MECHANICAL PARAMETERS OF DISPERSED SYSTEMS UNDER CYCLIC DEFORMATION WITH VARIOUS AMPLITUDES

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The mechanical behavior is reported for dispersed systems subject to cyclic deformation with or without steady-state flow. The mechanical characteristics are found to alter considerably.

Considerable theoretical and practical importance attaches to the effects of cyclic deformation on the mechanical behavior of dispersed systems, because we need to know the flow laws and because it may be possible to accelerate the processing of such systems, in particular dye and pigment pastes, as well as facilitating the design of processes for dispersing, transporting, and drying such materials.

There are many papers [1-12] on the effects of vibration on the mechanical properties of dispersed systems: concrete mixtures, bitumens, clay suspensions, etc., and it has been shown that the viscous behavior is much affected by vibration. However, these papers deal only with the effects of vibration on the viscosity and shear strength.

One can obtain more detailed information on the behavior of dispersed systems by employing polymer research methods, in particular cyclic shear, which gives the complex dynamic viscosity $\eta^* = \eta' - i\eta''$. The measurements are made with various strain amplitudes γ_0 and circular frequencies $\omega = 2\pi f$. From γ_0 we get the amplitude $\dot{\gamma}_{max} = \gamma_0 f$ of the deformation rate, while from η^* we get the complex shear modulus $G^* = \eta^* i\omega = G' + iG''$; where G' is the elastic modulus and G'' is the loss modulus.

The behavior of a viscoelastic material is considered to be linear if G^* is a function of frequency alone (is not dependent on γ_0); the structure is then unaltered. However, nonlinearity may set in at high amplitudes, $G^* = \psi(\gamma_0)$, and the structure changes. The threshold for this can be detected from the onset of nonlinearity. If the structure is disrupted, G' and G'' should decrease as γ_0 increases.

We have examined the nonlinear behavior of dispersed systems under cyclic and continuous shear strain, alone or combined.

We used copper phthalocyanin paste, which is used for bulk dyeing of viscose for fiber production. The paste contains also in a 1 : 1 ratio NF dispersal agent (sodium dinaphthyldimethane disulfonate) to prevent particle clumping, with 72 wt. % dry matter overall. The pigment particle size does not exceed 5 μm.

We used a coaxial-cylinder vibrorheometer [14] at 22°C over the range 6-110 Hz. The methods of measurement and calculation have previously been described [14, 15].

The following results were obtained in cyclic shear.

Figure 1 shows G' and G'' as functions of $\dot{\gamma}_{max}$ for several frequencies. The $G'(\dot{\gamma}_{max})$ and $G''(\dot{\gamma}_{max})$ curves show nonlinearity, but the oscillations remained reasonably sinusoidal, so the linear theory of viscoelasticity was used in the calculations.

The $G''(\dot{\gamma}_{max})$ curves for low $\dot{\gamma}_{max}$ represent a linear range, but this for $G'(\dot{\gamma}_{max})$ lies at values lower than those used here. Also, G' falls more rapidly than G'' in the nonlinear range.

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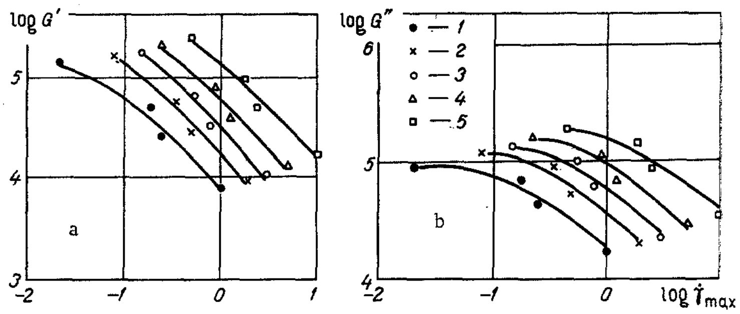

Fig. 1. Dependence on shear rate amplitude for: a) G'; b) G'' with log ω of: 1) 1.6; 2) 1.9; 3) 2.1; 4) 2.3; 5) 2.6.

In general, nonlinearity is seen earlier on the $G'(\dot{\gamma}_{max})$ curve for any dispersed system because such a system does not allow considerable reversible deformation under flow conditions and is disrupted even by small deformations [16].

G' and G'' increase with frequency in the linear and nonlinear ranges. Nonlinearity involves elimination of the low-frequency part of the complex dynamic modulus. Here there is a similarity in nonlinear behavior between dispersed (two-phase) and polymeric (single-phase) systems.

Figure 2 shows $|\eta^*|$ for the smallest $\dot{\gamma}_{max}$ as a function of frequency (curve 1) and also the effective viscosity η as a function of strain rate $\dot{\gamma}$ as measured in the steady state (curve 2). The $|\eta^*|(\omega)$ and $\eta(\dot{\gamma})$ curves are mutually displaced by a along the abscissa, and this quantity may be taken as approximately constant. The curves coincide if $\dot{\gamma} = a\omega$, which distinguishes dispersed systems from polymer ones, for which $|\eta^*| = \eta$ for $\dot{\gamma} = \omega$.

Figure 3 shows: I) $|\eta^*|$ as a function of $\dot{\gamma}_{max}$ for various ω; II) η as a function of $\dot{\gamma}$ for various ω. To the left of the $|\eta^*|(\dot{\gamma}_{max})$ curves is shown the tendency towards linear behavior. These curves have a single envelope, and the critical value γ_{max}^{cr} corresponds to the transition; this value increases with ω. The $|\eta^*|(\dot{\gamma}_{max})$ and $\eta(\dot{\gamma})$ curves confirm the view [13] that the nonlinearity mechanisms are similar in periodic shear and steady-state flow.

The $|\eta^*|(\dot{\gamma}_{max})$ and $\eta(\dot{\gamma})$ curves are mutually displaced on account of the relation between $\dot{\gamma}_{max}$ and $\dot{\gamma}$, since $\gamma_{max} = \gamma_0 f$; also, $\dot{\gamma}_0^{cr}$ (nonlinearity transition) is readily determined as a function of ω. As there is only 11% change in the frequency range used, one can put γ_0^{cr} = const approximately. Also, we put $\dot{\gamma} = a\omega$ for dispersed systems to get $\log \dot{\gamma}_{max} = \log \gamma_0(\omega/2\pi) = \log \dot{\gamma} + \log \gamma_0/2\pi a$. The envelope to curve 1 corresponds to $\gamma_0 = \gamma_0^{cr}$, so we have approximately that $\log \gamma_0^{cr}/2\pi a = 1.9$ (constant), so curves I and II may be superimposed with little error.

The following is the strain energy for a given $\dot{\gamma}_{max}^{cr}$ and corresponding ω:

$$E = \frac{4\pi^3 |\eta^*| (\dot{\gamma}_{max}^{cr})^2}{\omega}.$$

The critical E (nonlinearity transition) are independent of ω to a first approximation at $E_{cr} = 1.2 \cdot 10^2$ erg / cm^2, which is only 1/400 of the E_{cr} for P-20 polyisobutene [13]. This would appear to be the energy of the bonds between the particles.

We also used oscillations superimposed on steady-state flow [14]; Fig. 4 shows the shear stress τ as a function of f for various $\dot{\gamma}$ and $\log \gamma_0 = \bar{2}.44$ (constant). It is characteristic that there is a low-frequency part (0-25 Hz), where $d\tau/df$ is negative, and a part $f > 25$ Hz where τ is nearly independent of f. This occurs because: 1) the dynamic moduli and the resistance to steady-state flow increase with f in the linear and nonlinear regions for γ_0 constant; 2) the structure is disrupted as $\dot{\gamma}_{max}$ increases in the nonlinear region, so the dynamic moduli and the resistance decrease. It may be that in the first part the fall in the moduli and resistance due to disruption are much more pronounced than the increase with ω, while in the second part the two factors make equal contributions, and so τ becomes independent of f. This effect has been observed [12] in the displacement of dispersed systems by vibration.

Figure 5 shows that the curves shift to higher $\dot{\gamma}$ and alter in slope as γ_0 increases.

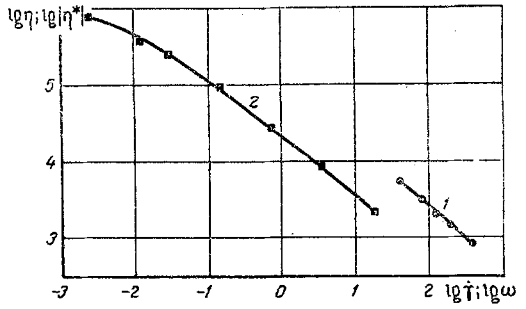

Fig. 2

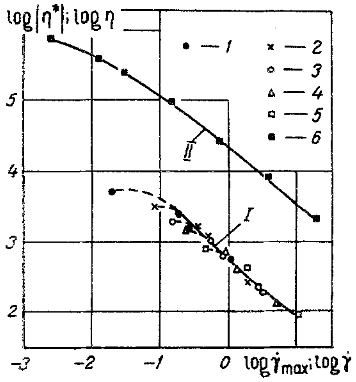

Fig. 3

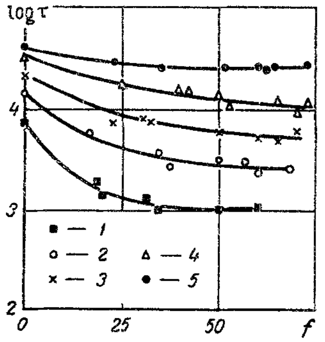

Fig. 4

Fig. 2. 1) $|\eta^*|$ as a function of ω; 2) η as a function of $\dot{\gamma}$.

Fig. 3. I) $|\eta^*|$ as a function of $\dot{\gamma}_{\max}$; II) η as a function of $\dot{\gamma}$ for log ω of: 1) 1.6; 2) 1.9; 3) 2.1; 4) 2.3; 5) 2.6. Curve 6 is from experiment.

Fig. 4. Shear stress τ as a function of f with $\log\gamma_0 = \bar{2}.44$ and $\log\gamma$ of: 1) $\bar{2}.44$; 2) $\bar{1}.15$; 3) $\bar{1}.85$; 4) 0.55; 5) 1.25.

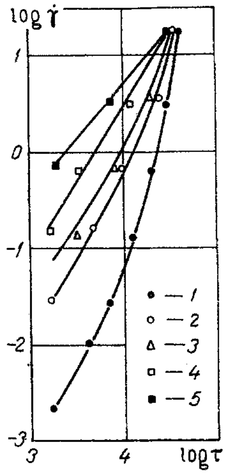

Fig. 5. Relation of τ to $\dot{\gamma}$ at 20 Hz for $\log\gamma$ of: 1) $-\infty$; 2) $\bar{2}.44$; 3) $\bar{2}.72$; 4) $\bar{2}.96$; 5) $\bar{1}.25$.

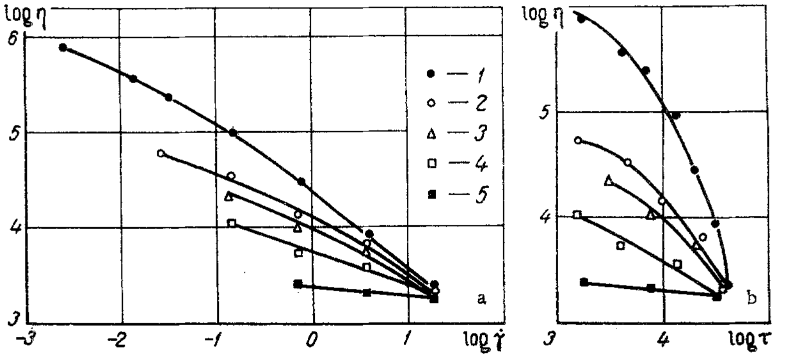

Fig. 6. Dependence of $\log\eta$ at 20 Hz on: a) γ; b) $\log\tau$ for $\log\gamma_0$ of: 1) $-\infty$; 2) $\bar{2}.44$; 3) $\bar{2}.72$; 4) $\bar{2}.96$; 5) $\bar{1}.25$.

Figure 6 shows that vibration greatly reduces η, e.g., at 20 Hz and $\log\gamma_0 = \bar{1}.25$, η is reduced by a factor 400 for $\log\tau = 3.2$. The effect is even larger at higher strain amplitudes.

These effects can be explained in terms of the flow mechanism. The flow resistance of a dispersed system is composed of: 1) that resistance for the medium; 2) the displacement resistance of the particles; 3) the flow resistance of the dispersion medium and particles. At low τ and γ, where the structure is only slightly disrupted, the vibrations reduce η considerably; higher τ and γ increase the extent of structure disruption, but at the same time the flow resistance of 3) increases, i.e., the proportion of the resistance related to structure disruption is reduced, and hence there is a marked reduction in η at low γ. Increased γ_0 cause more extensive disruption, which results in reduced η. Oscillations superimposed on a steady flow at low τ and $\dot{\gamma}$ greatly reduce the Newtonian viscosity, and the more so the greater the oscillation amplitude; but a dispersed system behaves as a non-Newtonian liquid at high τ and $\dot{\gamma}$.

NOTATION

η^*	is the complex viscosity;
η', η''	are the real and imaginary components of complex viscosity;
γ_0	is the deformation amplitude;
ω	is the circular frequency;
f	is the frequency;
$\dot{\gamma}_{\max}$	is the amplitude of deformation rate;
G^*	is the complex shear modulus;
G', G''	are the shear and loss moduli;
η	is the effective viscosity;
$\dot{\gamma}$	is the shear rate;
τ	is the shear stress;
E	is the strain energy.

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