RHEOLOGICAL PROPERTIES OF CONCENTRATED SUSPENSIONS IN THE PRESENCE OF THE WALL EFFECT

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The results of an experimental study of the flow in capillaries of filled (paste-like) composites with polymer binding are presented. It is shown that a considerable increase in the flow rate occurs owing to the wall effect. The graphic analysis method of calculating the latter is described.

Studies of the processes of flow of concentrated suspensions have acquired exceptional urgency in the last decade.

The solution of engineering and technological problems connected with the processing and transport of such media requires knowledge of their rheological characteristics, allowing one to calculate the resistance of the medium to shear, to establish the correlation between the chemical and rheological properties of the composite, and to determine the quality of the material [1, 2].

The rheological properties of fluid media can be determined on viscosimeters of various types. In accordance with the chosen channel geometry the experimental data in a study of the movement of media in a round tube should be taken on a capillary viscosimeter to avoid complicating effects.

As numerous studies have shown, the flow of concentrated suspensions in capillaries is often accompanied by a wall effect. A wall effect is observed in the flow of lubricants [3-5], peat pulps [6], various disperse systems [7-10], clay and cement solutions [11], polymer solutions [12-15], blood suspensions [16-23], food and pharmaceutical masses [24, 25], and highly-filled composites with polymer binding [26-28].

In a capillary viscosimeter the wall effect is manifested in an increase in the fluidity of the medium with a decrease in the capillary diameter and it leads to the incorrect interpretation of the experimental data obtained. Analysis of the data of a capillary viscosimeter in consistent variables still does not give an invariant flow curve. In this case to each capillary there corresponds its own dependence of τ_R on V_R, with higher velocity gradients (at the same τ_R) corresponding to capillaries of smaller radius.

In order to take the wall effect into account, in the presence of the latter the flow of concentrated suspensions is usually interpreted in the form of a stream of the suspension surrounded by an annulus of pure dispersion medium with a thickness δ [7, 17, 29-33]. The modeling of the influence of the boundary effect in the form of such an annulus is explained as follows.

Since the center of a single particle of the disperse phase cannot approach the solid wall to a distance less than the effective radius of the particle, the concentration of the suspension near the rigid boundary is decreased. This is equivalent to the existence near the wall of a layer of pure dispersion medium with a thickness equal to or somewhat greater than half the average effective particle radius [29].

Besides the "mechanical" effect indicated above, there are quite a few theoretical and experimental indications that single particles of a flowing suspension are subject to the

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TABLE 1. Characteristic Sizes of Capillaries

Number of group	Number of capillary	Radius R, cm	Length l, cm	$\frac{l}{d}$
I	1	0,09631	4,645	24,114
	2	0,09690	9,745	50,283
	3	0,09785	14,790	75,573
	4	0,09660	19,785	102,406
	5	0,09690	24,640	127,140
	6	0,09740	29,790	152,920
	7	0,09670	39,858	206,090
II	1	0,15828	4,650	14,689
	2	0,16057	9,645	30,033
	3	0,15822	14,990	47,370
	4	0,15938	19,845	62,256
	5	0,15870	29,820	93,950
	6	0,15870	39,890	125,670
III	1	0,24297	4,745	9,766
	2	0,24303	14,842	30,535
	3	0,24267	19,848	40,895
	4	0,24320	24,780	50,930
	5	0,24260	29,820	61,459
	6	0,24239	39,927	82,359
IV	1	0,33477	4,925	7,355
	2	0,31280	14,880	23,785
	3	0,31277	19,845	31,724
	4	0,31345	39,838	63,546

effect of a radial force directed toward the center [34-37]. The hypotheses are even advanced that the reduction in the apparent viscosity with a decrease in the capillary diameter is caused mainly by the radial displacement of the particles of the disperse phase toward the axis of the tube (the so-called "axial accumulation effect" [31]). The existing theoretical studies of this mechanism can be roughly divided into two groups: I) hydrodynamic and II) thermodynamic. The first is based on the assumption that the force producing the radial displacements arises due to the asymmetry of the spectrum of flow over the particles of the surrounding medium [7, 35], while the second is based on the principle of the minimum of energy dissipation in an irreversible process [38, 39]. According to this principle, a particle which is initially located at a point of velocity field with a nonzero velocity gradient should be displaced along the normal to the direction of flow to a region of lower gradients.

Thus, the majority of the theoretical studies explain the wall effect during the flow of concentrated suspensions by the absence of particles of the disperse phase in a narrow zone near the wall of the tube. The pushing back of particles from the wall owing either to "mechanical" or hydrodynamic effects (regardless of other effects) results not only in a decrease in the apparent viscosity of the suspension but also in a decrease in the concentration of the disperse phase in the tube [29, 30].

We studied the shear flow of a number of highly filled (paste-like) composites with polymer binding on the basis of the data of capillary viscosimetry. The volumetric filling of our systems far exceeded the critical value. As the binder (dispersion medium) in this case we used polyesters and epoxy resins and as filler we used inorganic salts of different degrees of dispersion.

The rheological properties of the composites were determined at a temperature of 323°K (the processing temperature under industrial conditions) and in a range of shear velocities corresponding to industrial values (10^{-2}-10^{2} sec^{-1}). In accordance with nature (a round tube), the experimental data were taken on a specially developed capillary viscosimeter. Composites with both a damaged and an undamaged structure were used for the studies.

In the tests with a damaged structure the measurements were conducted during the same time intervals following the end of the mixing in order to exclude the effect of structure formation. For the study of composites with an undamaged structure the latter were stored for a day following preparation.

The experimental data were taken on a whole series of preliminary calibrated capillaries which were divided into four groups (Table 1). Each group combines capillaries of about the same radius but of different lengths. The analysis of the results obtained

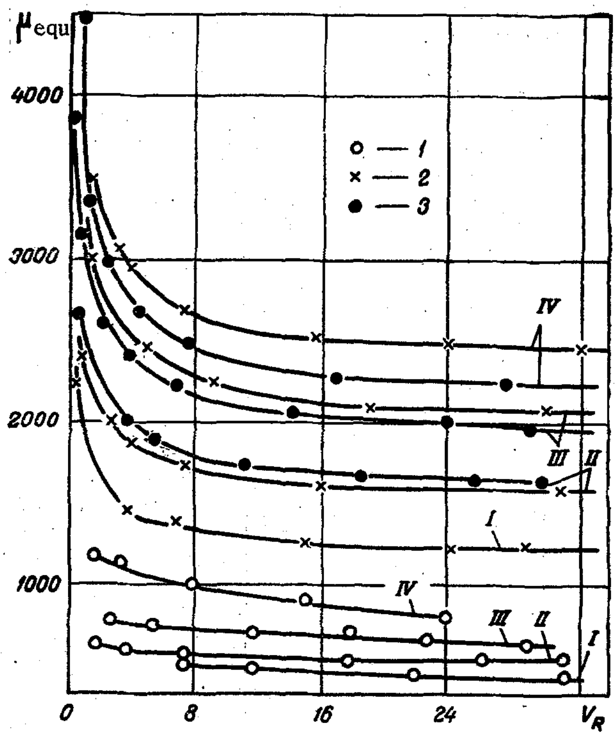


Fig. 1. Dependence of equivalent viscosity μ_{equ}, P, on the shear velocity V_R, sec^{-1}, obtained on capillaries I, II, III, and IV (capillaries I_7, II_6, III_6, and IV_4, respectively, in Table 1): 1) compound No. 1; 2) No. 2; 3) No. 3.

showed (Fig. 1) that the curves taken are noninvariant relative to the capillary diameter. The equivalent viscosity of the test composite decreases markedly with a decrease in the capillary diameter. A lower viscosity corresponds to a smaller capillary in this case regardless of the concentration of the compound. The composites studied behave as pseudoplastic media in the range of shear velocities of 0.1-30 sec^{-1} and obey a Newtonian law of internal friction when $V_R > 30$ sec^{-1}.

The flow curves obtained on the different capillaries proved to be noninvariant not only relative to the diameter, but also relative to the length of the capillary. It was established that the reason for the noninvariance of the flow curves relative to the capillary length is the pressure losses in the formation of the velocity profile. The degree of damage of the structure, proportional to l/d, also affects the trend of the curves. Dependences of τ_R on l/d constructed with V_R = const showed that the influence of entrance effects can be neglected only with ratios $l/d > 60$-70.

For the purpose of a more precise estimate of the wall effect the subsequent measurements were performed on composites with a damages structure. To completely eliminate the influence of entrance effects only capillaries with $l/d > 60$ were used in the tests. The flow curves obtained on such capillaries (Fig. 2) proved to be fully invariant relative to the capillary length. At the same time, stratification of the flow curves by diameters is observed even with capillaries having a ratio $l/d > 70$-80. Once again, the smaller τ_R correspond to smaller diameters for the same V_R. This points to the definite existence of a wall effect.

As already mentioned above, for the flow of concentrated suspensions the wall effect is usually modeled in the form of an annulus of pure dispersion medium of thickness δ surrounding a suspension core of radius $R - \delta$.

The presence of a boundary layer of dispersion medium of small thickness alters the structure of the stream. The increase in fluidity in the boundary layer in comparison with the fluidity in the volume leads to an increase in the flow rate. In this case the flow

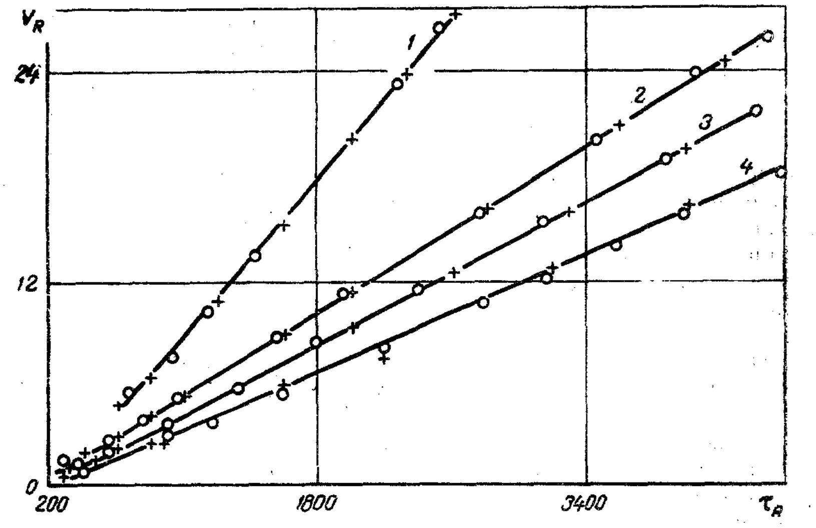


Fig. 2. Flow curves for compound No. 2: 1) capillaries I_6 and I_7; 2) II_5 and I_6; 3) III_5 and III_6; 4) capillaries IV_3 and IV_4. V_R, sec^{-1}; τ_R, N/m^2.

rate of the medium through capillaries when the continuity of the velocity profile is maintained can be represented in the form

$$Q = \pi \int_0^{R-\delta} v(r)\, d(r^2) + \pi \int_{R-\delta}^{R} u(r)\, d(r^2), \tag{1}$$

where the first integral represents the flow rate of the suspension through the core of the stream and the second represents the flow rate of the dispersion medium through the annulus of thickness δ. (It is assumed that established laminar flow occurs.)

Thus, in a strict solution of the stated problem one must know the velocity profiles in the core of the stream and in the boundary layer.

For small thicknesses of the boundary layer (in comparison with the radius of the capillary) one can approximately assume [40] that

$$Q \simeq \pi \int_0^{R-\delta} v(r)\, d(r^2). \tag{2}$$

In turn, integration of (2) by parts gives

$$Q \simeq \pi (R-\delta)^2 v(R-\delta) + \frac{\pi R^3}{\tau_R^3} \int_0^{\tau_{R-\delta}} \tau^2 f(\tau)\, d(\tau). \tag{3}$$

In the absence of a wall effect the flow rate of the medium through a round tube is determined by the equation [1]

$$\frac{4Q_0}{\pi R^3 \tau_R} = \frac{4}{\tau_R^4} \int_0^{\tau_R} \tau^2 f(\tau)\, d(\tau). \tag{4}$$

From a comparison of Eqs. (3) and (4) one can conclude (it is assumed that δ is very small in comparison with R) that the change in the flow rate owing to the wall effect is almost entirely determined by the value v(R − δ), i.e., by the velocity at the border of the boundary layer, called the slip velocity [$v(R-\delta) = v_{sl}$].

By introducing the effective slip coefficient $\beta = v_{sl}/\tau_R$ and taking $R - \delta \approx R$, we obtain

$$Q \simeq \pi R^2 \beta \tau_R + \frac{\pi R^3}{\tau_R^3} \int_0^{\tau_R} \tau^2 f(\tau)\, d\tau, \tag{5}$$

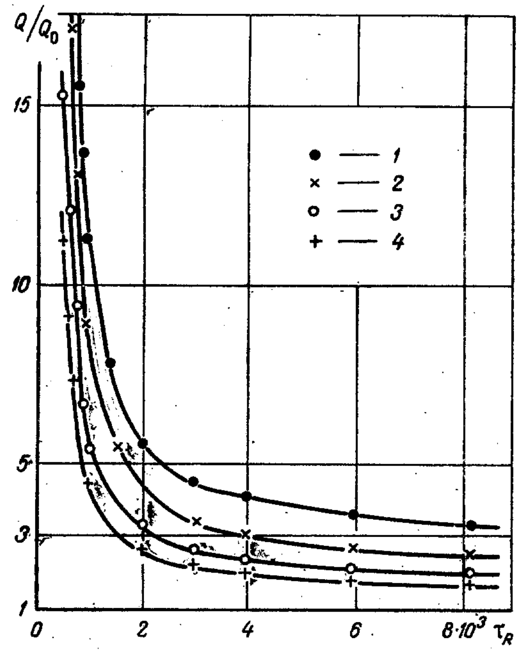


Fig. 3. Influence of wall effect on the flow of compound No. 2 (τ_R, N/m²): 1) capillary I_7; 2) II_6; 3) III_6; 4) IV_4.

from which

$$\frac{4Q}{\pi R^3\tau_R} \simeq \frac{4\beta}{R} + \frac{4}{\tau_R^4}\int_0^{\tau_R} \tau^2 f(\tau)\, d(\tau). \tag{6}$$

Equation (6), in contrast to Eq. (4), does not possess the property of uniqueness for a given τ_R, since it contains a term which depends on the radius. (The slip velocity v_{sl} depends only on the shear stress according to Oldroyd's argument [13].)

Thus, according to (6) the measured fluidity consists of two parts. The first is determined by the wall effect, while the second is due to shear flow, i.e.,

$$\varphi_{equ} = \frac{4\beta(\tau_R)}{R} + \varphi_0(\tau_R). \tag{7}$$

If the experimental curves of $\varphi_{equ}(\tau_R)$ are stratified by capillary diameters, then according to (7) one can conclude that there is anomalous flow near the wall. One must keep in mind, however, that in the case of the onset of nonlaminar flow the measured values of φ_{equ} may prove to be smaller than the calculated values and the points corresponding to large diameters will lie below the points obtained for small diameters, which could be interpreted incorrectly as proof of a wall effect. Therefore, the analysis of the experimental data must be approached carefully, especially for large τ_R.

On the basis of the family of curves of φ_{equ} as a function of τ_R obtained on capillaries of different diameters (but with the same ratio l/d) one can construct graphs of the dependence of φ_{equ} on $1/R$ at certain constant values of τ_R. The graphs constructed should, according to (7), consist of straight lines with a slope of 4β. Knowing β is a function of τ_R, one can determine the flow rate in the absence of a wall effect on the basis of (4) and (5) from the equation

$$Q_0 = Q - \pi R^2 \beta \tau_R. \tag{8}$$

However, recently published data on concentrated suspensions [5, 28] show that the condition of dependence of the slip velocity on the shear stress at the wall can be considered only as a first approximation, since v_{sl} actually depends not only on τ_R, but also on R. In particular, a linear dependence of φ_{equ} on $1/R^2$ is obtained in [28], while in [5] it is shown that there should be a linear dependence $\varphi_{equ} = f(1/R^{3/2})$.

In this connection the graphic analysis method was used in our studies for the determination of β.

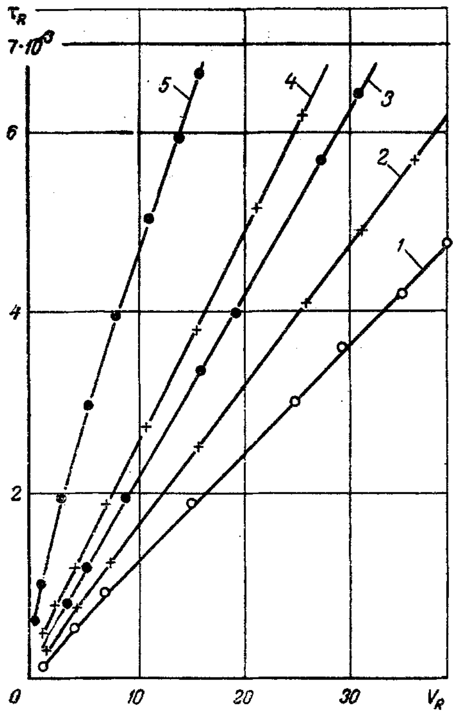
Suppose there is a series of consistent flow curves obtained on capillaries with a ratio $l/d > 70$–80 but of different diameters. We arbitrarily choose two of them, corresponding to the radii R_1 and R_2. Then, after the introduction of a correction for the boundary slippage, according to (8) the following equality should be satisfied (with the same τ_R):

$$\frac{4Q_1}{\pi R_1^3} - \frac{4\beta_1\tau_R}{R_1} = \frac{4Q_2}{\pi R_2^3} - \frac{4\beta_2\tau_R}{R_2}. \tag{9}$$

Assuming that β does not depend on the radius of the capillary, from (9) we obtain

$$\beta = \frac{R_1R_2(V_2 - V_1)}{4\tau_R(R_1 - R_2)}. \tag{10}$$

In fact, however, the values of β obtained on capillaries of different diameters differ somewhat from one another. By combining each capillary with all the others we obtain



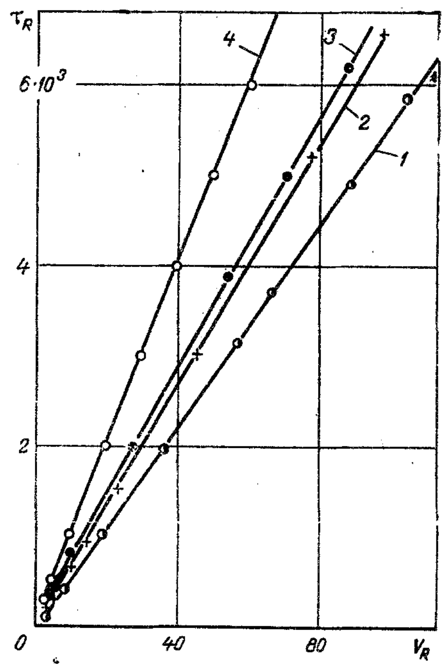


Fig. 4 Fig. 5

Fig. 4. Flow curves for compound No. 2 (τ_R, N/m^2; V_R, sec^{-1}): 1) capillary I_7; 2) II_6; 3) III_6; 4) IV_4; 5) invariant flow curve.

Fig. 5. Flow curves for compound No. 4 (τ_R, N/m^2; V_R, sec^{-1}): 1) capillary II_6; 2) III_6; 3) IV_4; 4) invariant flow curve.

a series of values of β whose arithmetic mean can be taken as the effective slippage coefficient $\overline{\beta}$ for a given value of τ_R. A similar separation is performed for all the successive values of τ_R.

Thus, we determined the values of $\overline{\beta}$ for all the compounds studied in the entire range of variation of τ_R. Then the values of Q_0 corresponding to each τ_R were found from Eq. (8).

Graphs of the dependence of the ratio Q/Q_0 on τ_R were constructed on the basis of the data obtained (Fig. 3). A decrease in the ratio Q/Q_0 with an increase in the capillary diameter and with an increase in τ_R was common to all the compounds studied. The influence of the wall effect here is especially great in the region of $\tau_R \leq 1000\ N/m^2$. With a further increase in τ_R the curves of $Q/Q_0 = f(\tau_R)$ become flatter and when $\tau_R > 5000\ N/m^2$ they approach a certain value of Q/Q_0, not equal to unity, however. (The smallest values of Q/Q_0 were obtained on capillary IV_4 and equalled about two.)

An analysis of the invariant flow curves constructed (see Fig. 4, for example) showed that in the absence of a wall effect the majority of suspensions studied behave like a Casson medium. Several (Fig. 5) are well described by the Shvedov–Bingham model. Both are characterized by a yield limit and a plastic viscosity which are easy to determine from the graphs of $\tau_R^{1/2} = f(V_0^{1/2})$ and $\tau_R = f(V_0)$ for Casson and Bingham media, respectively [1].

Thus, the determination of the rheological properties of concentrated suspensions, the capillary viscosimetry of which is complicated by the wall effect, can be reduced to the determination of the flow rate in a given range of variation of τ_R in the absence of a wall effect on the basis of the experimental data obtained in the presence of the latter. For the elimination of the influence of the wall effect it is necessary that the experimental data be taken on a series of capillaries of different radii (no less than three) and the measurements be conducted in the same range of variation of τ_R.

NOTATION

τ_R, shear stress at the wall; V_R, equivalent velocity gradient at the wall; R, radius of tube; δ, thickness of boundary layer; l, length of capillary; d, diameter of capillary; Q, flow rate of suspension through the capillary in the presence of a wall effect; r, current radius of capillary measured from the axis; v(r), velocity profile in the core of the stream; u(r), velocity profile in the boundary layer; Q_0, flow rate of liquid through the capillary in the absence of a wall effect; v_{sl}, slip velocity; β, effective slippage coefficient; φ_{equ}, equivalent fluidity; φ_0, equivalent fluidity in absence of wall effect; Q_1, flow rate measured on a capillary of radius R_1; Q_2, flow rate measured on a capillary of radius R_2; V_1, equivalent velocity gradient at the wall, measured on a capillary of radius R_1, $V_1 = 4Q_1/\pi R_1^3$; V_2, equivalent velocity gradient at the wall, measured on a capillary of radius R_2, $V_2 = 4Q_2/\pi R_2^3$; V_0, equivalent velocity gradient at the wall in the absence of a wall effect, $V_0 = 4Q_0/\pi R^3$.

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