The Rheological Properties of Concentrated Suspensions. III. Dynamic Properties and Their Correlations with Stationary Flow Properties

By Masaharu TAKANO

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In a previous paper[1] the construction and principles of a versatile rheometer have been described. The dynamic properties of concentrated suspensions at lower frequencies and stationary flow properties at very low rates of shear may be measured with this apparatus. Preliminary investigations of the dynamic properties of concentrated suspensions have been reported on in another previous paper.[2]

It is the purpose of the present paper to examine the concentration dependence of dynamic properties and their correlations with stationary flow properties and to prove the validity of theoretical considerations based on a network model.[3]

Experimental

Materials.—The fillers used in this work were barium sulfate of a chemical grade and barium sulfate coated with sodium stearate; both of these have very narrow size distributions. The mediums used were linseed oil and polyisobutylene whose number average molecular weight is 858. The characteristics of the materials are listed in Table I.

The Preparation of Suspensions.—The filler was dried at 110°C in a vacuum of 20 mmHg for three hours prior to the preparation of suspensions. Suspensions were prepared by ten "tight" passes of the mixed components through a three-roll paint mill, with a roll 5 cm. in diameter, 10 cm. long and with revolution velocities of 18, 60 and 170.5 r.p.m. The additive was adsorbed to the filler before the preparation of suspensions. Suspensions prepared in such a manner were kept at 30°C for six days before being measured.

Apparatus and Methods.—The apparatus used in this work has been described in detail in a previous paper.[1] The apparatus can be used as a rotational viscometer and as an oscillatory viscoelastometer under the same geometrical conditions. For this work, stationary flow properties at very low rates of shear and dynamic properties at lower frequencies (below 1 c.p.s.) were measured.

In simple shear experiments, the shearing stress, S, and the apparent rate of shear, $\dot{\gamma}$, at the surface of the inner cylinder were given as follows:

$$S=T/2\pi R_i^2 L=k\theta/2\pi R_i^2 L \tag{1}$$

$$\dot{\gamma}=2\omega/\{1-(R_i/R_o)^2\} \tag{2}$$

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1) H. Kambe and M. Takano, *Rept. Aeronaut. Res. Inst., Univ. Tokyo*, **28**, 159 (1963).

2) M. Takano and H. Kambe, *J. Japan Soc. Test. Matls. (Zairyô Shiken)*, **10**, 315 (May, 1961).

3) M. Takano, This Bulletin, to be published.

TABLE I. CHARACTERISTICS OF MATERIALS

Material	Viscosity* at 30°C poises	Density at 30°C g./cm³	Particle size μ		
			$(\overline{R})$	$(\overline{R^2})^{1/2}$	$(\overline{R^3})^{1/3}$
Barium sulfate	—	4.50	0.075	0.079	0.082
Linseed oil	59.3	0.960	—	—	—
Polyisobutylene	154.0	0.883	—	—	—

* Measured by a capillary viscometer.

TABLE II. EXPERIMENTAL CONDITIONS

Radius of outer cylinder	R_o	1.400 cm.	
Radius of inner cylinder	R_i	1.250 cm.,	1.000 cm.
Depth of outer cylinder		8.365 cm.	
Length of inner cylinder	L	5.000 cm.,	4.000 cm.
Maximum angular deflection of inner cylinder	θ_o	below 4 degrees	
Region of frequency	ν	from 0 to 1 c. p. s.	
Torsional constant	k	from 0 to 8.55×10^3 dyn.-cm./deg.	
Amplitude of shear strain (at wall of inner cylinder)	γ_{max}	below 0.685,	below 0.285
Amplitude of shear stress (at wall of inner cylinder)	S_{max}	below 11.7 dyn./cm²,	below 55.0 dyn./cm²
Range of revolution velocity of outer cylinder		from 0 to 400 r. p. m.	

where R_i and R_o are the radii of the inner and outer cylinders respectively; L is the length of the inner cylinder; T, the torque; k, the torsional constant of the inner cylinder; θ, the angular deflection of the inner cylinder, and ω, the angular velocity of the outer cylinder.

In dynamic measurements, the basic equation of the motion of the inner oscillatory unit is:[1,4,5]

$$(M+m+C)\mathrm{d}^2\theta/\mathrm{d}t^2+\{(\eta'/A)+B\}\mathrm{d}\theta/\mathrm{d}t+(G'/A)\theta=T \tag{3}$$

$$T=Ki_d-k\theta \tag{4}$$

where M, C, B and K are the instrument constants; m is the moment of inertia of the sample; A the shape factor; i_d, the current through a torque motor which gives torque to the inner cylinder, and η' and G' are the dynamic viscosity and the dynamic modulus of the sample respectively. When the moment of inertia of sample m is negligibly small compared to $(M+C)$ and the current, i_d, changes sinusoidally, the dynamic viscosity and the dynamic modulus are given by the following equations:[1,4,5]

$$\eta'=A[\{K'(f_{d_0}/f_{\theta_0})\sin d\}/\omega-B] \tag{5}$$

$$G'=A[K'(f_{d_0}/f_{\theta_0})\cos d-k+(M+C)\omega^2] \tag{6}$$

where f_{d_0} and f_{θ_0} are the amplitudes of the recorded curves of the current, i_d, and of the deflection, θ, respectively; K' is the instrument constant, and d, the phase lag between the current and the deflection.

The shape factor A and the phase lag d are given as follows:

$$A=(1/4\pi L)\{(1/R_i)^2-(1/R_o)^2\} \tag{7}$$

$$d=\cos^{-1}\{f^2{}_{\theta_0}+f^2{}_{d_0}-f^2{}_{s_0})/2f_{\theta_0}f_{d_0}\} \tag{8}$$

where f_{s_0} is the amplitude of recorded curve of difference between the current and the deflection.[1]

The dimensions of the assemblies of coaxial cylinders and the experimental conditions are listed in Table II. The temperature was maintained at 30±0.2°C during measurements. For Newtonian liquids, the dynamic experiments and the simple shear measurements were made within a range of error of ±10%.

Experimental Results and Discussion

The Influence of the Conditions of Mixing and Resting.—The rheological behavior of a disperse system is closely related to the state of the flocculation of its particles and is influenced by the conditions of preparation and resting.

For the study of the influence of mixing conditions, a small quantity of suspension was taken out after each pass through the mill and examined rheometrically. Figure 1 shows the relation between the dynamic properties of suspensions of barium sulfate in linseed oil and in polyisobutylene, with and without water added, and the number of passes through the mill.

In suspensions of barium sulfate in linseed oil with water added, the higher dynamic viscosity and dynamic modulus observed at the earlier stages of milling decrease rapidly with milling to limiting values which are almost independent of the amount of water. Without

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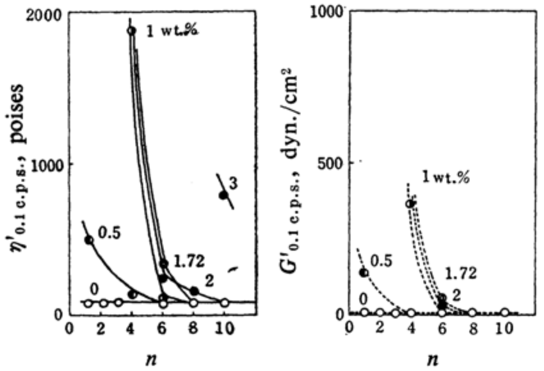
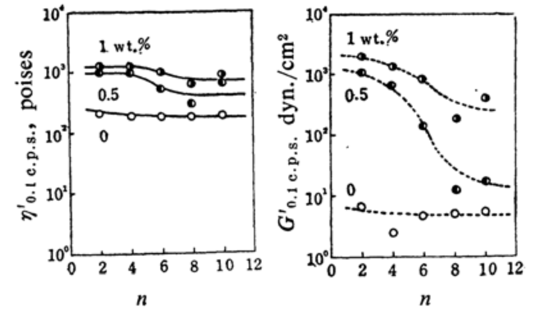
4) T. E. Morrisson, L. J. Zapas and T. W. DeWitt, *Rev. Sci. Instr.*, **26**, 357 (1955).

5) R. H, Shoulberg, F. H. Zimmerli and O. C. Kohler, *Trans. Soc. Rheology*, **3**, 27 (1959).



(a) 40 wt. % suspensions of barium sulfate in linseed oil, at 0.1 c.p.s., with or without water added.



(b) 10 wt. % suspensions of barium sulfate in polyisobutylene, at 0.1 c.p.s., with or without water added.

Fig. 1. Influence of the number of passes through the mill on the dynamic properties.

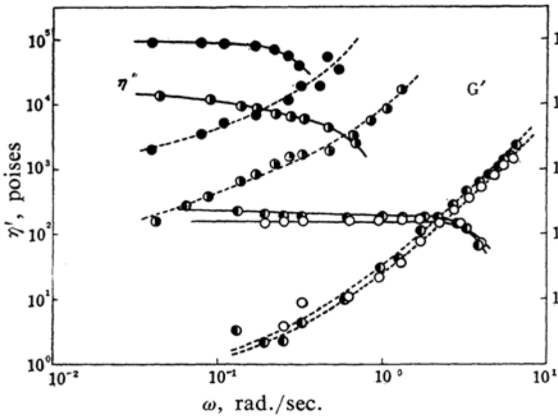


Fig. 4. Dependence of the dynamic properties on the concentration and the frequency in the suspensions of barium sulfate in polyisobutylene (30°C): ○, 0 wt. %; ◐, 10 wt. %; ◑, 20 wt. %; ●, 30 wt. %.

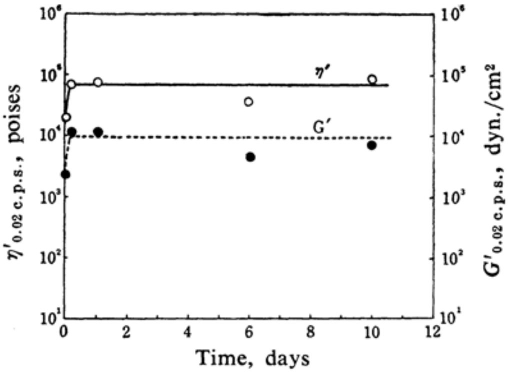


Fig. 2. Change in the dynamic properties with resting time, at 0.02 c.p.s., in 30 wt. % suspension of barium sulfate in polyisobutylene (30°C).

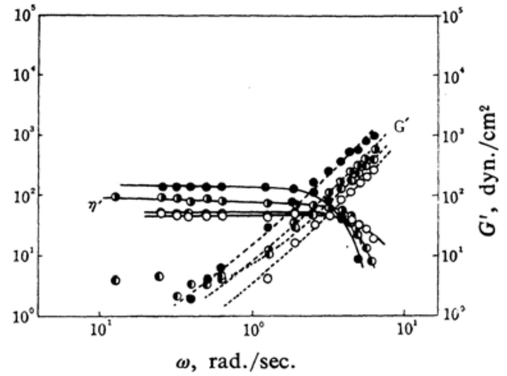


Fig. 3. Dependence of the dynamic properties on the concentration and the frequency in the suspensions of barium sulfate in linseed oil (30°C): ○, 0 wt. %; ◐, 10 wt. %; ◑, 30 wt. %; ● 50 wt. %.

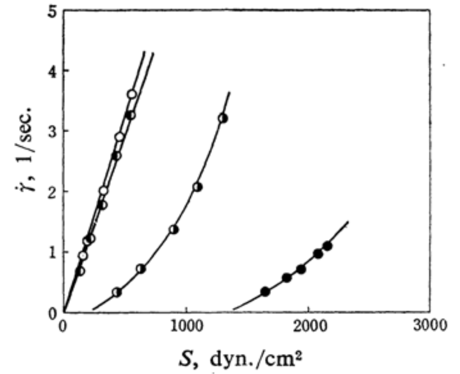


Fig. 5. Flow curves of the suspensions of barium sulfate in polyisobutylene at various concentrations (30°C): ○, 0 wt. %; ◐, 10 wt. %; ◑, 20 wt. %; ●, 30 wt. %.

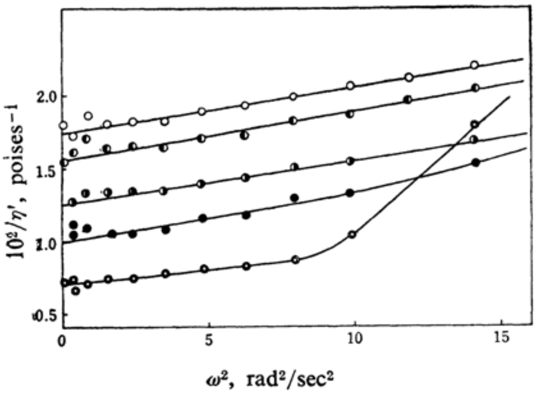


Fig. 6. Dependence of the dynamic viscosity on the concentration and the frequency in the suspensions of barium sulfate in linseed oil, with 0.5 wt. % water added (30°C): ○, 10 wt. %; ◐, 20 wt. %; ◑, 30 wt. %; ●, 40 wt. %; ◎, 50 wt. %.

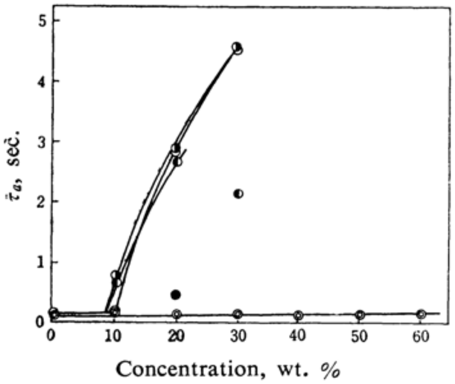
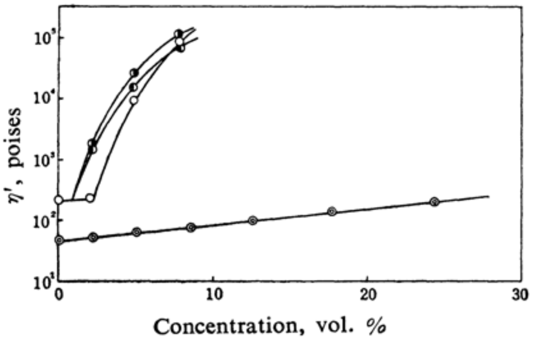
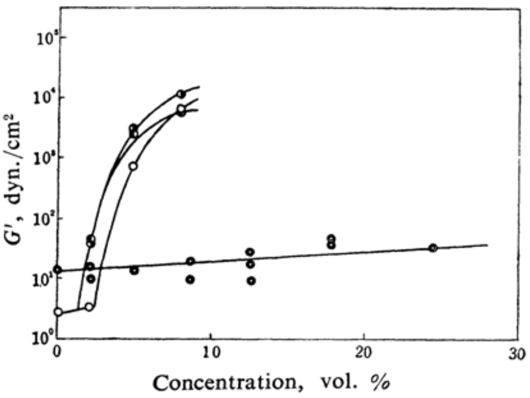


Fig. 7. Dependence of the apparent relaxation time on the concentration in various suspensions: ○, barium sulfate in polyisobutylene; ◐, barium sulfate in polyisobutylene, with 0.5 wt. % water added; ◑, barium sulfate in polyisobutylene, with 1.0 wt. % water added; ●, barium sulfate coated by 1 wt. % sodium stearate in polyisobutylene; ◎, barium sulfate in linseed oil, with or without water added.



(a) Dynamic viscosity.



(b) Dynamic modulus.

Fig. 8. Concentration dependence of the dynamic properties: ○, barium sulfate in polyisobutylene, at 0.02 c.p.s. ◐, barium sulfate in polyisobutylene, with 0.5 wt. % water added, at 0.02 c.p.s. ◑, barium sulfate in polyisobutylene, with 1.0 wt. % water added, at 0.02 c.p.s. ◎, barium sulfate in linseed oil, with or without water added, at 0.20 c.p.s.

water added, the dynamic properties of suspensions in linseed oil show no changes upon milling.

In suspensions of barium sulfate in polyisobutylene, the dynamic viscosity and dynamic modulus of suspensions are generally decreased by milling at the earlier stages and approach limiting values upon repeated passages through the mill.

Figure 2 shows the increase in the dynamic viscosity and dynamic modulus with resting time in a suspension of barium sulfate in polyisobutylene. The dynamic properties seem to have stationary values after resting for about three hours.

Data for suspensions which have been passed ten times through the mill and rested for three hours will be compared below.

The Concentration Dependence and Frequency Dependence of Dynamic Properties. — The dynamic viscosity and the dynamic modulus of suspensions are shown in Figs. 3 and 4 as functions of the frequency and of the concentration. Stationary flow curves of suspensions in polyisobutylene at various concentrations are illustrated in Fig. 5.

The linseed oil and polyisobutylene used in this work are viscoelastic by themselves. In a previous paper[3] it has been pointed out theoretically that the dynamic properties of concentrated suspensions are given approximately by the sum of the viscoelasticities of the medium and network-structures formed by suspended particles.

Assuming a suspension as a Maxwell body, we can get the apparent relaxation time, τ_a, from the following equation:

$$1/\eta'_s(\omega) = 1/\eta'_s(0) + (\tau_a{}^2/\eta'_s(0))\omega^2 \qquad (9)$$

where $\eta'_s(\omega)$ is the dynamic viscosity of the suspension at the angular frequency ω. Figure 6 shows the relation of $1/\eta'_s(\omega)$ to ω^2 for suspensions of barium sulfate in linseed oil. The apparent relaxation times obtained experimentally for various suspensions are listed in Table III. The apparent relaxation time generally increases with an increase in the concentration, as is shown in Fig. 7. In linseed oil, the apparent relaxation time of the suspension shows a slight change with the concentration. In polyisobutylene, on the other hand, the apparent relaxation time increases abruptly above a critical concentration, at which a network structure is formed by the particles in the medium.

TABLE III. APPARENT RELAXATION TIMES OF SUSPENSIONS OF BARIUM SULFATE IN LINSEED OIL AND POLYISOBUTYLENE (30°C)

Concentration wt. %		Na-stearate*	Apparent relaxation time of suspension, sec.	
$BaSO_4$	H_2O*		In linseed oil	In polyisobutylene
0	0	0	0.09	0.21
10	0	0	0.10	0.21
	0.5	0	0.13	0.70
	1.0	0	0.13	0.84
20	0	0	0.12	2.9
	0.5	0	0.15	2.7
	1.0	0	0.16	2.9
	0	1	—	0.48
30	0	0	0.17	4.6
	0.5	0	0.15	2.1
	1.0	0	0.14	4.6
40	0	0	0.18	—
	0.5	0	0.18	—
	1.0	0	0.19	—
	2.0	0	0.09	—
	3.0	0	1.4	—
	0	1	>5.0	—
50	0	0	0.19	—
	0.5	0	0.15	—
	1.0	0	0.21	—
60	0	0	0.18	

* Based on barium sulfate.

The concentration dependence of dynamic properties at a given frequency is shown in Fig. 8 and in Table IV. In polyisobutylene, the dynamic viscosity and dynamic modulus of a suspension increase abruptly above a critical concentration. The mean free energy of the activation for breaking links between particles, ΔF, and the mean number of links to be broken for the separation of two neighboring particles, σ', can be evaluated from the critical concentration $\phi'_{crit.}$[3,6] In suspensions of barium sulfate in polyisobutylene, the energy of interaction, ΔF, has the order of $33\sim34\,kT$, while the mean number of links,

TABLE IV. DYNAMIC PROPERTIES OF SUSPENSIONS OF BARIUM SULFATE IN LINSEED OIL AND POLYISOBUTYLENE (30°C)

Concentration		Na-stearate*	G' dyn./cm²	η' poises	G' dyn./cm²	η' poises
$BaSO_4$	H_2O*		In linseed oil, at 0.20 c.p.s.		In polyisobutylene, at 0.02 c.p.s.	
0	0	0	12.8	47.0	2.7	170.0
10	0	0	2.8	45.8	3.1	225.0
	0.5	0	16.2	54.9	43.1	1360.0
	1.0	0	8.7	48.4	36.9	1450.0
20	0	0	12.7	58.2	727.0	9420.0
	0.5	0	12.9	60.6	2180.0	14200.0
	1.0	0	11.3	62.6	2590.0	26300.0
	0	1	—	—	0.0	997.0
30	0	0	0.0	68.9	6180.0	85900.0
	0.5	0	19.3	74.6	10400.0	53100.0
	1.0	0	9.4	73.3	10700.0	106000.0
40	0	0	26.1	89.7	—	—
	0.5	0	16.1	95.9	—	—
	1.0	0	28.4	87.5	—	—
	1.72	0	8.1	81.0	—	—
	2.0	0	19.8	85.7	—	—
	3.0	0	—	—	—	—
	0	1	4030.0	—	—	—
50	0	0	38.0	135.0	—	—
	0.5	0	50.6	135.0	—	—
	1.0	0	42.1	143.0	—	—
60	0	0	32.4	180.0	—	—

* Based on barium sulfate.

TABLE V. CRITICAL CONCENTRATION AND THE INTERACTION PARAMETERS IN SUSPENSIONS OF BARIUM SULFATE IN POLYISOBUTYLENE (30°C)

Concn. of water (wt. % based on barium sulfate)	0	0.5	1.0
ϕ'_{crit} in η' (vol. %)	2.0	0.8	0.8
ϕ'_{crit} in G' (vol. %)	2.0	1.2	1.2
$\Delta F/\boldsymbol{k}T$ in η' ($\sigma'=1$)	33.3	34.2	34.2
$\Delta F/\boldsymbol{k}T$ in G' ($\sigma'=1$)	33.3	33.3	33.8
σ' in η'	1.49_1	1.49_2	1.49_2
σ' in G'	1.49_1	1.49_2	1.49_2
$\Delta F/\boldsymbol{k}T$ in η' ($\sigma'=1.49$)	32.9	33.8	33.8
$\Delta F/\boldsymbol{k}T$ in G' ($\sigma'=1.49$)	32.9	33.4	33.4

σ', is 1.49, as Table V shows. These values coincide well with those evaluated from the stationary flow properties.[6] In suspensions of barium sulfate in linseed oil, the concentration dependence of the dynamic viscosity and the dynamic modulus are given by the following equations (at 0.20 c.p.s.):

$$\eta'_s(0.20)=\eta'_m(0.20)\exp(5.53\,\phi) \tag{10}$$

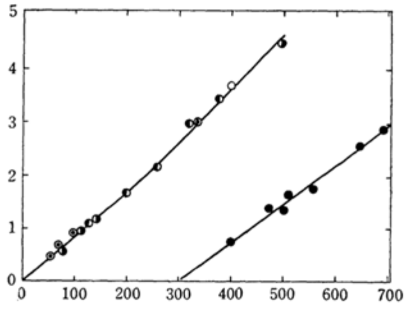
$$G'_s(0.20)=G'_m(0.20)\exp(3.92\,\phi) \tag{11}$$

where $\eta'_m(0.20)$ and $G'_m(0.20)$ are the dynamic viscosity and the dynamic modulus of an unfilled medium at 0.20 c.p.s. respectively, and where ϕ is the volume fraction of the filler. The increase in the apparent relaxation time with the concentration can be explained qualitatively by the difference in the concentration dependences between the dynamic viscosity and the dynamic modulus.

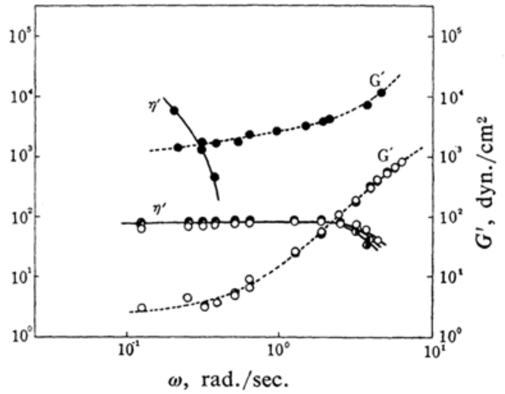
The Influence of Additions of Water and Sodium Stearate on the Dynamic Properties.— Dynamic properties also change upon the addition of additives which have an influence on the energy of interaction between particles, as is shown in Tables III, IV and V.

In relatively polar linseed oil, the dynamic viscosity and dynamic modulus of a concentrated suspension with water added increase in the earlier stages of milling, as is shown in Fig. 1. However, it is shown in Figs. 1, 8, 9 and Table IV that the dynamic properties decrease to limiting values upon milling, that these properties are slightly influenced by the amount of water, and that they are increased by coating particles with sodium stearate. The apparent relaxation time is also slightly influenced by the addition of water, as is illustrated in Table III.

In non-polar polyisobutylene, the dynamic viscosity and dynamic modulus of a concentrated suspension are increased by the addition of water independently of milling, as is shown in Figs. 1, 8, 10 and Table IV. The apparent relaxation time at lower concentrations also increases upon the addition of water, as Fig. 7 and Table III show. The critical concentration above which the dynamic properties increase appreciably is lowered, and the energy of interaction between particles, is increased by the addition of water, as is shown



(a) Flow curve.



(b) Frequency dependence of the dynamic properties.

Fig. 9. Influence of the addition of water and sodium stearate on rheological properties of 40 wt. % suspensions of barium sulfate in linseed oil: ○, without additive; ◐, with 0.5 wt. % water added; ◑, with 1.0 wt. % water added; ◉, with 2.0 wt. % water added; ●, coated by sodium stearate.

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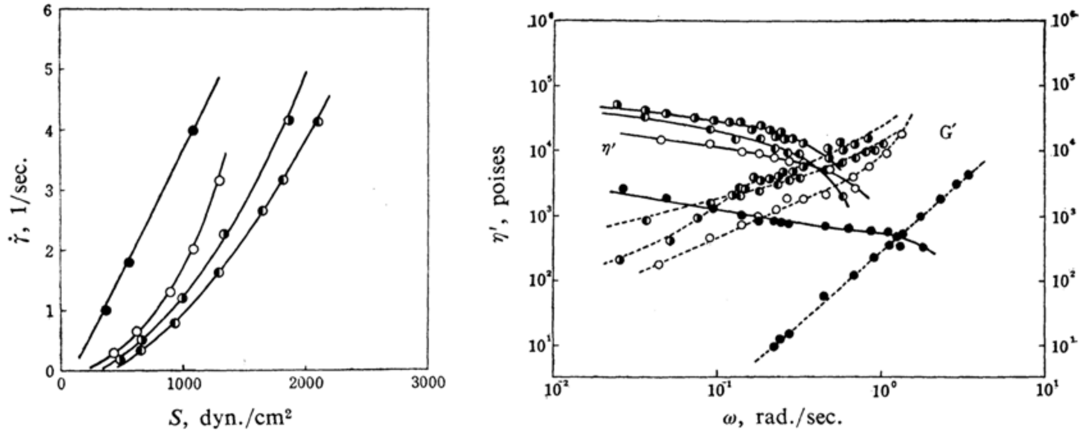
[6] M. Takano and H. Kambe, This Bulletin, to be published.



(a) Flow curve. (b) Frequency dependence of dynamic properties.

Fig. 10. Influence of the addition of water and sodium stearate on rheological properties of 20 wt. % suspensions of barium sulfate in polyisobutylene: ○, without additive; ◐, with 0.5 wt. % water added; ◑, with 1.0 wt. % water added; ●, coated by sodium stearate.

in Fig. 8 and Table V. The dynamic viscosity and dynamic modulus are decreased by coating particles with sodium stearate.

The change in the dynamic properties by additives must be attributed to the influence of the additive on the interactions between particles: van der Waals-London attractions,[7,8] capillary forces due to interfacial tension between additive and medium,[9-11] the repulsion of two electric double layers,[12] the entropic repulsion of adsorbed molecules of the medium on the surfaces of particles,[8,13] contractive forces arising from the elastic property of a medium when the medium is viscoelastic by itself,[14] and others. The diffusion of water into the polar medium must also be taken into account.

In the present experiments, it seems that capillary forces originating from the presence of water do not have a decisive effect on the interaction between particles at a stationary state of dispersion. The interfacial tension between water and linseed oil is larger than that between water and polyisobutylene, as shown in Table VI. Besides, it seems that water is adsorbed on the surfaces of particles without diffusion into the medium. If water adheres to the surfaces of particles, contractive forces originating from the viscoelastic properties of the medium may be decreased by the addition of water. In a previous paper,[3] the following equation has been derived for the frequency dependence of the dynamic viscosity:

TABLE VI. INTERFACIAL TENSION (26.3°C)

Interface	Interfacial tension* dyn./cm.
Water-Air	71.2
Linseed oil-Air	36.2
Polyisobutylene-Air	32.0
Linseed oil-Water	49.0
Polyisobutylene-Water	39.5

* Measured by Du Noüy's surface tension meter.

$$1/\{\eta'_s(\omega)-\eta'_m(\omega)\}=a+b\omega^2 \qquad (12)$$

where

$$a=\lambda^2{}_2\pi R_1/\boldsymbol{h}\exp(\Delta F/\boldsymbol{k}T)\,\sigma'(\phi-\phi'_{crit}) \qquad (13)$$

$$b=\boldsymbol{h}\pi R_1\exp(\Delta F/\boldsymbol{k}T)/4g^2{}_2\lambda^2{}_2\sigma'(\phi-\phi'_{crit}) \qquad (14)$$

In Eqs. 13 and 14, $\boldsymbol{h}$ and $\boldsymbol{k}$ are the constants of Planck and Boltzmann respectively; R_1 is the diameter of particles; λ_2, the distance by which particle moves whenever the secondary links between particles are broken reversibly; T, the absolute temperature; ΔF, the mean free energy of activation for breaking the links between particles; g_2, the mean stiffness of the secondary links, and σ', the mean number of links to be broken for separating two particles at very small deformations. If there are no

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7) H. C. Hamaker, *Physica*, **4**, 1058 (1937).

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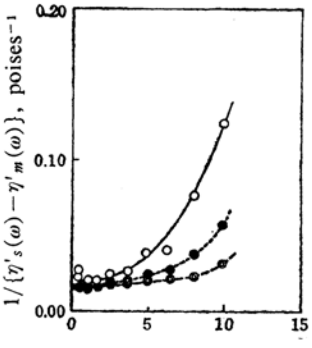

Fig. 11. Influence of the addition of water on the frequency dependence of the dynamic viscosity in 50 wt. % suspensions of barium sulfate in linseed oil: ○, without water; ◎, with 0.5 wt. % water added; ●, with 1.0 wt. % water added.

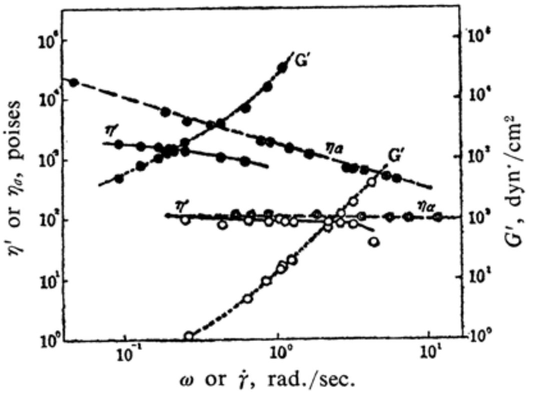

Fig. 12. Correlation between the dynamic properties and the apparent viscosity in 40 wt. % suspensions of barium sulfate in linseed oil: ○◎, with 2.0 wt. % water added (yield value, 0); ●◉, with 3.0 wt. % water added (yield value, 1280 dyn./cm²).

contractive forces arising from the viscoelastic property of the medium, the values of a and b must be effectively independent of the frequency. Figure 11 shows the relation of $1/\{\eta'_s(\omega)-\eta'_m(\omega)\}$ to ω^2. However, it has been assumed that the dynamic viscosity of a medium involving particles at the volume fraction ϕ is given by the following equation:[15]

$$\eta'_m(\omega)=\eta'_{mo}(\omega)(1+2.5\phi+7.17\phi^2+16.2\phi^3)$$

where $\eta'_{mo}(\omega)$ is the dynamic viscosity of an unfilled medium. The dependence of b on the frequency apparently decreases on the addition of water. Such a tendency is observed both in polar and in non-polar media.

The magnitude of the van der Waals-London attraction between two spherical particles can be approximately evaluated as in a previous paper.[6] The change in dynamic properties by additives can be explained at least qualitatively by considering van der Waals-London attractions between particles.[6] However, other forces must also be taken into account, particularly such forces as the contractive forces of the medium. In a polar medium, the repulsion of two electric double layers may have an influence on the interaction between particles. In a medium with a high molecular weight, the entropic repulsion of adsorbed macromolecules may be considered between particles.

The Correlation between Dynamic Properties and Stationary Flow Properties. — In unfilled media and pseudo-plastic suspensions, the apparent viscosity at lower rates of shear coincides with the dynamic viscosity at lower frequencies. In plastic suspensions, however, the former does not generally coincide with the latter.

In plastic suspensions, the apparent viscosity at lower rates of shear may be higher or lower than the dynamic viscosity at lower frequencies when they are compared with each other on the same time scale. Figures 12 and 13 show the shear-rate dependence of the apparent viscosity, along with the frequency dependence of dynamic viscosity and dynamic modulus. In a series of suspensions of barium sulfate in polyisobutylene, the apparent viscosity in simple shear experiments is lower than the dynamic viscosity on the same time scale. Such a tendency is observed independently of the presence of water. In suspensions of barium sulfate in linseed oil, with a large quantity of water added, the apparent viscosity is higher than the dynamic viscosity on the same time scale.

These correlations between the apparent viscosity and the dynamic viscosity are at least qualitatively explained by the network model described in the previous paper.[3] The dynamic viscosity at very small deformations, $\eta'_s(\omega)$, and the apparent viscosity, η_a, are given by the following equations:

$$\eta'_s(\omega)=\eta'_m(\omega)+(2/\pi R_1)g_2\{\tau_2/(1+\tau^2{}_2\omega^2)\}\sigma'(\phi-\phi'_{crit}) \tag{15}$$

$$\eta_a=S/\dot\gamma=\eta_{pl}+S_o/\dot\gamma \tag{16}$$

where η_{pl} and S_o are given as follows:

$$\eta_{pl}=\eta_m+(R_1^2/3)(g_1+g_2)\tau_2\{(6/\pi R_1^3)+(3\eta\dot\gamma/kT\pi\phi_c)\}\sigma(\phi-\phi_{crit}) \tag{17}$$

$$S_o=(R_1^2/3)g_1\gamma_1\{(6/\pi R_1^3)$$

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[15] V. Vand, *J. Phys. and Colloid Chem.*, **52**, 277, 300 (1949).

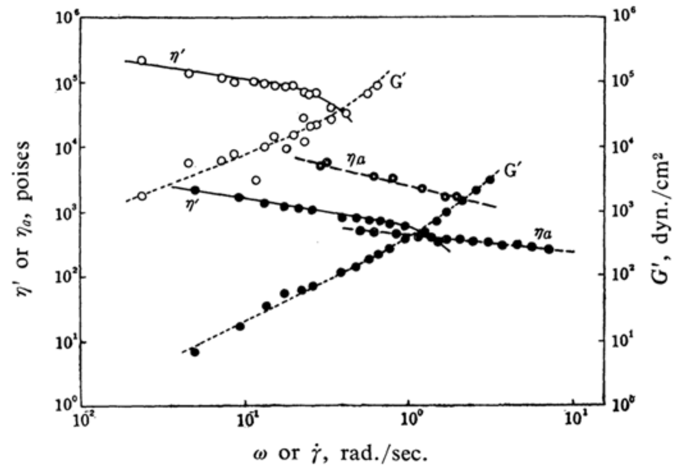


Fig. 13. Correlation between the dynamic properties and the apparent viscosity in suspensions of barium sulfate in polyisobutylene: ●◉, 10 wt. % suspension with 1.0 wt. % water added (yield value, 130 dyn./cm²); ○◎, 30 wt. % suspension with 1.0 wt. % water added (yield value, 1500 dyn./cm²).

$$+(3\eta\dot{\gamma}/kT\pi\phi_c)\}\sigma(\phi-\phi_{crit}) \tag{18}$$

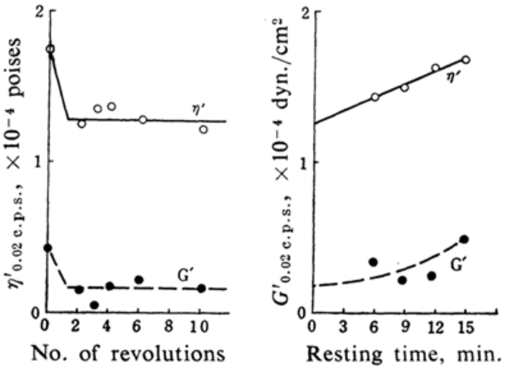
where g_1 is the mean stiffness of the primary links; τ_2, the relaxation time of the secondary links; γ_1, the mean strain of the primary links in the stationary flow; ϕ_c, the mean fraction of the volume occupied by particles in a multiple flocculate, and σ and ϕ_{crit} are the mean number of links to be broken for separating two particles and the critical concentration above which stationary links between particles would appear respectively at the shear-rate of $\dot{\gamma}$.³⁾ Equations 17 and 18 can be approximated by the following equations at very low rates of shear;³⁾

$$\eta_{pl}=\eta_m+(g_1+g_2)\tau_2(2/\pi R_1)\sigma'(\phi-\phi'_{crit}) \tag{17'}$$

$$S_o=(2/\pi R_1)g_1\gamma_1\sigma'(\phi-\phi'_{crit}) \tag{18'}$$

In pseudo-plastic suspensions, the apparent viscosity at a zero rate of shear must be equal to the dynamic viscosity at zero frequency because, in Eqs. 17′ and 18′, γ_1 and g_1 are effectively zero and $\eta'_m(0)$ is generally equal to η_m.

In plastic suspensions, the apparent viscosity must be infinite at a zero rate of shear if a remarkable change in the structure of the network is not effected by shearing forces, whereas the dynamic viscosity has a finite value on the same time scale. Such a case is encountered in suspensions of barium sulfate in linseed oil, with a large quantity of water added. However, if the network is broken appreciably by shearing forces, the apparent viscosity may occasionally be lower than the dynamic viscosity at a finite rate of shear, as in suspensions of barium sulfate in polyisobutylene, since in Eqs. 17 and 18 σ is decreased and ϕ_{crit} is increased by shearing forces.³⁾ Figure 14 shows the fall of dynamic properties by shearing actions and their restoration by resting the solution in a 20 wt. % suspension of barium sulfate in polyisobutylene. The abscissas represent the number of repeated revolutions at a given rate of shear (3.78 sec⁻¹) and the resting time after 30 revolutions. In this system, it seems that the network is easily broken down by shearing actions and that it takes at least fifteen minutes for the restoration of the broken network-structure. The discrepancy between the apparent viscosity and the dynamic viscosity at lower rates of shear seems to be related to the sensitivity of the network structure to shearing forces and



(a) Structure break down with shearing actions ($\dot{\gamma}$=3.78 sec⁻¹).

(b) Structure restoration after 30 revolutions.

Fig. 14. Change in the dynamic properties with shearing conditions in 20 wt. % suspension of barium sulfate in polyisobutylene.

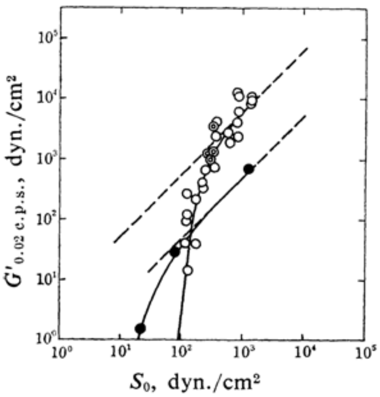


Fig. 15. Correlation between the dynamic modulus and the yield value: ○, suspensions of barium sulfate in polyisobutylene; ●, suspensions of barium sulfate in linseed oil, with water added; ◎, suspensions of barium sulfate coated by sodium stearate in linseed oil.

to the time necessary for the restoration of broken structures. Besides, it is likely that the discrepancy between viscosities is independent of the magnitude of yield value in stationary flow experiments, as is shown in Figs. 12 and 13.

The correlation of the dynamic modulus at a frequency of 0.02 c. p. s. and the yield value obtained by extrapolation to zero shear-rate in stationary flow experiments are shown in Fig. 15. The dynamic modulus apparently increases with an increase in the yield value.

According to theoretical considerations based on a network model,[3] the dynamic modulus, $G'_s(\omega)$, is given by the following equation at very small deformations:

$$G'_s(\omega)=G'_m(\omega) + (2/\pi R_1)\{g_1+g_2\tau_2^2\omega^2/(1+\tau_2^2\omega^2)\}\sigma'(\phi-\phi'_{crit}) \tag{19}$$

where $G'_m(\omega)$ is the dynamic modulus of a medium involving particles. If the dynamic modulus of the medium is negligibly small compared to that of the network structure formed by particles at lower frequencies and if the network is not changed by shearing forces, the dynamic modulus at lower frequencies must be approximately proportional to the yield value given by Eq. 18′ at very low rates of shear. Consequently, the slope in Fig. 15 must be approximately equal to unity. In the experimental results, the slope seems to approach unity only at higher concentrations, where stronger network structures may be formed by particles. The deviation from the theoretical prediction at lower concentrations seems to be connected with the amplitude dependence of the dynamic modulus. If the network structure is sensitive to shearing forces, it is likely that the network is broken down irreversibly at lower concentrations and that the dynamic modulus decreases with an increase in the amplitude of oscillation, since measurements are made with a constant amplitude of the activating current, i_{d_o}.

In suspensions of barium sulfate in polyisobutylene, the time dependence of the apparent viscosity resembles that of the dynamic viscosity, as is shown in Fig. 13. However, it is dangerous to attribute two behaviors to the same mechanism. As has been described in a previous paper,[3] the dependence of the apparent viscosity on the rate of shear is connected with the structural changes of the network caused by shearing forces, whereas the frequency dependence of the dynamic viscosity originates mainly from the relaxation of the network structures formed by particles in the medium. For the elucidation of the correlation between the dynamic properties and stationary flow properties of concentrated suspensions, further investigation of the amplitude dependence of rheological properties is necessary.

The Amplitude Dependence of Dynamic Properties.—In unfilled media and non-flocculated systems, the dynamic properties fall well within the linear viscoelasticity at smaller amplitudes of oscillation.

In flocculated systems, however, the dynamic viscosity and the dynamic modulus inevitably decrease with an increase in the amplitude of oscillation.[16-18] Figure 16 shows the amplitude dependence of the dynamic properties in a 10 wt. % suspension of barium sulfate in polyisobutylene, with 0.5 wt. % water added. In Fig.

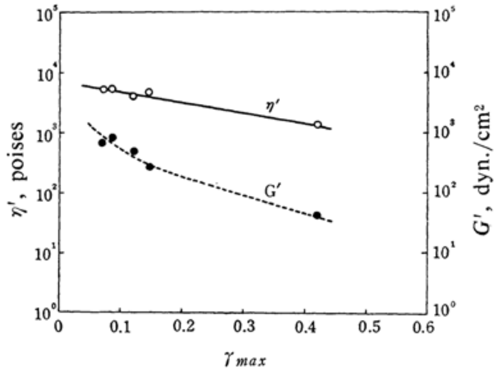


Fig. 16. Amplitude dependence of the dynamic properties in a 10 wt. % suspension of barium sulfate in polyisobutylene, with 0.5 wt. % water added, at 0.02 c.p.s.

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16) M. Senō, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 66 (1957).
17) R. B. Stambaugh, *Ind. Eng. Chem.*, **34**, 1358 (1942).
18) A. R. Payne, *J. Appl. Polymer Sci.*, **3**, 127 (1960).

16, the maximum shear strain at the wall of the inner cylinder, γ_{max}, is calculated as follows :19)

$$\gamma_{max,\, r=R_i} = 2\theta_0 R_0^2/(R_0^2 - R_i^2) \tag{20}$$

The amplitude dependence of the dynamic modulus is more remarkable than that of the dynamic viscosity. The amplitude dependence of the dynamic properties in flocculated systems is caused by the structural change in the network formed by particles and by the non-linearly elastic nature of the links between particles. In a previous paper,3) it has been theoretically pointed out that the dependence of the dynamic viscosity on amplitude mainly originates from the structural change in the network, while that of the dynamic modulus originates from both the structural change and the non-linearly elastic nature of the links between particles. According to theoretical considerations based on a network model,3) we obtain the following approximation at lower frequencies:

$$\begin{aligned}&\{G'_s(\omega)-G'_m(\omega)\}_{\dot{\gamma},f}/\{G'_s(\omega)-G'_m(\omega)\}_{\dot{\gamma},f\fallingdotseq 0}\\ &\quad\fallingdotseq\{(g_1)_{\dot{\gamma},f}/(g_1)_{\dot{\gamma},f\fallingdotseq 0}\}\{\eta'_s(\omega)-\eta'_m(\omega)\}_{\dot{\gamma},f}/\\ &\quad\{\eta'_s(\omega)-\eta'_m(\omega)\}_{\dot{\gamma},f\fallingdotseq 0}\end{aligned} \tag{21}$$

where the subscripts s and m represent the values of the suspension and the medium respectively, and $\dot{\gamma}$ and f represent the experimental conditions of the rate of shear and the shearing forces. In flocculated systems, since $G'_m(\omega)$ and $\eta'_m(\omega)$ may be negligibly small compared to $G'_s(\omega)$ and $\eta'_s(\omega)$, we have, approximately:

$$\begin{aligned}&\{G'_s(\omega)\}_{\dot{\gamma},f}/\{G'_s(\omega)\}_{\dot{\gamma},f\fallingdotseq 0}\\ &\quad\fallingdotseq\{(g_1)_{\dot{\gamma},f}/(g_1)_{\dot{\gamma},f\fallingdotseq 0}\}\{\eta'_s(\omega)\}_{\dot{\gamma},f}/\{\eta'_s(\omega)\}_{\dot{\gamma},f\fallingdotseq 0}\end{aligned} \tag{22}$$

Consequently, the difference between the amplitude dependences of dynamic properties, as shown in Fig. 16, may be regarded as a measure of the non-linearity of the elastic nature of the links between particles.

The experimental data given in this paper were obtained with a given amplitude of torque acting on the inner cylinder. The amplitude of the deflection of the inner cylinder was consequently decreased with an increase in the frequency. As a result of these features in dynamic properties and dynamic experiments, the apparent relaxation time of suspensions may be slightly shorter than those evaluated in the present experiments. Dynamic properties were measured with as small an amplitude as possible.

Summary

The dynamic properties and stationary flow properties of suspensions of barium sulfate in polyisobutylene and in linseed oil have been measured by the use of an electrically-recording rotational rheometer.

The concentration dependence, the influence of mixing conditions, the effects of the addition of water and of sodium stearate on the dynamic viscosity and the dynamic modulus, and the correlation of the dynamic properties with stationary flow properties have been examined experimentally.

In suspensions of barium sulfate in linseed oil, the dynamic viscosity and dynamic modulus increase monotonously with an increasing concentration, and no critical concentration is observed up to the highest concentration. The apparent relaxation time shows a slight increase with an increase in the concentration of particles.

In suspensions of barium sulfate in polyisobutylene, the dynamic viscosity and dynamic modulus increase abruptly above a critical concentration. The apparent relaxation time also increases remarkably above the critical concentration. The mean free energy of the activation for breaking links between particles and the mean number of links to be broken for the separation of two neighboring particles have been evaluated as 33∼34 kT and 1.49 respectively.

The influence of additives on dynamic properties resembles that on stationary flow properties and can be explained qualitatively by assuming a van der Waals-London attraction between particles. However, in a viscoelastic medium, contractive forces arising from the elastic property of the medium seems to be altered by the addition of additives.

For pseudo-plastic systems, the dynamic viscosity coincides with the apparent viscosity at lower frequencies. However, for plastic systems, the apparent viscosity may be higher or lower than the dynamic viscosity at lower frequencies, depending on the sensitivity of the network structures formed by particles and on the time necessary for the restoration of broken structures. The dynamic modulus at lower frequencies increases with an increase in the yield value, while the former increases proportionally to the latter at higher concentrations also.

The non-linearity of dynamic properties has been observed as a feature of their amplitude dependence. The change in the dynamic modulus is more remarkable than that in the dynamic viscosity.

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19) Th. Schwedoff, *J. de Phys.*, (2), **8**, 341 (1889).

The experimental results described above at least qualitatively agree with the theoretical predictions based on a network model.

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Aeronautical Research Institute
The University of Tokyo
Meguro-ku, Tokyo