The Rheological Properties of Concentrated Suspensions. IV. The Viscoelastic Properties of Concentrated Dispersions in Molten Polymers

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The effects of fillers on the equilibrium modulus of solid polymers and on the viscosity of molten polymers have been studied extensively.[1-4] The viscoelastic properties of filled polymers have also been much investigated.[5-7] However, these investigations have mainly been concerned with properties in the transition region from flexible to glasslike consistency and have not attempted to extend the experiment to the molten state. Very little work has been done on the viscoelastic properties of filled molten polymers.

In the transition region, it has been observed experimentally that if particles are dispersed homogeneously and too apart from each other to be bridged by single polymer molecules, the relaxation spectrum of the polymer is essentially unaffected by the filler on the high frequency side, although it is broadened on the lower frequency side because of the suppression of the molecular motion of the polymer by dispersed particles.[6-8] In suspensions of finer particles, however, the aggregation of the particles may also complicate circumstances. In such a case, when particles approach each other, each particle may be bonded to others by single polymer molecules and the whole system may act as a highly crosslinked polymer.[3,8,9] Furthermore, additional forces, e. g., van der Waals-London attraction, should also be considered between particles. It is evident that the concentration dependence of dynamic properties cannot be described in terms of the volume-filling properties alone in concentrated dispersions of fine particles.[4,8,10]

It is the purpose of this paper to examine experimentally the dependence of the dynamic properties of concentrated dispersions in the molten polymer on the concentration, the particle size and the amplitude of oscillations.

We have studied the dynamic viscosity and the dynamic modulus of disperse systems containing fillers of various particle sizes. In order to eliminate complex chemical crosslinking, we chose an uncrosslinked polyethylene containing non-interacting fillers, that is, small glass spheres, barium sulfate powder and calcium carbonate powder.

Experimental

Materials.—The medium used in this work is a melt of a low density polyethylene, "Sumikathene F-70-6," whose number average molecular weight is 28000, with a melt index of 7, a melting temperature of 109~112°C, and a density of 0.921 g./cm^3 at 23°C.

The fillers used in this work are two kinds of barium sulfate, two kinds of calcium carbonate,

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[1] E. Guth, *J. Appl. Phys.*, **16**, 20 (1945).

[2] H. M. Smallwood, ibid., **15**, 758 (1944).

[3] A. M. Bueche, *J. Polymer Sci.*, **15**, 105 (1955); **25**, 139 (1957).

[4] J. Furukawa, *Chem. High Polymer, Japan* (*Kôbunshi Kagaku*), **6**, 265 (1949).

[5] S. Nohara, ibid., **12**, 527 (1955).

[6] R. F. Landel, *Trans. Soc. Rheology*, **2**, 53 (1958).

[7] A. R. Payne, "Rheology of Elastomers," Ed. by P. Mason and N. Wookey, Pergamon Press, London (1958).

[8] J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons Inc., New York (1961).

[9] P. J. Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).

[10] Y. Satô and J. Furukawa, *Rubber Chem. Technol.*, **35**, 857 (1962); Y. Satô, *High Polymers* (*Kôbunshi*), **7**, 396 (1958); *J. Solid State Phys.* (*Busseiron Kenkyû*), **2**, No. 2, 854, 871 (1957); **2**, No. 3, 1, 12, 274, 294, 404, 422 (1958).

and four kinds of glass spheres with various particle sizes. Calcium carbonate and barium sulfate powders were chosen because of their approximately spherical shapes and the narrow distributions of particle sizes. Besides, their dielectric constants are nearly equal to those of glass spheres and may be regarded as chemically inactive to polyethylene. The particle sizes were determined microscopically or electron-microscopically. Details of the size analyses, expressed on a statistical basis, are listed in Table I. The statistical diameters are defined as follows :[11]

Number average diameter : $d_n = \sum nd / \sum n$

Mean surface diameter : $d_s = (\sum nd^2 / \sum n)^{1/2}$

Mean volume diameter : $d_v = (\sum nd^3 / \sum n)^{1/3}$

Mean volume-surface diameter :

$$d_{vs} = (\sum nd^3 / \sum nd^2)$$

where n is the number of particles contained in a small size range, the mid value of which is d. The mean diameters were determined by measuring one hundred particles.

The Preparation of the Suspensions.—The fillers were dried at 110°C, in a vacuum of 20 mmHg, for three hours. Polyethylene was milled at 105± 2°C for two minutes prior to mixing it with particles through a plastic roll-mill, the roll of which was 3 inches in diameter, 7.5 inches long, and with revolution velocities of 18 and 20 r. p. m. After the filler had been added to the molten polyethylene, the suspension was milled for seven minutes and finished as a sheet about 2 mm. thick. A circular disk 2 cm. in diameter was cut off from the sheet and used as a specimen. The effect of the oxidation and shear degradation of polyethylene during milling on the dynamic properties seemed to be negligibly small compared to the effect of the filler. The dynamic viscosity, η', and the dynamic modulus, G', of milled polyethylene are not altered from those of raw polyethylene after 10 min. milling.

Apparatus and Methods. — The cone-and-plate rheometer used in this work has been described in detail in previous papers.[12-14] The apparatus can be used essentially as a rotationally oscillatory viscoelastometer, at small deformations. A feature of the rheometer is the completely automatic electrically detecting and recording system. The oscillatory torque is supplied to the shaft of the movable cone by a torque motor. The clearance between the cone and the plate is sufficiently large so that the dispersed particles do not interfere with the measurements. The dimensions of the assemblies of cone-and-plate and of coaxial coni-cylinders are as follows :

(a) Cone and plate : the angle between cone and plate is 9°58′, the radius of the cone is 1.002 cm. and the tip of the cone is truncated by 1/100 mm.

(b) Coaxial coni-cylinders : the angle between the conical end of the inner cylinder and the plane bottom of the outer cylinder is 19°58′, the radii of the inner and outer cylinders are 0.501 cm. and 0.951 cm. respectively, the depth of the outer cylinder is 0.683 cm. and the tip of the inner cone is truncated by 1/100 mm.

Since the assemblies are made so small in size, as has been described above, great care must be paid to the accuracy of the distance between cone and plate. The distance between the truncated cone tip and the stationary plate was held at 1/100 mm., within a margin of error of ±2/1000 mm., by using a micrometer unit with an electric contact. The shape factor was determined experimentally. The dynamic viscosity and the dynamic modulus were calculated from the amplitude ratio and the phase lag between the recorded curves of torque and deflection.

Experiments were made at a torsional constant of 2.39×10^4 dyn.-cm./rad. In this case, the moment of inertia of the oscillatory unit was 50± 0.5 dyn.-cm.-sec^2/rad., the amplitude of the angular deflection of the cone was below 4 degrees, and the amplitude of the torque could be varied from 0 to 3×10^3 dyn.-cm. The dynamic viscosity, η', and the dynamic modulus, G', were measured at frequencies from 1/100 to 75/100 c. p. s. The temperature was varied from 155 to 230°C within a margin of error of ±1°C. During the experiments a stream of hot nitrogen gas was supplied to the atmosphere in order to avoid the rapid oxidation of the specimen.

Experimental Results

The Thixotropic Behavior of Filled Systems. —In such a highly viscous medium as molten polyethylene, the state of the dispersion of particles seems to be determined essentially by the mechanical conditions of milling. The dynamic viscosity and the dynamic modulus of filled systems changed almost not at all during measurements in suspensions of glass spheres and in those of calcium carbonate of larger particle sizes. Table II and Fig. 1 show the time dependence of dynamic properties in a suspension of calcium carbonate. In suspensions of barium sulfate of finer particles, however, the dynamic viscosity and the dynamic modulus increased with time under periodic strains. Figure 2 shows the change in dynamic properties with time in such a filled system. Measurements were made with a given amplitude of torque, 1.8×10^3 dyn.-cm., in an atmosphere of nitrogen gas. The increase in the dynamic viscosity and in the modulus is not due to any chemical changes in the specimen but to structural changes in the network formed by the agglomeration of particles in such a highly viscous medium. No gel fraction could be obtained practically

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[11] G. F. Eveson, *J. Oil and Colour Chem. Assoc.*, **40**, 456 (1957).

[12] H. Kambe, *J. Japan Soc. Test. Matls.* (*Zairyô Shiken*), **8**, 354 (1959).

[13] H. Kambe and M. Takano, *Rept. Aeronaut. Res. Inst., Univ. Tokyo*, **28**, 159 (Rept. No. 377, 1963).

[14] H. Kambe and M. Takano, ibid., **28**, 175 (Rept. No. 378, 1963).

TABLE I. CHARACTERISTICS OF FILLERS

Filler	Glass sphere				$CaCO_3$		$BaSO_4$	
	I	II	III	IV	I	II[a]	I	II
Number average diameter, μ	91.1	49.5	32.3	24.0	2.28	0.04	0.265	0.075
Mean surface diameter, μ	91.5	51.2	32.9	24.8	2.65	—	0.283	0.079
Mean volume diameter, μ	92.2	52.0	33.8	25.6	2.99	—	0.311	0.082
Mean volume-surface diameter, μ	93.5	53.5	35.6	27.3	3.80	—	0.375	0.088
Density at 25°C g./cm^3	2.36				2.71		4.47	
Dielectric constant e. s. u.	7∼10[b]				8.8[c]∼9.15[d]		10.2∼10.25[c]	

a) Hakuenka CC (calcium carbonate coated by calcium stearate).

b) F. Keller, *Z. tech. Physik.*, **13**, 237 (1932) ; A. Güntherschulze and F. Keller, *Z. Physik.*, **75**, 78 (1932).

c) F. Wachholtz and A. Franceson, *Kolloid Z.*, **92**, 75 (1940).

d) P. Schupp, *Z. Physik.*, **75**, 84 (1932).

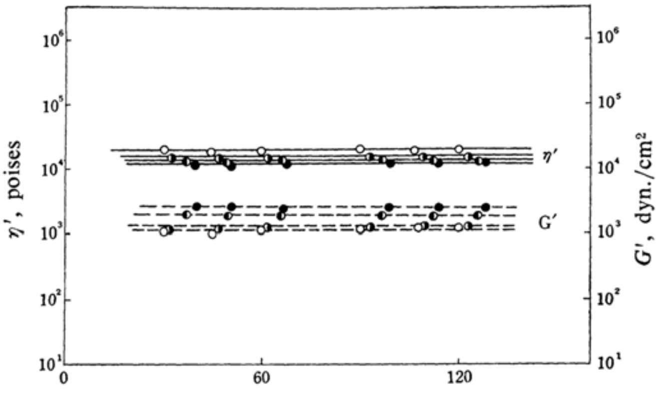

Fig. 1. Change in the viscoelastic properties with time in 28.6 wt.% suspension of calcium carbonate-I in polyethylene (210°C) : ○, 0.02 c. p. s.; ◑, 0.05 c. p. s.; ◐, 0.08 c. p. s.; ●, 0.10 c. p. s.

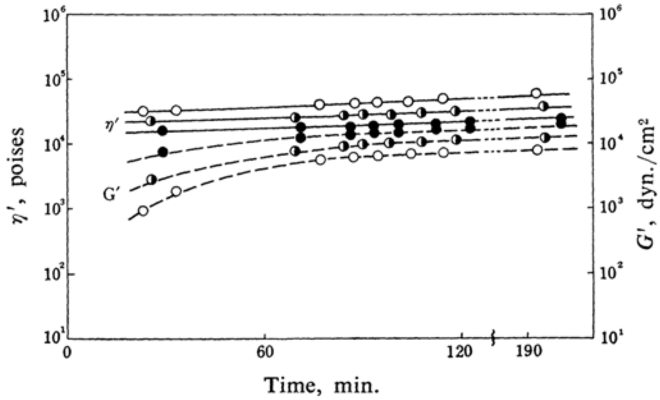

Fig. 2. Change in the viscoelastic properties with time in 28.6 wt.% suspension of barium sulfate-II in polyethylene (210°C) : ○, 0.02 c. p. s.; ◑, 0.05 c. p. s.; ●, 0.10 c. p. s.

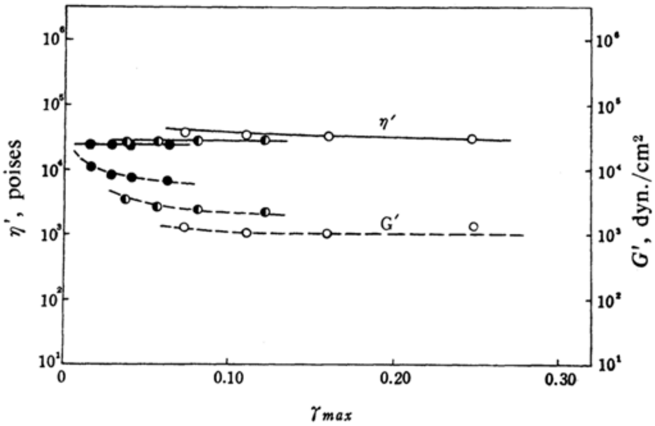

Fig. 3. Amplitude dependence of the viscoelastic properties in 60 wt. % suspension of calcium carbonate-I in polyethylene (210°C) : ○, 0.02 c. p. s.; ◐, 0.05 c. p. s.; ●, 0.10 c. p. s.

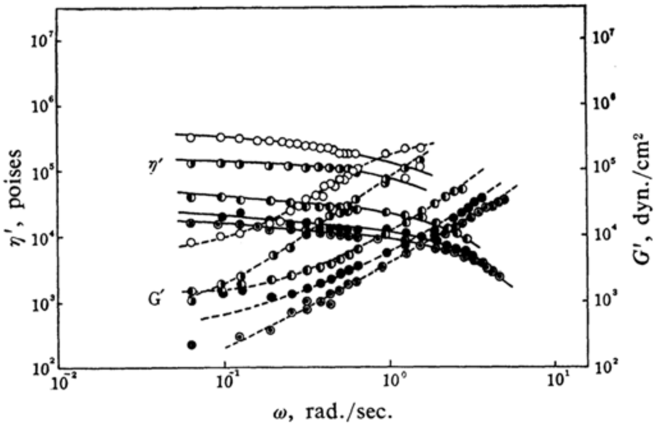

Fig. 4. Dependence of the viscoelastic properties on the concentration and the frequency in suspensions of glass sphere-I in polyethylene (200°C) : ⊙, 0 wt.% ; ●, 28.6 wt.% ; ◐, 60.0 wt.% ; ◑, 75.0 wt.% ; ○, 80 wt.%.

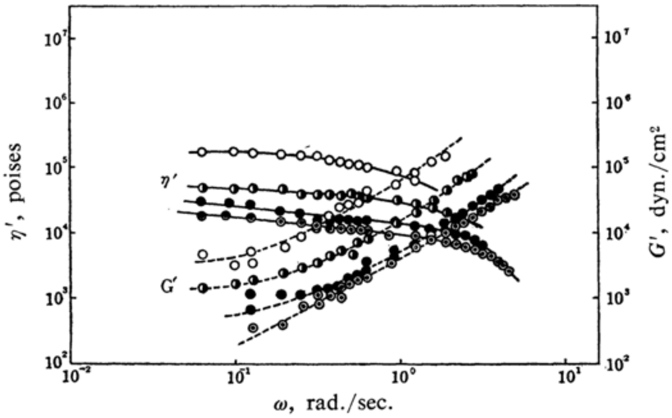

Fig. 5. Dependence of the viscoelastic properties on the concentration and the frequency in suspensions of glass sphere-IV in polyethylene (200°C) : ⊙, 0 wt.% ; ●, 28.6 wt.% ; ◑, 60.0 wt.% ; ○, 75.0 wt.%.

TABLE II. DEPENDENCE OF DYNAMIC PROPERTIES ON TIME

(a) 28.6 wt.% suspension of calcium carbonate-I in polyethylene (210°C)

Frequency, c. p. s. 0.02

Time min.	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
30	0.212	1.02	1.86
45	0.233	0.90	1.68
60	0.220	1.07	1.82
90	0.213	1.11	1.94
107	0.214	1.15	1.88
120	0.212	1.15	1.89

Frequency, c. p. s. 0.05

Time min.	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
32	0.146	1.12	1.41
47	0.151	1.13	1.37
62	0.153	1.12	1.37
93	0.148	1.10	1.42
109	0.147	1.17	1.43
123	0.155	1.05	1.33

Frequency, c. p. s. 0.08

Time min.	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
37	0.101	1.99	1.27
49	0.109	1.75	1.24
67	0.106	1.84	1.25
97	0.102	1.82	1.33
112	0.107	1.68	1.25
126	0.109	1.73	1.23

Frequency, c. p. s. 0.10

Time min.	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
39	0.090	2.59	1.18
51	0.091	2.42	1.18
68	0.091	2.36	1.22
99	0.089	2.41	1.23
114	0.091	2.36	1.20
128	0.093	2.09	1.19

(b) 28.6 wt.% suspension of barium sulfate-II in polyethylene (210°C)

Frequency, c. p. s. 0.02

Time min.	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
23	0.113	0.96	3.04
33	0.104	1.81	3.07
77	0.065	5.47	3.76
87	0.061	5.94	3.80
94	0.060	6.02	4.05
104	0.054	7.23	4.14
114	0.051	7.22	4.83
192	0.050	7.10	5.49

Frequency, c. p. s. 0.05

Time min.	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
25	0.063	2.81	2.18
69	0.045	7.63	2.30
84	0.041	8.35	2.52
90	0.040	8.85	2.59
98	0.038	9.39	2.49
108	0.036	9.88	2.76
118	0.034	11.1	2.74
195	0.031	10.3	3.83

Frequency, c. p. s. 0.10

Time min.	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
29	0.036	7.52	1.69
71	0.030	11.9	1.66
86	0.028	13.8	1.64
93	0.026	15.4	1.66
101	0.026	14.4	1.88
112	0.024	16.6	1.72
122	0.022	17.8	1.93
200	0.020	20.3	2.16

in hot tetralin. Furthermore, the dependence of dynamic properties on the amplitude was examined, since dynamic properties at lower frequencies are very sensitive to structural change in a network formed by particles.[15-17] Table III shows typical data of the amplitude dependence of dynamic properties in various suspensions. The maximum shear strain, γ_{max}, is defined as follows:[18] in an assembly of cone and plate,

$$\gamma_{max}=\theta_o/\beta$$

and in an assembly of coaxial cylinders,

$$\gamma_{max}=2\theta_o R_o^2/(R_o^2-R_i^2)$$

where θ_o is the amplitude of deflection; β, the angle between cone and plate, and R_i and R_o, the radii of the inner and the outer cylinder respectively.

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[15] A. R. Payne, *J. Appl. Polymer Sci.*, **3**, 127 (1960).

[16] M. Senō, *J. Chem. Soc., Japan Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 66 (1957).

[17] M. Takano, This Bulletin, **36**, 1418 (1963).

[18] Th. Schwedoff, *J. de Phys.*, (2), **8**, 341 (1889).

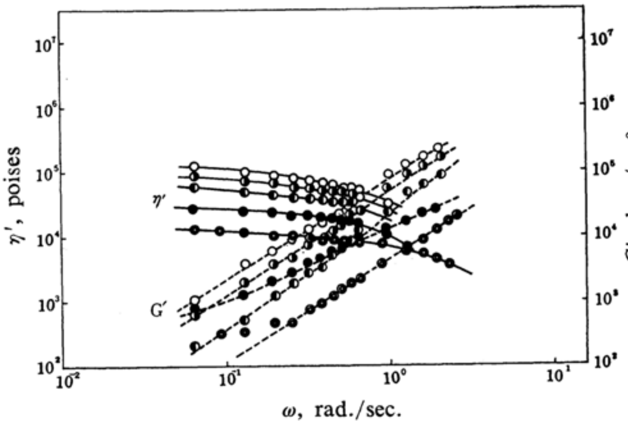

Fig. 6. Dependence of the viscoelastic properties on the concentration and the frequency in suspensions of calcium carbonate-I in polyethylene (210°C) : ◎, 0 wt.% ; ●, 16.7 wt.% ; ◐, 54.5 wt.% ; ◑, 60.0 wt.% ; ○, 66.7 wt.%.

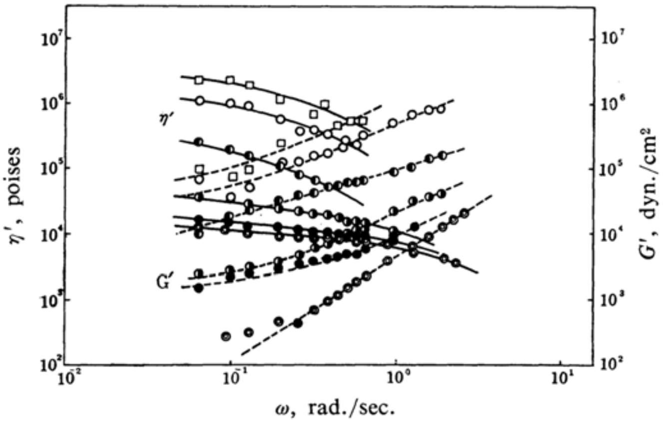

Fig. 7. Dependence of the viscoelastic properties on the concentration and the frequency in suspensions of barium sulfate-II in polyethylene (210°C) : ◎, 0 wt.% ; ●, 16.7 wt.% ; ◑, 28.6 wt.% ; ◐, 37.5 wt.% ; ○, 44.4 wt.% ; □, 50.0 wt.%.

Whereas in the dynamic properties of suspensions at lower concentrations the linearity of viscoelasticity holds well, the dynamic properties of concentrated suspensions depend on the amplitude, even at very small deformations.[15,19] The dynamic viscosity and modulus seem to fall off with an increase in amplitude beyond a kind of yield strain whose magnitude depends on the concentration and on the particle size of the filler. These phenomena coincide with a common characteristic of thixotropic systems, the breaking of certain linkages strained beyond their elastic limits.

As the viscoelastic properties depend on their mechanical history in such thixotropic systems, great care must be paid to the mechanical conditions of preparation and experimentation. In suspensions of glass spheres and of calcium carbonate of larger particle sizes, the dependence of the dynamic modulus on the amplitude of oscillation is more remarkable than that of the dynamic viscosity, as is shown in Table III and Fig. 3. According to theoretical considerations based on a network model,[17] the decrease in dynamic viscosity is mainly due to structural changes in the network formed by particles, while the decrease in dynamic modulus is due to both the structural change in the network and the nonlinear characteristics of the links between particles.

The Dependence of Dynamic Properties on the Concentration and Frequency.—As has been described above, dynamic properties depend on the amplitude of oscillation as well as on the frequency and concentration of filler, especially

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[19] R. B. Stambaugh, *Ind. Eng. Chem.*, **34**, 1358 (1942).

TABLE III. DEPENDENCE OF DYNAMIC PROPERTIES ON AMPLITUDE OF OSCILLATION

(a) 75 wt.% suspensions of glass spheres in polyethylene (200°C)

Filler		I			II	
Frequency, c. p. s.		0.02			0.02	
	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises
	0.130	2.98	13.8	0.135	3.41	12.3
	0.109	2.00	11.3	0.115	3.12	12.6
	0.107	3.54	14.1	0.110	2.39	11.1
	0.098	2.20	12.6	0.100	3.36	12.3
	0.085	3.46	14.7	0.070	3.54	12.7
	0.058	3.88	14.0	0.044	3.57	11.8

Filler		III			IV	
Frequency, c. p. s.		0.02			0.02	
	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises
	0.107	7.82	13.6	0.115	4.67	16.2
	0.092	8.35	13.6	0.101	4.34	15.8
	0.086	6.34	12.8	0.086	4.35	15.7
	0.081	6.82	13.7	0.082	4.63	17.0
	0.059	6.39	13.1	0.056	5.07	17.3
	0.041	6.73	12.8	0.039	5.67	15.4

(b) Suspensions of calcium carbonate-I in polyethylene (210°C)

Concn. of filler wt.%		28.6			60.0	
Frequency, c. p. s.		0.02			0.02	
	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises
	0.357	0.343	1.52	0.249	1.39	3.22
	0.234	0.973	1.70	0.160	0.99	3.31
	0.206	0.484	1.52	0.110	1.05	3.43
	0.181	1.02	1.52	0.073	1.30	3.59
	0.135	1.26	1.36			

Concn. of filler wt.%		60.0			60.0	
Frequency, c. p. s.		0.05			0.10	
	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises
	0.122	2.22	2.96	0.063	6.74	2.49
	0.081	2.47	2.88	0.040	8.01	2.62
	0.056	2.71	2.93	0.028	8.25	2.53
	0.037	3.34	2.74	0.016	10.4	2.40

(c) Suspensions of barium sulfate-II in polyethylene (210°C)

Concn. of filler wt.%		28.6			60.0	
Frequency, c. p. s.		0.02			0.02	
	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises	γ_{max}	$G' \times 10^{-3}$ dyn./cm^2	$\eta' \times 10^{-4}$ poises
	0.139	7.60	2.79	0.017	7.59	25.4
	0.104	7.40	3.46	0.008	15.2	46.6
	0.069	8.55	3.01	0.007	21.2	63.1
	0.053	8.57	3.53	0.005	16.0	142.0
	0.038	8.93	3.08	0.004	18.8	121.0
				0.004	14.3	101.0

TABLE IV. DEPENDENCE OF DYNAMIC PROPERTIES ON CONCENTRATION

(a) Suspensions of glass spheres in polyethylene (0.02 c. p. s., 200°C)

Filler	I			II		
Concn. wt.%	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
0		0.65	1.51			
16.7	0.213	0.75	1.50	0.193	1.49	2.60
28.6	0.178	6.09	3.19	0.200	0.24	2.74
28.6*	0.177	1.66	2.64	0.223	0.28	2.26
44.5	0.176	2.71	2.40	0.199	0.70	3.00
54.5	0.208	0.87	2.63	0.197	1.09	4.40
60.0	0.179	2.13	3.72	0.183	1.60	4.54
61.5	0.176	1.99	3.74	0.184	1.41	4.27
66.7	0.186	0.74	4.07	0.160	1.45	6.04
75.0	0.088	2.20	12.6	0.083	2.39	11.1
80.0	0.054	7.14	28.8	—	—	—

Filler	III			IV		
Concn. wt.%	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
16.7	0.214	0.57	1.91	0.208	1.15	2.16
28.6	0.210	0.62	3.06	0.206	1.20	2.78
28.6*	0.222	0.42	2.35	0.204	0.72	2.72
44.5	0.231	0.19	2.48	0.195	1.08	3.36
54.5	0.196	0.23	3.57	0.206	0.64	3.78
60.0	0.191	1.12	4.24	0.171	1.74	4.50
61.5	0.192	0.63	4.56	0.190	0.72	4.97
66.7	0.173	0.93	5.73	0.182	1.03	5.36
75.0	0.093	6.34	12.8	0.085	4.35	15.7
80.0	0.056	12.1	25.2	—	—	—

* Prepared under the same condition with the other.

(b) Suspensions of calcium carbonate in polyethylene (0.02 c. p. s., 210°C)

Filler	I		
Concn. wt.%	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
0		0.55	1.33
16.7	0.229	1.36	2.31
28.6	0.209	1.07	3.05
28.6*	0.153	1.25	3.46
37.5	0.186	1.00	4.04
44.5	0.167	0.55	3.96
44.5*	0.169	1.09	3.85
50.0	0.118	0.46	5.32
54.5	0.196	0.49	4.58
60.0	0.093	2.09	7.11
66.7	0.078	3.87	9.10
66.7*	0.080	7.04	7.56
73.3	0.041	21.3	15.2
	0.037	26.3	22.7
	0.019	30.4	46.7
80.0	0.007	58.3	134.0
	0.005	99.2	164.0

Filler II

Concn. wt.%	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
18.8	0.272	1.20	1.54
	0.113	0.93	1.41
	0.027	1.32	1.13
31.7	0.014	46.5	42.8
	0.005	29.3	50.2
41.2	0.0044	269.0	154.0
	0.0037	445.0	146.0
48.4	0.0022	550.0	760.0
	0.0018	757.0	453.0
	0.0015	179.0	325.0

* Prepared under the same condition with the other.

(c) Suspensions of barium sulfate in polyethylene (0.02 c. p. s., 210°C)

Filler I

Concn. wt.%	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
0		0.55	1.33
16.7	0.220	1.17	2.55
27.5	0.227	1.23	2.37
43.2	0.221	1.75	3.09
60.3	0.016	124.0	49.5
69.7	0.004	424.0	398.0

Filler II

Concn. wt.%	γ_{max}	$G'\times10^{-3}$ dyn./cm^2	$\eta'\times10^{-4}$ poises
16.7	0.152	2.65	1.22
28.6	0.069	8.55	3.01
	0.038	8.93	3.08
37.5	0.030	28.6	13.6
	0.022	27.8	14.1
44.5	0.007	41.7	93.5
	0.006	138.0	86.1
50.0	0.007	81.4	86.3
	0.002	90.2	184.0
54.5	0.003	282.0	252.0
	0.003	258.0	201.0
60.0	0.004	143.0	101.0
	0.003	239.0	278.0
66.7	0.007	134.0	95.2
	0.003	235.0	324.0

in thixotropic systems. In such filled systems, therefore, it is very difficult to obtain the exact frequency dependence of dynamic properties, independent of the amplitude. Figures 4—7 show the frequency dependence of the dynamic viscosity and the dynamic modulus obtained by a given amplitude of torque in the range of 1.6∼2.0×10^3 dyn.-cm. at various concentrations and in various suspensions.

In suspensions of glass spheres, the amplitude dependence of the dynamic properties may be ignored within the range of experimental error of ±10%, as shown in Table III. In suspensions of calcium carbonate and barium sulfate of smaller particle sizes, the dependence of the dynamic properties on the amplitude exceeds the range of experimental error because of their thixotropic nature. In the latter case, therefore, the frequency dependence curve represents only a qualitative tendency.

However, it is evident that the dynamic modulus at lower frequencies increases with an increase in the concentration of filler, and that the superposition of the frequency dependence curves with respect to the concentration of filler can not be made as simply as was done in polymer solutions by Ferry.[20] Table IV shows the concentration dependence of the dynamic properties of suspensions of glass spheres, calcium carbonate and barium sulfate at a given frequency, 0.02 c. p. s. In order to confirm the reproducibility of these data, some suspensions were prepared twice; the dynamic viscosity and modulus were then measured under nearly the same mechanical conditions. In thixotropic suspensions, it is essentially impossible to obtain the limiting values of dynamic properties independent of the mechanical history. In thixotropic suspensions of calcium carbonate-I, the particles are relatively large and the restoration of the network broken by shearing forces requires a long time; therefore, the dynamic viscosity and modulus of these systems fall off appreciably after large deformations. The data listed in Table IV were obtained with as small a strain as possible. In suspensions of barium sulfate-II, the dynamic viscosity and modulus increase with time, as has been described above; therefore, data were obtained after heating the suspension for about two hours. By conditioning the system in such a way, the scattering of data could be reduced tolerably. Figures 8 and 9 show the dependence of the dynamic viscosity and the dynamic modulus at a given frequency, 0.02 c. p. s., on the volume fraction of the filler. The volume fraction of the filler has been calculated by assuming that the density of molten polyethylene is 0.76 g./cm³ at 200~210°C;[21,22] the thermal expansion of the filler may be ignored, as the volume expansion of the filler is negligibly small compared to that of the polymer.

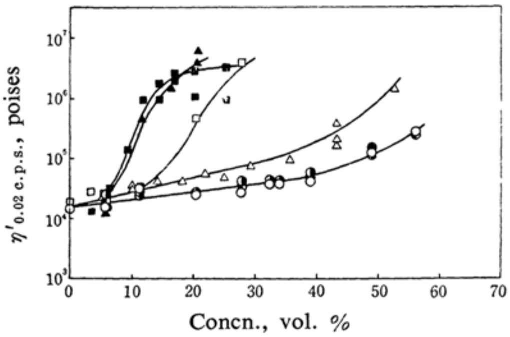

Fig. 8. Dependence of the dynamic viscosity on the concentration, at 0.02 c. p. s., in various suspensions: ○, glass sphere-I; ◑, glass sphere-II; ◐, glass sphere-III; ●, glass sphere-IV; △, calcium carbonate-I; ▲, calcium carbonate-II; □, barium sulfate-I; ■, barium sulfate-II.

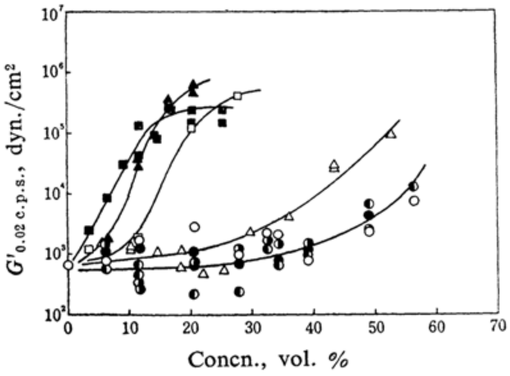

Fig. 9. Dependence of the dynamic modulus on the concentration, at 0.02 c. p. s., in various suspensions: ○, glass sphere-I; ◑, glass sphere-II; ◐, glass sphere-III; ●, glass sphere-IV; △, calcium carbonate-I; ▲, calcium carbonate-II; □, barium sulfate-I; ■, barium sulfate-II.

In suspensions of glass spheres, the concentration dependence of the dynamic viscosity at a frequency of 0.02 c. p. s. closely follows a generalized Robinson formula:[23,24]

$$\ln(\eta'/\eta'_0) = K\phi/(1-S'\phi)$$

where η'_0 is the dynamic viscosity of an unfilled polymer; ϕ, the volume fraction of the filler, and K and S', 2.5 and 1/0.74 respectively. The concentration dependence of the dynamic modulus resembles that of the dynamic viscosity.

In thixotropic suspensions of calcium carbonate and barium sulfate, the concentration dependence of the dynamic viscosity can not be represented by such a simple formula. The dynamic viscosity and the modulus increase more remarkably with an increase in the concentration. In suspensions of finer particles, the dynamic viscosity and the modulus suddenly increase beyond a sort of critical concentration. In suspensions of glass spheres of larger particles, no such critical concentration could be observed up to the highest concentration used in our experiments. In suspensions of calcium carbonate of an intermediate particle size, also, no such critical concentration could be observed. It is evident that the critical concentration depends on the particle size and that the effect of a filler on the dynamic properties of molten polymer can not be described in terms of the volume-filling properties alone. Although the filler used in

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[21] I. Sakurada and A. Nakajima, *Chem. High Polymer, Japan* (*Kôbunshi Kagaku*), **3**, 91 (1946).

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TABLE V. APPARENT COEFFICIENTS OF TEMPERATURE DEPENDENCE OF DYNAMIC VISCOSITY AT 0.02 c. p. s.

(a) Suspensions of glass spheres in polyethylene (200°C)

Filler Concn. wt.%	I ΔH kcal./mol.	II ΔH kcal./mol.	III ΔH kcal./mol.	IV ΔH kcal./mol.
0	11(11)			
54.5	10(16)	13(15)	12(16)	13(14)
60.0	12(13)	13(15)	11(14)	13(17)
61.5	14(14)	12(13)	14(16)	13(17)
66.7	14(21)	12(13)	—(16)	13(17)
75.0	15(16)	16(18)	15(14)	13(17)
80.0	16(18)	—	11(14)	—

(b) Suspensions of calcium carbonate and barium sulfate in polyethylene (210°C)

Filler Concn. wt.%	Calcium carbonate-I ΔH kcal./mol.	Barium sulfate-II ΔH kcal./mol.
0	11	
16.7	11	11(15)
28.6	—	18(22)
37.5	—	7(13)
44.5	12	5(13)
54.5	12	—

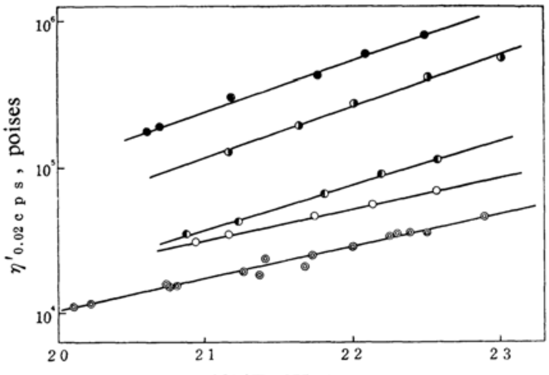

Fig. 10. Temperature dependence of the dynamic viscosity at 0.02 c. p. s. for suspensions of glass sphere-I in polyethylene with various concentrations : ◎, 0 wt.% ; ○, 54.5 wt.% ; ◐, 66.7 wt.% ; ◑, 75.0 wt.% ; ●, 80.0 wt.%.

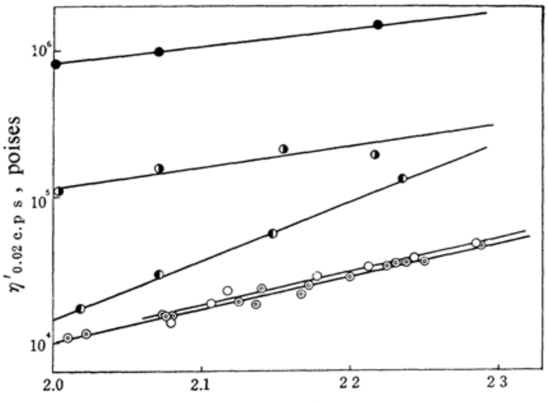

Fig. 11. Temperature dependence of the dynamic viscosity at 0.02 c. p. s. for suspensions of barium sulfate-II in polyethylene with various concentrations : ◎, 0 wt.% ; ○, 16.7 wt.% ; ◐, 28.6 wt.% ; ◑, 37.5 wt.% ; ●, 44.5 wt.%.

the present experiment has a perfectly or approximately spherical shape, the shape of particles also seems to have a great influence on the concentration dependence of dynamic properties, as our other experiments have discovered.

The Dependence of Dynamic Properties on the Temperature. — According to the experimental results described above, it is evident that particles aggregate in concentrated suspensions of finer particles, whether they are covered by polymer molecules or not. An examination of the temperature dependence of dynamic properties will present information on the nature of links between particles. Figures 10 and 11 show the temperature dependence of the dynamic viscosity at a frequency of 0.02 c. p. s. The coefficients of the temperature dependence of the dynamic viscosity calculated from the slopes of the above curves are listed in Table V. However, these values are not the true activation energies for a viscous flow at zero rate of shear, because the dynamic viscosity depends on the frequency and the temperature. Therefore, they are only approximate values of the activation energies for flow. The values in parentheses have been approximately calculated from the temperature dependence of the shift factor as determined by the frequency dependence curves at 200 or 210°C and by the dynamic properties at a frequency of 0.02 c. p. s. at various temperatures. As Table V shows, the apparent coefficients of the temperature dependence for a viscous flow in various suspensions agree approximately with that of unfilled polyethylene. Consequently, in suspensions of finer particles, it is likely that dispersed particles are covered by polymer molecules and are bridged by single molecules at higher concentrations.

Discussion

As is shown in Figs. 8 and 9, the dynamic properties depend appreciably on the particle size of the filler. The effect of particle size on the melt viscosity and on the elasticity of rubber has been discussed by Furukawa⁴⁾ and Bueche³⁾ in detail. However, according to Furukawa's theory, the logarithmic relative viscosity of filled molten polymer must be proportional to the specific surface area and to the volume ratio of dispersed particles to polymer:

$$\ln(\eta/\eta_o) = (a + b/\boldsymbol{R}T)(1 + SM/\alpha A\rho)X$$

where η and η_o are the viscosities of filled and unfilled polymers; a and b are constant; M is the molecular weight of the polymer; ρ, the density of the polymer; α, the surface area occupied by an adsorbed polymer molecule; $\boldsymbol{R}$, the gas constant; A, Avogadro's constant; S, the specific surface area per unit volume, and X, the volume ratio of the filler to the polymer. The dynamic viscosity at lower frequencies may be approximately equal to the melt viscosity. Figure 12 shows the relation of the relative dynamic viscosity at a frequency of 0.02 c. p. s. to the volume ratio of the filler. The linear relation expected by Furukawa's theory can not be observed, even in the suspensions of glass spheres of larger particle sizes. This means that the effect of the filler on the dynamic viscosity at small strains can not be described only in terms of an increase in the volume of particles caused by adsorbed polymer molecules but that it is rather closely connected with the network structure formed by particles bridged by single polymer molecules. Bueche has suggested that the effective number, ν, of polymer segments which can act as a molecular spring is given by the following equation:

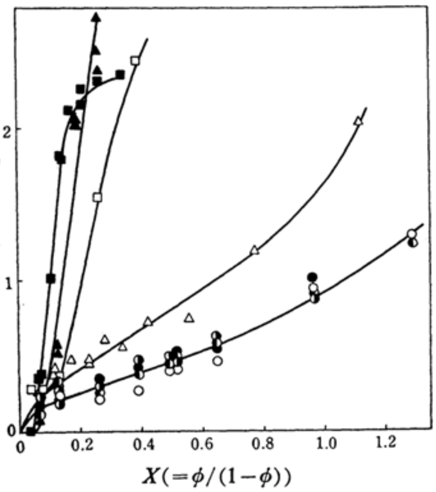

Fig. 12. Relation between the relative dynamic viscosity at 0.02 c.p.s. and the volume ratio of filler to polymer: ○, glass sphere-I; ◑, glass sphere-II; ◐, glass sphere-III; ●, glass sphere-IV; △, calcium carbonate-I; ▲, calcium carbonate-II; □, barium sulfate-I; ■, barium sulfate-II.

$$\nu = N\{(1-1/N)^n - (1-n/N)\}$$

where N is the number of linear polymer molecules and n, the number of points of adherence. In the case of spherical particles with the radius r, we have:³⁾

$$n = 3fv_2/r$$

and

$$N = \rho v_1/m$$

where f is the number of points of adherence per unit area; m, the mass of a polymer molecule, and v_1 and v_2 the volume fractions of the polymer and the filler respectively. Bueche's theory predicts that the first few filler particles will be relatively ineffective and that at higher concentrations the number of molecular springs will approach³⁾

$$\nu = n - N = 3fv_2/r - \rho v_1/m$$

The critical volume ratio beyond which dynamic viscosity and modulus increase appreciably is, therefore, given by:

$$X_c = \rho r/3mf = A\rho r/3Mf$$

As $\rho = 0.76$ and $M = 2.8 \times 10^4$ in the present experiments, we have

$$X_c = 2.73 \times 10^{18} d/f$$

and

$$1/f = 3.66 \times 10^{-19} X_c/d$$

where d is the mean volume-surface diameter of the particles.

In suspensions of barium sulfate-II and -I, the values of X_c are 0.06 and 0.12 respectively, as shown in Figs. 8 and 9. Therefore, the surface area necessary for one point of adherence, $1/f$, are 25 Å^2 and 12 Å^2 for barium sulfate-II and -I respectively. In suspensions of calcium carbonate-II, X_c is 0.06, and so the value of $1/f$ is 55 Å^2. The value of $1/f$ seems to be decreased by a decrease in the particle size. If we assume that the surface area necessary for one point of adherence, $1/f$, is 10 Å^2 for particles larger than that of calcium carbonate-I, the critical volume ratio, X_c, is expected to be 0.72 in suspensions of calcium carbonate-I. In suspensions of glass spheres, the critical volume ratio, X_c, is expected to be near to the closest packing.

Furthermore, if particles are covered by polymer molecules and are bridged partially by single molecules, it is expected that the dynamic viscosity and the modulus will increase as the mean distance between the surfaces of the particles approaches the molecular dimension of the polymer. Assuming that the particles of calcium carbonate and barium sulfate have also a perfectly spherical shape, we can calculate the mean distance between the surfaces of particles, δ_m, by the following equation:

$$\delta_m = d\{(\phi_c/\phi)^{1/3}-1\}$$

where ϕ_c is the volume fraction at the closest packing, 0.7405. Figure 13 shows the relation of the relative dynamic viscosity at a frequency of 0.02 c. p. s. to the mean distance between the surfaces of the particles at the various concentrations, 6.1, 11.4, 20.5 and 27.9 vol. %. The root-mean square end-to-end separation of polyethylene, the number average molecular weight of which is 28000, is 97 Å, and the end-to-end separation at maximum extension is 2540 Å.[25] The relative dynamic viscosity apparently increases as the mean distance between the surfaces of particles approaches the molecular dimension of the polymer. Therefore, it may be concluded that the dispersed particles are covered by polymer molecules and that in suspensions of finer particles they are partially bridged by single molecules.

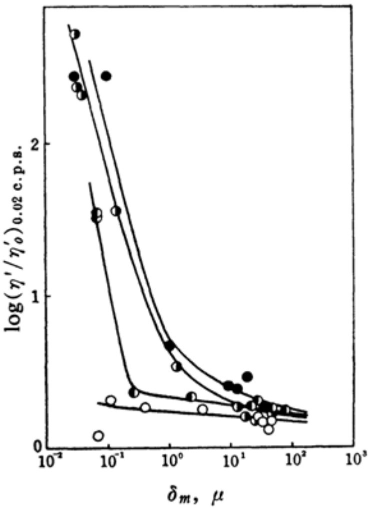

Fig. 13. Relation between the relative dynamic viscosity at 0.02 c. p. s. and the mean distance between surfaces of particles: ○, 6.1 vol.%; ◐, 11.4 vol.%; ◑, 20.5 vol.%; ●, 27.9 vol.%.

If particles sufficiently approach each other, the van der Waals-London attraction may also be considered among neighboring particles. The energy of interaction between two neighboring particles covered by polymer molecules is given by the following equation;[26]

$$\Delta F = (A_m^{1/2}-A_p^{1/2})^2 d/24(\delta+2\Delta)$$

where A_m and A_p are the Hamaker parameters of the medium and of the particles respectively, Δ is the thickness of the layer of bound polymer molecules, and δ, the distance of the closest approach of the covered surfaces. The magnitudes of the Hamaker parameters A_m and A_p evaluated from the dielectric constants of the polymer and of the particles are approximately 2×10^{-12} and 6×10^{-13} ergs.[27]

Therefore, the energy of interaction due to the van der Waals-London attraction is

$$\Delta F = 1.70\times10^{-14} d/(\delta+2\Delta)$$

and the additional shear modulus due to the van der Waals-London attraction, ΔG, is

$$\begin{aligned}\Delta G &\fallingdotseq N_a(d+2\Delta)(d^2\Delta F/d\delta^2)/3\\ &= 1.13\times10^{-14} N_a(d+2\Delta)d/(\delta+2\Delta)^3\end{aligned}$$

where N_a is the number of links between particles per unit cross-sectional area which transmit forces from one part of the sample to the other. If all the dispersed particles are involved in a flocculate, N_a is given approximately by $2\phi\sigma(d+2\Delta)/\pi d^3$; thus we have

$$\Delta G \fallingdotseq 7.20\times10^{-15}\phi\sigma(d+2\Delta)^2/d^2(\delta+2\Delta)^3$$

where σ is the parameter depending on the network structure and with values in the range of 1∼3.[17] When the thickness of the layer of a bound polymer, Δ, is negligibly small compared to the diameter of the particles, we have approximately:

$$\Delta G \fallingdotseq 7.20\times10^{-15}\phi\sigma/(\delta+2\Delta)^3$$

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[25] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York (1953), p. 415.

[26] M. J. Vold, *J. Colloid Sci.*, **16**, 1 (1961).

[27] M. Takano and H. Kambe, This Bulletin, **36**, 1424 (1963).

In this case, the additional shear modulus due to the van der Waals-London attraction is independent of the particle size, and if particles approach each other within 100Å at a concentration of 10 vol. %, the magnitude of the additional shear modulus, ΔG, may be in the order of $10^2\sim10^3$ dyn./cm^2. This order seems to be sufficiently small compared to the observed order of the modulus, $10^4\sim10^6$ dyn./cm^2. Therefore, the van der Waals-London attraction seems to be of secondary importance in the forces between particles.

Summary

The dynamic viscoelastic properties of molten polyethylene with various fillers have been measured in nitrogen gas at frequencies from 0.01 to 0.75 c. p. s. The dynamic viscosity and dynamic modulus have been measured at the temperatures of 150~230°C.

Glass spheres, calcium carbonate powder and barium sulfate powder have been used as fillers. The average diameter of the particles covers the range of $0.04\sim91\,\mu$. The polyethylene used was one of a low density, "Sumikathene F-70-6," whose number average molecular weight is 28000.

The dynamic viscosity and modulus of molten polyethylene are increased by the addition of fillers. The viscoelastic properties at low frequencies depend differently on the concentration in each suspension. In suspensions of glass spheres of the larger particle sizes (particle diameter: 24.0, 32.3, 49.5 and 91.1 μ), the concentration dependence of the dynamic viscosity, η', follows a generalized Robinson's formula:

$$\ln(\eta'/\eta'_0)=K\phi/(1-S'\phi)$$

where η'_0 is the dynamic viscosity of polyethylene; ϕ, the volume fraction of the suspended particles, and K and S', 2.5 and 1/0.74 respectively, regardless of the particle size. In suspensions of calcium carbonate of the intermediate particle size (particle diameter: 2.4 μ), the dependence of the dynamic viscosity on the concentration and on the amplitude of oscillation is observed more remarkably than that in suspensions of glass spheres. In suspensions of calcium carbonate and barium sulfate of the smaller particle sizes (particle diameter: 0.04, 0.08 and 0.27 μ), the dynamic viscosity and modulus increase appreciably above a critical concentration of the filler, a point which depends on the particle size. Beyond this critical concentration, the particles seemed to be linked with each other by single polymer molecules.

The dynamic viscosity and modulus at lower frequencies increase remarkably as the mean distance between the surfaces of particles becomes less than the molecular dimension of the polymer. In suspensions of the larger particles of glass spheres, this critical concentration can not be observed up to the highest concentration.

The temperature dependence of the dynamic viscosity at lower frequencies approximately agrees with that of unfilled polymers.

The dependence of dynamic properties on the time and on the amplitude of oscillations is observed in suspensions of calcium carbonate and in those of barium sulfate of comparatively small particles. In the barium sulfate suspensions of the finest particles, the dynamic viscosity and modulus increase with time under periodic strains and decrease with the increase in the amplitude of oscillations. The amplitude dependence of the dynamic modulus is more remarkable than that of the dynamic viscosity generally. In such thixotropic suspensions, the dynamic properties were measured with as small a strain as possible.

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