NOTATION

p, pressure; V, molar volume; T, temperature; x, concentration; u, speed of ultrasound; ρ, density; β_s, adiabatic compressibility; e, internal energy; k, Boltzmann's constant; $g_{ij}(r)$, radial distribution function for mixture of particles with effective interaction pair potential $\varphi_{ij}(r)$; ε and σ, parameters of Lennard-Jones potential; m, molecular mass; c(r), direct correlation function.

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DEPENDENCE OF THE VISCOSITY OF PLASTISOLS ON TEMPERATURE AND TIME

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The method of rapid heating of the medium was used for investigating the dependence of the viscosity of polyvinyl chloride plastisols on the temperature and time in connection with isothermal molding in casting practice.

For injection molding in long molds with small clearances, plastisols are often used; these are materials consisting basically of a mixture of a polymer and a plasticizer. Fixation of the mold is attained by gelling the polymer material at elevated temperatures where the viscosity of the system rapidly increases up to curing. To optimize casting and choose correctly its parameters, it is important to know the rheological properties of the processed plastisols.

It was found that the temperature has a considerable effect on the gelling process of industrial plastisols above 40-60°C. At low temperatures, where the viscosity does not change with time, the rheological properties of plastisols in steady shear have been accurately determined (viz., e.g., [1]). It is interesting to investigate the behavior of these

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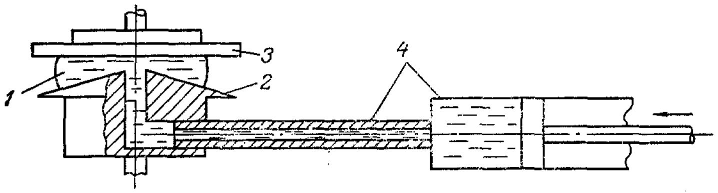

Fig. 1. Diagram of the injection of plastisol into the gap between the cone and plane of the rheogoniometer.

media at elevated temperatures in connection with isothermal casting conditions. At such temperatures the behavior of viscosity in dependence of the temperature and time was studied either qualitatively under isothermal conditions [1, 2] or with the temperature increasing with time [3].

We investigated the industrial plastisol of polyvinyl chloride (PVC).* Preliminary experiments showed that with $\gamma > 10\ \mathrm{sec}^{-1}$ and $T \lesssim 56°C$ this plastisol flows like a Newtonian liquid with the so-called lowest Newtonian viscosity η_∞ which does not change with time at a fixed temperature. When $\gamma < 10\ \mathrm{sec}^{-1}$, viscosity increases with decreasing γ. The stress in these experiments (γ = const) attains a constant value practically instantaneously, i.e., such a medium does not have a characteristic time. First we will examine the motion of polyvinyl chloride plastisol for flow with the lowest Newtonian viscosity (when the mold is being filled, the strain rate averaged over the clearance is $\gamma \gg 10^{-1}\ \mathrm{sec}^{-1}$) and in the range of temperatures at which gelling proceeds noticeably ($T \gtrsim 56°C$). In this range viscosity does not depend on the strain rate. It decreases with increasing temperature at the initial instant, but then it increases with time in the process of gelling, and more intensely so, the higher the temperature is.

We studied the rheological properties of PVC base plastisol on a standard rheogoniometer with a cone–plane unit which was placed in a thermostated chamber. In rheological investigations it is usual to charge the material between the cone and the plane (the plane is first raised and then lowered), and then to thermostat it. It must be pointed out that the thermostating to a specified temperature has to take a fairly long time (e.g., heating material from 22 to 70°C takes more than an hour). For studying the isothermal processes occurring fairly rapidly in time, the ordinary procedure of charging and subsequent thermostating of the specimen is unsuitable. Speeding up the heating of the medium can be attained in two ways: by injecting the material into the working unit (cone–plane) previously heated to the specified temperature. In our work we used the second method which is simpler. The time t^* needed for heating the liquid injected into the preheated unit is less than 1 sec ($t^* < h_{\max}^2/\xi$).

For injecting the liquid 1 (Fig. 1) into the gap between the plane 3 and the cone 2, a cylindrical hole with d = 4.2 mm was drilled into the latter. Into the hole a pipe (d_p = 4 mm) 14 cm long was inserted. The pipe was connected to an ordinary medical syringe 4 (for 20 ml) instead of the needle.

At the time of injection we opened a small slit in the thermostat chamber; through it we inserted the pipe of the syringe into the hole in the cone, and for a time of the order of 10 sec we injected the liquid; after that we plugged up the hole and closed the chamber again. Within that time the temperature of the working unit remained practically unchanged. During injection we usually raised the upper plate by 0.5 mm above the cone because this facilitates injection. When injection of the liquid was finished, the plane with the cone were joined again, with the chamber closed. Thus from the start of injecting to the start of the testing no more than 15-20 sec passed.

The tests were carried out in the temperature range 68-100°C. It was demonstrated that at 68°C there is initial (up to 2 min) steady flow with constant viscosity (viscosity plateau), and then viscosity begins to increase linearly (Fig. 2a).† We note that the viscosity

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* Composition of the plastisol: 50% polyvinyl chloride, 47.7% plasticizer, the rest are special-purpose additives (stabilizers, dyestuffs, etc.).

† When the time was longer (not shown in Fig. 2a), the growth rate of the viscosity decreased somewhat.

TABLE 1. Coefficients Determining the Viscosity of Plastisols at Different Temperatures

T, °C	21	40	56	68	82	92	100
a, Pa·sec	—	—	—	$4{\cdot}10^{-4}$	$4{\cdot}10^{-3}$	$2{,}7{\cdot}10^{-2}$	$2{,}7{\cdot}10^{-1}$
b, Pa	3,5	1,3	0,58	0,4	0,29	0,19	—

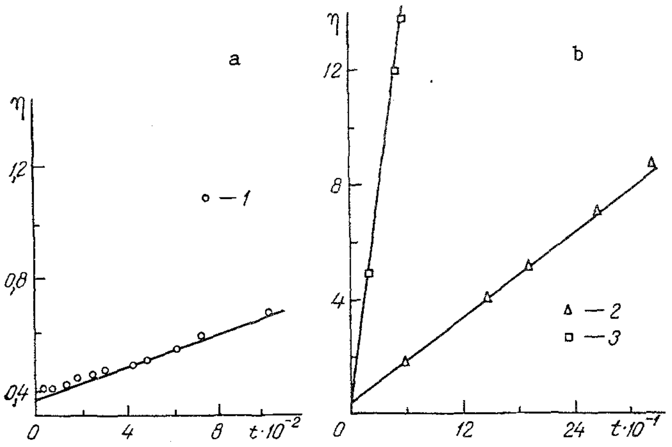

Fig. 2. Dependences of η_∞ (Pa·sec) on time t (sec) for γ = 36 $\sec^{-1}$ and different experimental temperatures, °C: a) 1) 68; b) 2) 92, 3) 100.

on the plateau practically corresponds to the length of the line segment intercepted by the straight line $\eta_\infty(t)$ on the axis η_∞. During the process of gelling the viscosity was practically independent of whether shear strain ($\gamma \leq 36$ $\sec^{-1}$) was effected continuously or only at instants of discrete measurements.

At 82, 92, and 100°C we found solely linear dependences of the viscosity η_∞ on time t (since the time interval was so short, the plateau was not investigated). Figure 2b shows only the dependences $\eta_\infty(t)$ at 92 and 100°C.

Thus, with fixed temperature, the dependence of the viscosity η_∞ on time t may be assumed with a practical degree of accuracy to be the following:

$$\eta_\infty = a(T)t + b(T), \tag{1}$$

where $a(T)$ = const and $b(T)$ = const at fixed temperature.

The dependence ln $a(T)$ turned out to be linear (Table 1), hence follows that

$$a(T) = a(T_0)\exp[m(T - T_0)], \tag{2}$$

where m = 0.22; T_0 is some fixed temperature, °K.

The dependence ln b(1/T) is also linear (see Table 1),* hence follows that

$$b(T) = b(T_0)\exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{3}$$

for $(T - T_0)/T_0 \ll 1$

$$b(T) = b(T_0)\exp[-k(T - T_0)], \quad k = E/RT_0^2, \tag{4}$$

where E = 8.4 kcal/mole, R = $2{\cdot}10^{-3}$ kcal/mole.

Thus, for a PVC base plastisol with initial viscosity (t = 0) the Arrhenius dependence on the temperature is fulfilled (see, e.g., [5]). For T_0 = 68°C k ≈ $4{\cdot}10^{-2}$.

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* The values of b for T ≳ 82°C were determined at the places where the straight lines (Fig. 2b) intersected the axis η_∞.

It follows from (2) and (4) for certain constants that the decrease of b(T) proceeds much more slowly than the increase of $a(T)$. For instance, when the temperature changes from 92 to 100°C, b(T) decreases by a factor of 1.3 whereas $a(T)$ increases by a factor of 9.

We note (without presenting experimental values) that when we regard the dependence of the viscosity on temperature and time in the range where the viscosity depends on the strain rate, then

$$\eta = \eta_\infty \varphi(\dot{\gamma}), \quad \varphi \geqslant 1, \tag{5}$$

where η_∞ was determined in (1)-(3), and φ is a function of the strain rate γ only.

Dependences (1)-(3), (5) turned out to be correct (with a somewhat lower accuracy of description of the experiment) also for PVC plastisol* with distinct thixotropic properties. With T_0 = 68°C, $a(T_0)$ = 0.1 Pa, $b(T_0)$ = 1.4 Pa·sec, m = 0.22, E = 5.3 kcal/mole. In this plastisol with distinct anomaly of viscosity, maximal stress was attained instantaneously upon specification of shear intensity with constant strain rate ($\gamma > 1$ sec^{-1}), and then the stress decreased to a steady value with viscosity η. The maximal stress depended on the time of "recovery" of the medium between experiments, and it tended to a steady value for short times (a few seconds) of recovery. As regards filling of the molds, where the strain rates change fairly continuously with time, the thixotropic nonsteady phenomena may be neglected.

Proceeding from the above-described rheological properties of plastisols, we want at the end to draw some conclusions concerning the isothermal filling of thin molds with them (at mean strain rates γ corresponding to a viscosity that does not depend on γ). It follows from dimensional considerations that the time required for filling the mold t_f is correlated with the injection pressure P by the following formula:

$$t_f = \frac{b}{P} f\left(\frac{a}{P}\right), \quad \lim_{x \to 0} f(x) = c, \tag{6}$$

where f is a monotonically increasing function, and c is a constant depending on the geometric parameters of the mold.

When the gelling of the plastisol is slight, expression (6) for filling of the mold is simplified:

$$t_f = \frac{b}{P} c.$$

NOTATION

γ, shear strain rate; T, temperature; η_∞, lowest Newtonian viscosity; t^*, time required for heating the liquid; h_{max}, largest gap between cone and plane of the rheogoniometer; ξ, thermal diffusivity; d, hole diameter; d_p, diameter of the syringe pipe; t, duration of the experiment; a and b, parameters determining the rheological behavior of the medium; m and k, constants determining the rate of change of the temperature-dependent parameters a and b; P, pressure of the injection into the mold; t_f, time required for filling the mold; f and c, function and constant, respectively, depending on the geometric parameters of the molds; η, effective viscosity; φ, component of the viscosity η depending solely on γ; E, activation energy of viscous flow; R, gas constant.

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*In percentage composition the plastisol was similar to the first one, differing only in the brands of the PVC and of the plasticizer.