduced by the factor of  $5 \cdot 10^4$ .

## LINEAR VISCOELASTICITY

Measurements of the frequency dependence of the complex modulus in the linear deformation region are nondestructive mechanical spectrometry and supply data on relaxational properties of the original of material structure. In Refs. 11 and 21, for the frequency region corresponding to fluidity (I) and transition into the highly elastic state<sup>13</sup> (II), there has been shown that the temperature frequency superposition principle is applicable to filled systems, while the temperature-frequency shift factor ( $a_T$ ) and the apparent activation heat of viscoelastic relaxation times ( $\Delta H_a$ ) being subject to no changes up to a certain filler concentration. When this critical concentration ( $C_k$ ) is exceeded,  $a_T$  and  $\Delta H_a$  start increasing, a fact which, according to Ref. 24, evidences a qualitative structure alteration and is apparently caused by the influence of the interaction between boundary layers. This influence is not only substantially dependent on dispersity (specific surface) of particles, but also varies in the action duration region corresponding to glass transition point, towards increasing critical concentration values.

Reference 11 also distinguishes between filled ( $C < C_k$ ) and highly filled ( $C > C_k$ ) systems and suggests a criterion for the division of the former from the latter according to relaxational properties.

If  $C < C_k$ , then the frequency relationships between real  $G'(\omega)$  and imaginary  $G''(\omega)$  parts of the complex modulus are brought into coincidence by means of multiplying the modulus values by a constant factor which is dependent only on the volume filling degree  $b(c)$ . For solid viscoelastic bodies (or high-elasticity region), this was predicted in Ref. 5 and experimentally shown in Ref. 25. The ratios between shear moduli constituents of the composite and the matrix at the same deformation frequencies are equal to one another and to the initial (Newtonian) viscosities ratio, i.e.  $G'_K/G'_M = G''_K/G''_M = \eta_{0K}/\eta_{0M} = \eta_{rel}$ . Note that experimentally determined values  $b(C)$  substantially exceed those calculated from the "hydrodynamic" effect of rigid particle presence,<sup>11</sup> estimated by the relationships presented in any of Refs 26–28. For calcium carbonate particles in 8% polyisobutylene solution in cetane, this excess is approximately 2.6, i.e. effective volume filling degree is  $C_e = aC$ , where  $a = 2.6$ . Here, by knowing the specific surface of particles it is possible to calculate the effective thickness of the boundary layer. Thus, relaxation time spectrum  $\lg H(\lg \theta)$  of a filled system and relaxation time spectrum of the matrix feature the same shape, but the former is shifted upwards along the ordinate axis; in other words, the frequency dependence of

the loss angle tangent is not related to the degree of filling. Temperature changes equally shift the matrix and composition spectra along the time base.  $\eta_{rel}(C)$  is not a function of temperature.

If  $C > C_k$ , then the apparent activation heat for viscoelastic relaxation times rises with filler concentration. In the low frequency region, the increase rate for the complex shear modulus constituent values due to frequency rise is slower than those of the matrix and of filled compositions (provided the same frequencies are used), whereas the loss angle tangent values are smaller than those of the matrix and of filled compositions. The spectrum changes its shape (in log coordinates) due to increased contribution to the region of high relaxation times. When  $C > C_k$  the concentration function of the initial viscosity is not invariant under temperature, and  $\eta_{rel} = f(C, T)$ .

It should be emphasized that previous ideas of the frequency-concentration superposition as valid<sup>29-31</sup> have not been confirmed both for filled and highly filled systems.

For fluid polymers (melts and concentrated solutions), the original structure is characterized, along with the initial viscosity, by the initial pseudo-equilibrium modulus of high elasticity  $G_{e0} = \lim_{\sigma_{12} \rightarrow 0} (\sigma_{12}/\gamma_e)$ . These two parameters are determined at strain rates  $\dot{\gamma} \rightarrow 0$ , and goes down to the linear viscoelasticity theory. If the relaxation time spectrum is known, its zero moment is equal to the glassline shear modulus

$$m_0 = \int_{-\infty}^{\infty} H(\theta) d \ln \theta = G_0$$

the first moment

$$m_1 = \int_{-\infty}^{\infty} \theta H(\theta) d \ln \theta = \lim_{\omega \rightarrow 0} G''/\omega = \eta_0$$

is equal to the initial viscosity; the second moment

$$m_2 = \int_{-\infty}^{\infty} \theta^2 H(\theta) d \ln \theta = \lim_{\omega \rightarrow 0} G'/\omega^2 = \alpha_0$$

is equal to the initial normal stress factor. The initial pseudo-equilibrium modulus is defined as the ratio

$$G_{e0} = \frac{\eta_0^2}{\alpha_0} = \left[ \int_0^{\infty} H(\theta) d\theta \right]^2 / \int_0^{\infty} \theta H(\theta) d\theta = \frac{1}{J_{e0}}$$

where  $J_{e0}$  is initial pseudo-equilibrium compliance. At the zero spectrum moment, all relaxation times make equal contributions to be determined on the basis of valid measurement results not only in the regions of fluidity and transition into high elasticity region but also in the high frequency region, up to glassy region. For fluid polymers, such a wide range usually is not

covered experimentally. With the moment number increasing, a progressively larger contribution is made by high relaxation times, and therefore within the frequency band used, they have been determined more confidently. It has been stated that, for filled melts and solutions, the initial moduli ratio for the composite and the matrix is equal to their initial viscosity ratio— $G_{e0K}/G_{e0M} = \eta_{0K}/\eta_{0M}$ . In highly filled melts and solutions, the modulus dependence on the filler content near  $C_k$  may pass through a local minimum, and it may turn out that  $G_{e0K} < G_{e0M}$ . Such pattern of the concentration dependence can be explained by the formation of a secondary network at  $C > C_k$  due to boundary layer interactions. By the formation of two interpenetrating networks, namely a fluctuation matrix meshing network and the above secondary network, compliance values are additive. In principle, such compound systems are thermorheologically complex,<sup>32</sup> but the temperature-time superposition according to Williams–Landel–Ferry is also applicable at  $C > C_k$ , when in the considered relaxation regions of fluidity and transition into high elasticity state. In general, except for a narrow region whose  $G_{e0K}$  corresponds to the above minimum, the initial moduli of both highly filled and filled systems increase, thus causing elasticity reduction as filler content becomes larger.

## STEADY SHEAR FLOW

### Viscosity

There is no commonly accepted view on the flow mechanism in filled polymer melts. As asserted in a number of papers, filled compositions are characterized by a plastic flow with fluidity limit, as distinct from anomalous viscous flow in matrixes. Such conclusions are based on the investigative results for carbon-black-loaded elastomers<sup>33</sup> noted for forming “carbon-black structures”.<sup>34</sup> Some highly dispersed fillers with less than  $1 \mu\text{m}$  particle sizes also produce such interstructural effects in polymers. The present review deals with compositions where the presence of the Newtonian flow at low shear rates is indisputable, e.g. cases of more than  $1 \mu\text{m}$  size particles or their aggregates dispersed in a polymer matrix.<sup>35</sup> Filler concentration is also restricted by a limit value corresponding to the starting moment of dilatancy onset in the flow treated by Reynolds. Therefore, in the compositions under consideration, as in bulk polymer melts, the initial viscosity specifies a material in the case of a flow with an intact structure as shown by a complete set of relaxational processes, a fact which is confirmed by the equality of its values found experimentally and computed from relaxation time spectra, i.e. on the basis of two independent values.<sup>11, 22</sup>



The relation between the shear stress and the shear rate in a steady-shear flow is reflected in a flow curve. Flow curves fit for the same composition at different temperatures and are brought into coincidence by means of a shift factor whose values are the same as for viscoelastic relaxation times, which is evidence for the identical nature of viscoelastic relaxation processes in the regions of fluidity and of transition into high elasticity state, as well as of viscous flow mechanisms.<sup>11</sup>

Ideas concerning the hydrodynamic effective filling are insufficient for describing the non-Newtonian flow, since a relative viscosity increase due to filler particles introduced into the matrix will be, as a rule, an ambiguous function of the filler concentration; and it depends on whether the relative viscosity is considered at the same shear rates or shear stresses. Approaches to treating these two correlation methods are presented in Ref. 11.

Prediction of the composite viscosity dependence on the basis of matrix viscosity data is possible if a generalized dependence of the reduced viscosity ( $\eta_r = \eta/\eta_0$ ) on the shear rate can be successfully derived. Ref. 36 shows melts to have such a reduction, provided the product samples compared are characterized by the same type of molecular-weight distribution and provided  $M \gg M_c$ , where  $M_c$  is some critical molecular weight at which the fluctuation network starts its onset. At  $C < C_k$  fillings, it should have been expected that values  $\eta(\dot{\gamma})$  of the matrix and composite will be brought into coincidence by means of linear coordinate conversion. In such a situation, the characteristic relaxation time ratio of the composite and matrix viscous flows  $\theta_K/\theta_M = a$  should be considered as a factor of increasing average effective matrix shear rate  $\dot{\gamma}_K a = \dot{\gamma}_m$ . Then, matrix viscosity and two parameters  $b(c)$  and  $a(c)$  being the functions in a general case of effective filling degree, will describe composite viscosity  $\eta_K(\dot{\gamma}) = b(C)\eta_M(\dot{\gamma}a)$ . The above assumption has been confirmed.

When  $C > C_k$ , such a reduction type takes place starting from definite  $\dot{\gamma}$  and corresponding  $\sigma_{12}$ , which are structure strength indices for the secondary network.<sup>11</sup> When considering  $\eta_{rel} = \eta_K/\eta_M$  at equal  $\sigma_{12}$  values, only a slight  $f(C)$  dependence on  $\sigma_{12}$  was observed. This fact served as a basis for deriving the log arithmetic additivity rule,<sup>37</sup> or the variable separation rule<sup>38</sup> reduced to  $\eta_{rel}|_{\sigma_{12}=\text{const}} = f(C_e)$ , where  $f(C_e)$  is the function only of volume filling and not of shear rate or shear stress. The results presented in Refs 11 and 22 and analysis of the data given in a number of other papers supply no confirmation to this rule for filled systems. This rule finds reflection in flow curve ( $\sigma_{12} - \dot{\gamma}$ ) shifts only along the  $\lg \sigma_{12}$  axis to  $\lg \mathcal{C}$ , and in dependence coincidence in  $\lg(\eta/\eta_0) - \lg \sigma_{12}$  and  $\lg(\eta/\eta_0) - \lg(\dot{\gamma}\eta_0)$  coordinates which is true for the temperature-rate superposition. At  $C < C_k$  fillings, the concentration reduction in a flow curve is realized by a shift along the  $\lg \sigma_{12}$  axis to  $\lg \mathcal{C}$  and along the  $\lg \dot{\gamma}$  axis to  $\lg a$ . Flow curves and thus the viscosity versus shear rate de-

pendences in highly filled systems, i.e. at  $C > C_k$  filler concentrations, cannot be brought into coincidence by means of linear coordinate conversion.

### High elasticity

When flowing, polymer melts and concentrated solutions are accumulating elastic energy which, after unloading the material, causes recoverable strain (recovery) and which, in case of a simple shear flow, manifests in the onset of the normal stress difference components. Under the conditions of a steady shear flow, the highly elastic strain thus accumulated is constant. In case of an elastic fluid with a rather general hereditary function, with respect to directly proportional tangential stresses and to the quadratic dependence of the first normal stress difference versus shear rate the recoverable strain  $\gamma_0$ , coincides with the strain derived from the relation  $\gamma_e = P_w/2\sigma_{12}$ . Increasing  $\sigma_{12}$  the recoverable strain in the pre-stationary region of active loading (at  $\sigma_{12} = \text{const}$ ) and that of recovery in the passive region ( $\sigma_{12} = 0$ ) are quite distinct, i.e. the recoverable strain accumulation process in the active region differs substantially from the recovery kinetics in the passive region. At definite values of  $\dot{\gamma}$  expressed by a step function stress overshoot is observed in the prestationary region. In Ref. 39 this phenomenon in melts and solutions is explained as being due to the onset of long-lived kinetic highly-elastic flow units (clusters) and due to variations in the flow mechanism. The cluster flow pattern has been found to be possible in polymer solutions and in polydisperse by molecular weight melts. In monodisperse by molecular weight melts, the cluster flow mechanism onsets concomitantly with a flow stability loss, and with a transition into forced highly elastic state when a steady-state flow becomes impossible. Clusters accumulate energy which, in the process of recovery measurements, partially returns into the system and partially seems to dissipate. The cluster flow pattern is realized when

$$\frac{dE_e}{d\dot{\gamma}} = \sigma_{12} \frac{d\gamma_e}{d\dot{\gamma}}$$

is diminishing with  $\dot{\gamma}$  increasing, i.e.  $d^2E_e/d\dot{\gamma}^2 \leq 0$ . This pattern corresponds to a partial transition of macromolecules into a mechanically induced nematic phase with predominantly macromolecule orientation within a cluster. The second criterium is  $d^2E_e/d\dot{\gamma}_e^2 = d\sigma_{12}/d\dot{\gamma}_e \leq 0$ . Shear rates corresponding to the criterion of cluster flow onset will be designed as  $\dot{\gamma}_{K1}$ , and those corresponding to the second criterium—as  $\dot{\gamma}_{K2}$ . The  $\dot{\gamma}_{K2}/\dot{\gamma}_{K1}$ , ratio rises drastically as MWD-polymer expands. In a uniform shear rate field,  $\dot{\gamma}_{K1}$ , corresponds to a loss of the flow stability. In capillary rheometers, the loss of stability occurs at  $\dot{\gamma}_{K2}$ . The latter can be explained by the damping effect of wall-separated melt layers and by cluster migration towards the center.

Thus, the shear rate range from  $\dot{\gamma}_{K1}$  to  $\dot{\gamma}_{K2}$  should be considered as a metastable region, and that upwards of  $\dot{\gamma}_{K2}$  as an unstable region. However, in the case of a steady shear flow, the contribution of clusters (consisting of macromolecules that have escaped out of the "meshing network") into  $\gamma_e$  is relatively small and predominantly affects the recovery process. This may serve as an explanation for systematically observed  $\gamma_0 > \gamma_e$ . Of essential interest is the fact stating that if a matrix is of entropic nature, then the entropic character of  $\gamma_e$  is preserved for the matrix-based composites, provided that the temperature-rate superposition holds true.<sup>40</sup> A question has emerged—that of a temperature dependence of the  $\gamma_e/\gamma_0$  ratio. Evidently, it is  $\gamma_e = P_w/2\sigma_{12}$  that characterizes elastic energy of the fluctuation network in the course of a steady shear flow, rather than recovery which is accompanied by an alteration of the polymer structure sustained during the steady flow.

The importance of measuring  $P_w$  for filled compositions under steady shear flow conditions is therefore quite obvious. Discrete disperse solid particles may serve to some extent as a model of clusters and, as will be shown further on, determining their effect on  $\sigma_{12} = f(\dot{\gamma})$  and  $P_w = f(\dot{\gamma})$  is of fundamental significance.

Figure 1 schematically shows the results of determining the functions for

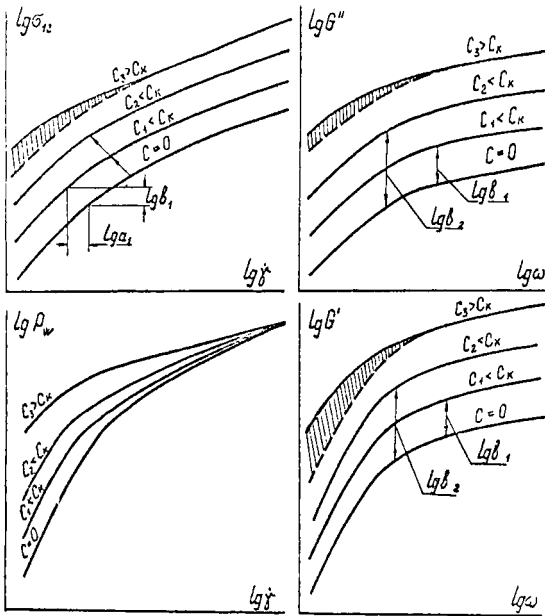


FIGURE 1 Dependences  $\sigma_{12}(\dot{\gamma})$ ,  $P_w(\dot{\gamma})$ ,  $G''(\omega)$  and  $G'(\omega)$  with filler concentration  $c$  used as a parameter.

8% polyisobutylene Π200 solution in cetane and for compositions made on the basis of this solution and filled to 5, 10 and 15% of the volume with calcium carbonate particles at 60°C. As may be seen, at  $C < C_k$  the matrix and composite flow curves are brought into coincidence by means of linear coordinate conversion, whereas for  $P_w(\dot{\gamma})$  a function of such a coincidence is unachievable.  $\sigma_{12}$  value at any of the shear rates examined increases with filler concentration, whereas with shear rate becoming higher,  $P_w$  tends to the matrix  $P_w$  values at high shear rates. Frequency dependences of the complex shear modulus constituents for the same samples are presented for comparison.

Figure 2 shows a plot of  $\sigma_{12K}/\sigma_{12M}$  and  $P_{WK}/P_{WM}$  ratios versus shear rate.

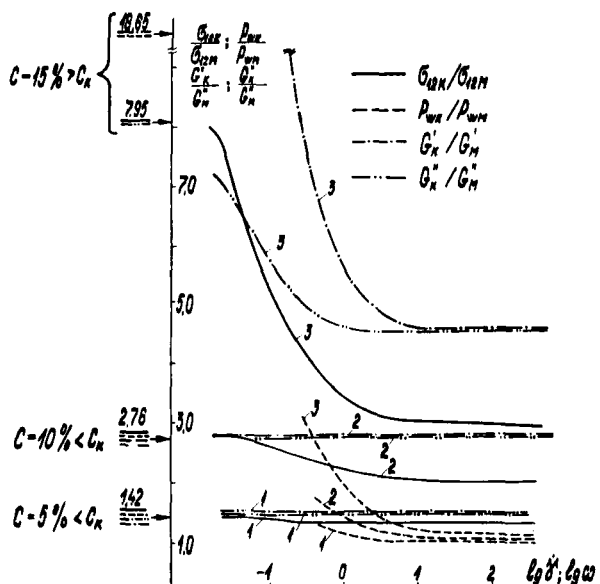


FIGURE 2 Values of  $\sigma_{12K}/\sigma_{12M}$  and  $P_{WK}/P_{WM}$  versus  $\dot{\gamma}$ , and values of  $G'_K/G'_M$  and  $G''_K/G''_M$  versus  $\omega$ . Volume filling  $C = 5\%$  - 1,  $10\%$  - 2,  $15\%$  - 3. The same ratios at  $\dot{\gamma} \rightarrow 0$  and  $\omega \rightarrow 0$  are indicated by arrows.

Arrows to the left of the abscissa axis indicate the ratio values for initial viscosities and initial normal stress factors. Furthermore,  $G'_K/G'_M$  and  $G''_K/G''_M$  ratios at  $\omega = \dot{\gamma}$  frequencies are presented for comparison. Note that the latter ratios characterize the loading rate effect and, contrary to  $\sigma_{12K}/\sigma_{12M}$  and  $P_{WK}/P_{WM}$ , do not reflect the stress level effect which offsets relaxation transitions due to emerging forced fluidity and forced high elasticity.<sup>30</sup> The above flow features of filled systems are caused by an increase of the number of effective entanglements per molecule as a result of filling, and by changes of that number as a function of shear strain intensity. As shear strain intensity

risers, physical filler–filler couplings (i.e. secondary network at  $C > C_k$ ) and subsequently polymer–filler coupling are reversibly destroyed, i.e. the probability of such coupling formations diminishes. Starting from definite  $\dot{\gamma}$  values, these fluctuation entanglements have no time to form; a fluid polymer is a system composed of a matrix and a filler with a boundary layer; the filler is not included in the entanglement network and, therefore cannot effect  $P_w$  which, in this particular case, is caused only by the matrix being capable of larger recoverable strains. In the course of filling,  $\sigma_{12K}/\sigma_{12M}$  increases with the number of effective entanglements per molecule. As the straining intensity rises, this ratio as compared at equal  $\dot{\gamma}$  values, decreases with the number of effective entanglements diminishing; the more the filler concentration, the more pronounced the above decrease. Starting from definite shear rates when additional entanglements caused by the filler presence are destroyed,  $\sigma_{12K}/\sigma_{12M}$  value becomes stabilized, but at larger  $\dot{\gamma}$  as distinct from  $P_{WK}/P_{WM} \rightarrow 1$  it tends to a constant value larger than unity. This is due to purely hydrodynamic effects as opposed to high elastic effects and, as observed, when introducing any rigid inclusions into a viscous fluid. Thus, the filler having a close-to-spherical shape and no physical couplings with the matrix, produces, with increasing viscosity, no changes in  $P_w$  and  $\alpha$  values as compared with those of the matrix. Therefore, it may be concluded that, with  $C$  increasing,  $\dot{\gamma}$  values diminish, and at equal  $\dot{\gamma}$  modulus  $G_e$  becomes higher. The  $P_{WK}/P_{WM}$  ratio is a measure for the effect produced by additional couplings formed by the filler and being maintained at a given rate of the steady shear flow. “Destruction” of the polymer–filler couplings is understood as particles escaping out of the entanglement network with preserved interaction between the filler and  $M < M_c$  molecular-weight molecules; in other words, the above mechanism is not similar to vacuole formation which is known for filled rubbers.

In the low shear rate region  $P_w \sim \sigma_{12}^2$ . With shear rate rising and the initial structure partially destroyed,  $P_w \sim \sigma_{12}^\alpha$  where  $\alpha = f(\sigma_{12})$  and possesses a minimum whose value diminishes in inverse proportion to the filler concentration. In the region corresponding to higher rates  $\alpha \rightarrow 2$  the effective shear modulus values are substantially higher than those in the low shear rate region. In the course of straining melts, no high shear rate region of the shear modulus constancy is observed, since the material loses its flow stability well below these shear rates (Figure 3).

Figure 4 illustrates a shear rate dependence of accumulated strain  $\gamma_e = P_w/2\sigma_{12}$  of the matrix, i.e. of polyisobutylene solution in cetane (a typical highly elastic liquid), as well as changes in this strain due to introduction of the filler. It also shows  $\text{ctg } \delta = G'/G''$  values which are compared with  $\gamma_e$ , provided  $\dot{\gamma} = \omega$ . Equivalence between  $\gamma_e = f(\dot{\gamma})$  and  $\text{ctg } \delta = f(\omega)$  is expected.<sup>46</sup> However, for the matrix, this correlation is observed only within a

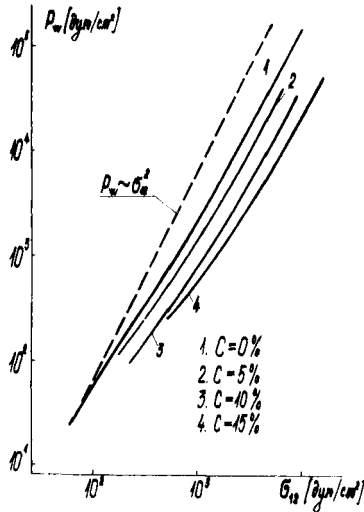


FIGURE 3  $P_w(\sigma_{12})$ . Volume filling: matrix—1.5%—2, 10%—3, 15%—4.

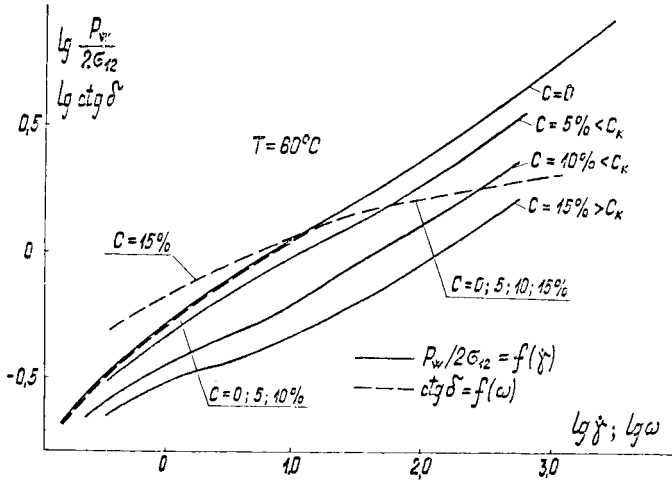


FIGURE 4 Accumulated elastic strain  $P_w/2\sigma_{12} = f_1(\dot{\gamma})$  and  $ctg \delta = f_2(\omega)$ .

narrow shear rate and frequency range, namely within flow region ( $ctg \delta < 1$ ). For filled compositions, this correlation is not observed, since their  $ctg \delta = f(\omega)$  values do not change as compared with those of the matrix, contrary to  $\gamma_e(\dot{\gamma})$ .

### $\sigma_{12}(\gamma_e)$ dependence at simple shear

According to the kinetic theory of rubber high elasticity and on the basis of the Mooney–Rivlin potential, this dependence should be linear, i.e.  $G_e = \text{const}$ . These potentials and implied conclusions suitable for determining steady state strains in cross-linked rubbers are extensively used for investigating high elasticity of melts under the conditions of steady-shear flow, i.e. under quasi equilibrium conditions.<sup>42</sup> Figure 5 schematically shows  $\sigma_{12}(\dot{\gamma})$  and  $\sigma_{12}(\gamma_e)$  dependence for polymer solutions. With polymer concentration  $\varphi$  in solution rising, no lower Newtonian viscosity  $\eta_m$  is reached, since elastic turbulence emerges before corresponding shear rates. Introducing a low molecular-weight solvent into a polymer decreases the “network” density and leads to reduction of  $G_{e0}$  and  $G_e$  and to higher  $\gamma_e$  at the same  $\dot{\gamma}$  values,<sup>41</sup> whereas introducing solid particles (of the filler concentration less than  $C_K$ ) leads to higher initial network thickness of initial modulus  $G_{e0}$  and of  $G_e$  values as compared at the same  $\sigma_{12}$  values, and to lower  $\gamma_e$  at the same  $\dot{\gamma}$  values.

Regions marked by dotted lines in Figure 5 are probably due to incompleteness of the pre-stationary flow region.<sup>39</sup> Filling of melts and solutions at

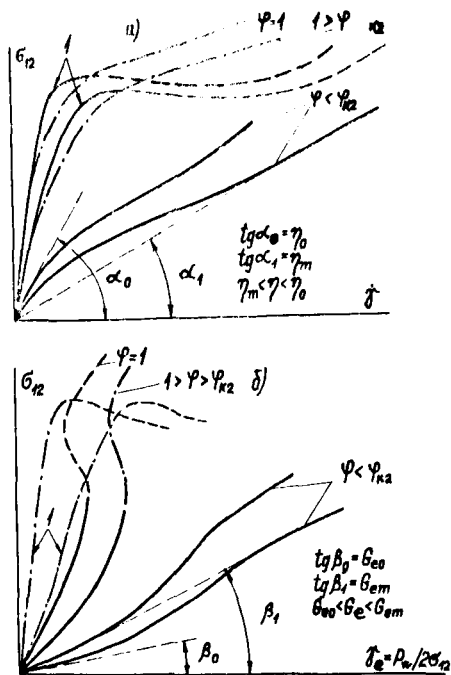


FIGURE 5 Flow curves and  $\sigma_{12}(\gamma_e)$  dependences versus concentration of a high molecular-weight polymer in the solution. 1—Narrow MWD polymers.

$\varphi > \varphi_K$  leads to a higher modulus and to a lower maximum  $\gamma_e$  values at which elastic stability loss (i.e. lower  $\gamma_e$  at higher  $\sigma_{12}$ ) occurs. Of illustrative value are also more abundant results of determining polymer extrudate swelling after leaving the nozzle and the effect of filling on such swelling (Figure 6). On descendant part of the  $\sigma_{12} - D/D_0$  plot, no steady shear flow for

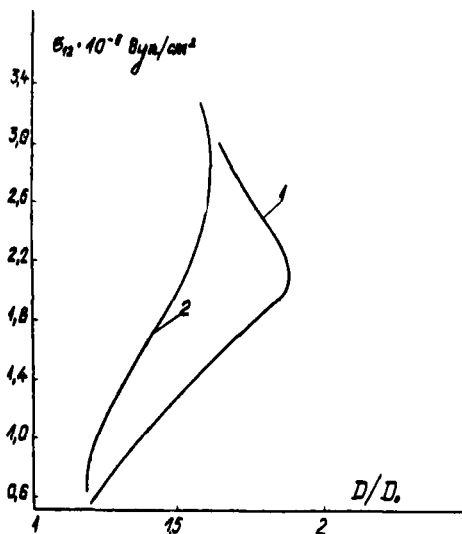


FIGURE 6 Extrudate swelling. 1—Matrix. 2—Filled systems.

the material occurs in the nozzle. Higher  $L/D$  ratios, where  $L$  is a length of the nozzle, may require a substantial increase of the input pressure from the reservoir to the nozzle, taking into account melt compressibility effect.

Filling can be seen to cause no essential changes in the pattern of  $\sigma_{12}(\gamma_e)$  dependence as determined by the polymer matrix.

The concentration dependence of flow and strain curves ( $\sigma_{12} - \gamma_e$ ) of polymer solutions should be distinguished not only for  $\varphi_K$  in the sense stated in Ref. 41 and designated further on as  $\varphi_{K1}$ , but also for  $\varphi_{K2}$  starting from which flow curves for  $\sigma_{12} = \text{const}$  show a "spurt" and the  $\sigma_{12} - \gamma_e$  dependence begins to manifest ambiguity. In the first case, the transition of some macromolecules into a highly elastic state does not lead to a loss of flow stability; at  $\varphi > \varphi_{K2}$ , when macromolecules pass to a highly elastic state the steady-shear flow becomes unachievable. Filling decreases the solution concentration  $\varphi_K$  while increasing the number of the network entanglements.

*Periodical shear* ( $|\dot{\gamma}| = |\gamma| \omega \cos \omega t$ ) with finite amplitudes permits the acquisition data unavailable under the steady flow conditions and, as emphasized in Ref. 34, of considerable importance for polymer physics: using stress as a parameter



and varying the loading rate through a set of constant stress amplitude values enables the relaxation spectrum and its changes to be studied versus the stress magnitude. A review of the most significant results for periodical shear deformation of polymers and a physical interpretation of changes of relaxation spectrum versus  $|\sigma_{12}|$  are given in Ref. 13. A considerable applied importance of this type of deformation is indicated for intensifying technological processes. The character of deformation dependence  $|\sigma_{12}| - |\dot{\gamma}|$  is determined entirely by the frequency deformation region. At low frequencies, the "flow" region is noted for the same mechanism as in case of a steady shear flow. At high frequencies, with higher deformation amplitudes in the region of transition into a highly elastic state and in the highly elastic state fractions of definite molecular weight pass selectively into clusters. Thus, the range of frequencies corresponding to fluidity gives no advantages as compared with the steady shear flow: at these frequencies,  $\text{tg } \delta$  in the nonlinear deformation region up to destruction will diminish with deformation amplitudes increasing. Within the range of frequencies corresponding to the transition from a highly elastic state into a glasslike state the conditions of periodical deformation are possible only within the linear region. Thus, for technological purposes a considerably wide frequency range is of interest; this range corresponds to the transition from a fluid state into a highly elastic state and to the highly elastic state when  $\text{tg } \delta$  increases with  $|\dot{\gamma}|$ . Deformation at ultrasonic frequencies of finite amplitudes can essentially facilitate a number of technological processes due to mechanical and thermal destruction in thin layers of the material at the interface of the setting surface of the processing equipment.<sup>43</sup> Furthermore, in some cases the effect can be achieved under unsteady conditions.

Specific features of the periodical deformation at finite amplitudes of linear monodisperse polymers are treated in Ref. 44. As shown above, shear rate in the matrix of filled compositions is higher than the effective shear rate in the material. Therefore for filled systems the deformation amplitude corresponding to a transition to nonlinear deformation region is reduced.

At  $C > C_K$ , nonlinearity at low frequencies is caused by small extreme deformation amplitudes of the secondary "network", and relaxation transitions are shifted to a higher frequency region, as compared with the matrix. Therefore, the technologically effective range for many filled systems coincides with that readily realizable in the engineering sense. Note that periodical straining of materials includes rolling<sup>45</sup> and calendaring.

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