

Rheological Properties of Iron Oxide Particle Suspensions

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Synopsis

Viscosities of γ -Fe₂O₃ dispersions in epoxy resin, phenol resin, and polyvinyl butyral solutions are measured at shear rate D from 19.2 to 384 sec⁻¹. Volume fraction of γ -Fe₂O₃ in these dispersions ranges from about 0.002 to 0.03. The concentration dependence of relative viscosity η/η_s is closely represented by the Mooney equation. From this equation, intrinsic viscosity $[\eta]$ of suspensions is found to decrease from 46.1 at $D = 19.2$ sec⁻¹ to 14 at $D = 384$ sec⁻¹ for epoxy resin solution. The high $[\eta]$ value indicates the existence of flocs containing immobilized liquid. By increasing the shear rate, the average floc size is reduced to a point where at an infinite shear rate, only small clusters or possibly particles remain. Of the three polymers, the lowest $[\eta]$ value is obtained in the dispersion of the phenol resin solution.

INTRODUCTION

Recently, the recording density of magnetic disks and tapes used as a peripheral memory of the computer has been increasing. The improvement in the degree of dispersion of the particles in recording media is the most important factor for increasing recording density. Hence, the development of magnetic paints with a high degree and stability of dispersion has been demanded.

These properties of dispersion are mainly dependent on interaction forces between the dispersed particles. In order to clarify the interaction, it is essential to investigate the particle structure in magnetic paints. The particle structure of suspensions has been characterized by various methods. In one of them, it is considered that the rheological properties of suspensions reflect the structure of the particles. This article clarifies the nature of the particle structure of magnetic paints by investigating their dependence on shear rate and particle concentration in various polymer solutions.

EXPERIMENTAL

Material

An acicular γ -Fe₂O₃ obtained from Pfizer Co. was used as the magnetic iron oxide material. According to Pfizer, this material has low oil adsorption (35.3/100 g), a 4.65 g/cm³ density, and a tap density of 0.73 g/cm³. Powder was dried for 5 hr at 120°C before preparing dispersions.

The characteristics of three polymer solutions used as dispersion media are shown in Table I. Mixture of cyclohexanone, isophorone, and dioxane was used as solvents of these solutions.

A dispersion of γ -Fe₂O₃ in a polymer solution was prepared by ball-milling for 48 hr.

TABLE I
Characteristics of Various Polymer Solutions Used in Dispersions

Polymer	Soln conc., wt %	Viscosity, Pa Sec
Epoxy resin (Epikote 1007)	20.0	0.52
Phenol resin (Methylon 75108)	55.0	0.58
PVB (polyvinyl butyral)	3.1	0.54

Viscosity Measurement

Viscosities were measured with a Tokyo-Keiki cone-plate-type viscometer calibrated with standard viscosity fluids. Temperature was maintained at $22 \pm 1^\circ\text{C}$. The viscometer cone radius was about 1 in. Viscosities were measured at rotational speeds between $0.5\text{--}100\text{ min}^{-1}$. Consequently, shear rate D ranged from 1.92 to 384 sec^{-1} . The shear stress was obtained from the torque reading on the viscometer dial and calibration factors. Viscosity was defined as shear stress divided by shear rate.

In measuring viscosities, a dispersion was first sheared at the highest speed. The torque was recorded after it attained a constant value. Shear rate was decreased stepwise with the steady-state torque being measured at each step.

EXPERIMENTAL RESULTS

Viscosity Data

Plot of shear stress (N/cm) against shear rate D (sec^{-1}) are shown in Figure 1 for five dispersions in epoxy resin solution having volume fractions ϕ of iron oxide from 0.0021 to 0.0206 . It is clear that yield values are nearly zero.

From these results, the relation between viscosity η and ϕ at various shear rates was shown as in Figure 2.

Results almost the same as those were obtained for two other polymer solutions.

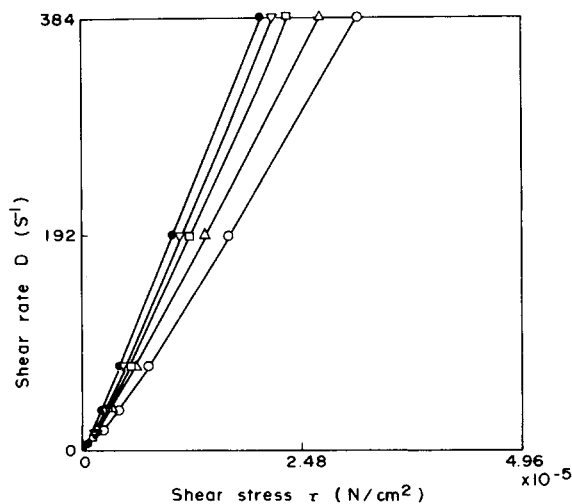


Fig. 1. Relations between shear rate and shear stress for dispersions of iron oxide in epoxy resin solutions. \circ , $\phi = 0.0206$; \triangle , $\phi = 0.0145$; \square , $\phi = 0.0084$; ∇ , $\phi = 0.0042$; \bullet , $\phi = 0$.

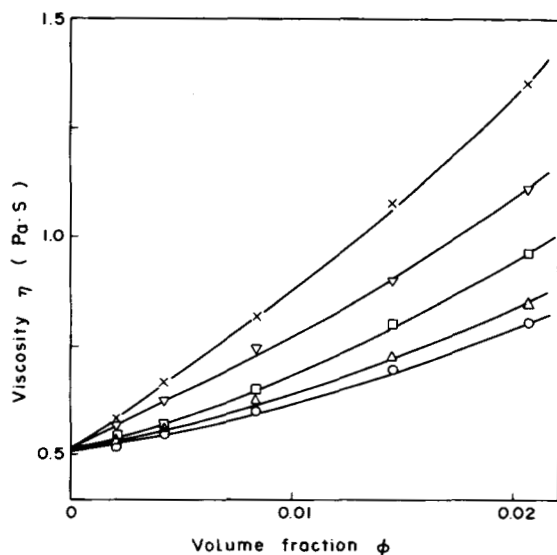


Fig. 2. Dependence of viscosity on volume fraction of iron oxide for dispersions in epoxy resin solutions. \circ , $D = 384 \text{ sec}^{-1}$; Δ , $D = 192 \text{ sec}^{-1}$; \square , $D = 76.8 \text{ sec}^{-1}$; ∇ , $D = 38.4 \text{ sec}^{-1}$, \times , $D = 19.2 \text{ sec}^{-1}$.

Application of Mooney Equation

Various equations concerning fluid characteristics in dispersions have been proposed.¹⁻⁷ Some of these can be applied to dispersions of acicular particles such as iron oxide. Dispersions in our work were found to be successfully represented by the Mooney equation,^{2,3}

$$2.303 \log (\eta / \eta_s) = [\eta] \phi / (1 - \phi / \phi_m) \tag{1}$$

where η_s is solution viscosity, $[\eta]$ is the intrinsic viscosity of the suspended particles not the polymer, and ϕ_m is considered to be an empirical constant. In the original derivation, ϕ_m was the maximum volume fraction of particles. Actually,

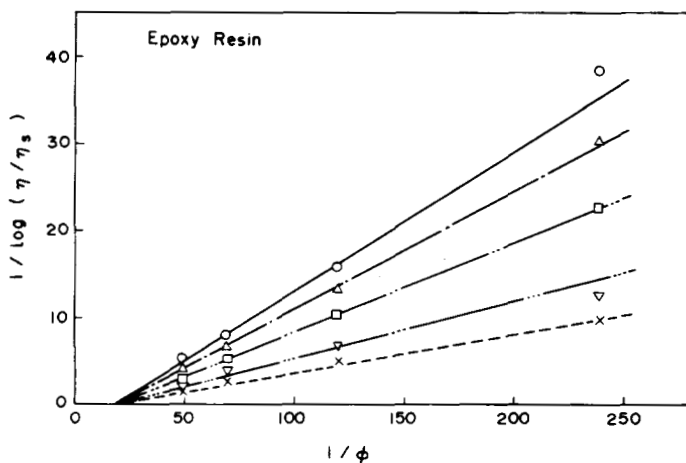


Fig. 3. Applicability of Mooney equation in evaluating intrinsic viscosity of epoxy resin. \circ , $D = 384 \text{ sec}^{-1}$; Δ , $D = 192 \text{ sec}^{-1}$; \square , $D = 76.8 \text{ sec}^{-1}$; ∇ , $D = 38.4 \text{ sec}^{-1}$; \times , $D = 19.2 \text{ sec}^{-1}$.

Mooney used the symbol $k = 1/\phi_m$ and termed it a crowding factor. Equation (1) predicts that $\eta/\eta_s \rightarrow \infty$ as $\phi \rightarrow \phi_m$.

To determine whether data conform to eq. (1), the equation is rewritten:

$$1/\log(\eta/\eta_s) = 2.303/[\eta]\phi - 2.303/[\eta]\phi_m \quad (2)$$

Thus, a plot of the left side against $1/\phi$ should yield a straight line. The parameter $[\eta]$ is obtained from the slope. The good fit of the viscosity data to the Mooney equation is shown in Figures 3-5. Intrinsic viscosities obtained from these data are shown in Figure 6 and Table II.

DISCUSSION

Intrinsic Viscosity

To interpret intrinsic viscosity data, it is first necessary to consider the expected behavior at infinite dilution of the dispersion.

The intrinsic viscosity of a dispersion of rigid spheres is 2.5 according to Einstein. The specific viscosity of an infinitely dilute dispersion of spherical flocs is given by

$$\eta_{sp} = 2.5\phi_f + [\eta]_{pp}\phi_{pp} \quad (3)$$

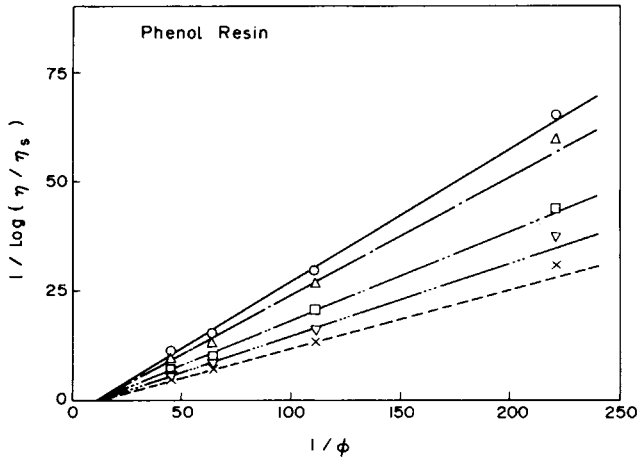


Fig. 4. Applicability of Mooney equation in evaluating intrinsic viscosity of phenol resin. O, $D = 384 \text{ sec}^{-1}$; Δ , $D = 192 \text{ sec}^{-1}$; \square , $D = 76.8 \text{ sec}^{-1}$; ∇ , $D = 38.4 \text{ sec}^{-1}$; x, $D = 19.2 \text{ sec}^{-1}$.

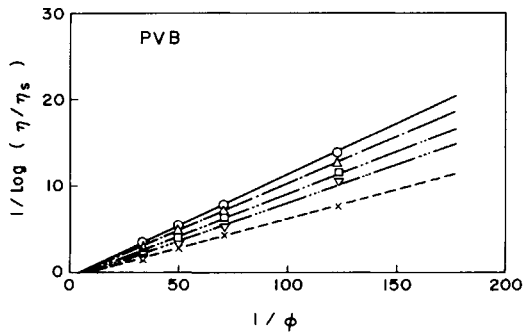


Fig. 5. Applicability of Mooney equation in evaluating intrinsic viscosity of PVB. O, $D = 384 \text{ sec}^{-1}$; Δ , $D = 192 \text{ sec}^{-1}$; \square , $D = 76.8 \text{ sec}^{-1}$; ∇ , $D = 38.4 \text{ sec}^{-1}$; x, $D = 19.2 \text{ sec}^{-1}$.

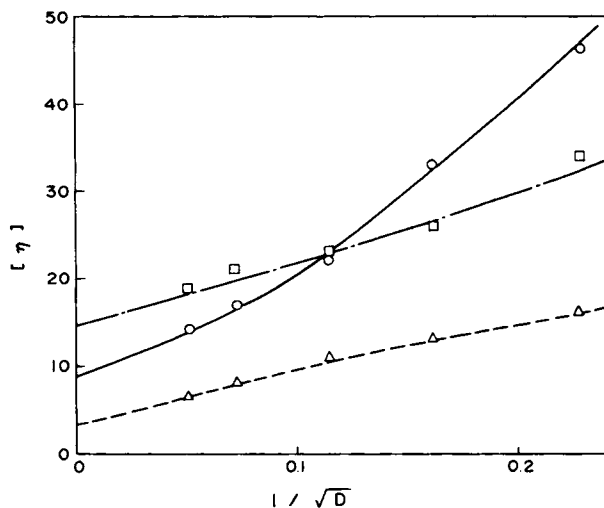


Fig. 6. Plots of $[\eta]$ from Mooney equation against $1/\sqrt{D}$. \circ , epoxy resin; Δ , phenol resin; \square , PVB.

where ϕ_f is the floc volume fraction and $[\eta]_{pp}$ and ϕ_{pp} are the intrinsic viscosity and volume fraction of particles that do not reside in a floc. From the relation, $[\eta] = (\eta_{sp}/\phi)_{\phi \rightarrow 0}$, we assumed the following in dilute dispersion

$$\eta_{sp} = [\eta]\phi \quad (4)$$

where ϕ is the volume fraction of particulate matter in the dispersion. Elimini-

TABLE II
Rheological Properties for Dispersions of Iron Oxide in Various Polymer Solutions

Polymer	D (sec ⁻¹)	$[\eta]^a$	ϕ_{ppf}^b	θ^c sec ⁻¹	α (D/θ)
Epoxy resin	19.2	46.1	0.054	3.77	5.1
	38.4	32.9	0.076	3.77	10.2
	76.8	2.9	0.114	3.77	20.4
	192	17.1	0.146	3.77	50.9
	384	14.0	0.179	3.77	102
	∞	0.0 ^d	0.278 ^d		
Phenol resin	19.2	16.1	0.155	3.33	5.8
	38.4	13.2	0.189	3.49	11.0
	76.8	11.0	0.227	3.64	21.1
	192	8.2	0.304	3.72	51.6
	384	0.6	0.380	3.77	102
	∞	3.0 ^d	0.833 ^d		
PVB	19.2	33.9	0.074	3.73	5.1
	38.4	26.2	0.095	3.90	9.8
	76.8	23.0	0.109	4.08	18.8
	192	20.9	0.120	4.16	46.2
	384	18.9	0.132	4.21	91.2
	∞	14.5 ^d	0.173 ^d		

^a Intrinsic viscosities evaluated from the Mooney equation.

^b ϕ_{ppf} volume fraction of iron oxide in a floc.

^c θ , rotary diffusion constant.

^d Values obtained by extrapolation in Fig. 6.

nation of η_{sp} between eq. (3) and eq. (4) gives:

$$\phi/\phi_f = 2.5/[\eta] + [\eta]_{pp}\phi_{pp}/[\eta]\phi_f \quad (5)$$

If the tendency for floc formation is appreciable, then $\phi_{pp} \ll \phi_f$ and $[\eta]_{pp} < [\eta]$. Hence, eq. (5) reduces to:

$$\phi_{ppf} = \phi/\phi_f = 2.5/[\eta] \quad (6)$$

for

$$\phi_{pp} \ll \phi_f$$

where ϕ_{ppf} is the volume fraction of primary particles in a floc.

In many dispersions, especially those of particulate solids in pure liquid, attracting forces between particles cause the formation of loose clusters or flocs whose most probable shape is spherical. Liquid is immobilized within the floc. Thus, floc size is given by an effective hydrodynamic volume V_{ef} . Although a floc affects viscosity in the same manner as spherical particles of volume V_{ef} , a floc no doubt deforms readily and its effective size decreases with increasing shear rate.

For uniform dispersions of prolate ellipsoids having axial ratio P of 5 and 10, for example, the intrinsic viscosities in the limit of zero shear rate are 5.8 and 13.6, respectively, according to Scheraga.⁸ With increasing shear rate, the major axis of the ellipsoids becomes progressively more highly oriented in the flow direction, producing a reduction in $[\eta]$. The orientation is opposed by the Brownian motion of the particles. A measure of the disorientation rate in a quiescent dispersion is the rotary diffusion constant θ , which for $P > 5$ is given by the approximation relation⁹:

$$\theta = kT(3 \ln P + 0.57)/8\pi\eta_s a^3 \quad (7)$$

where kT is the product of Boltzmann's constant and the absolute temperature, and a is the length of the major axis. Hence, in considering the shear rate dependence of $[\eta]$, the key parameter is not D but the ratio $D/\theta = \alpha$. Specially, if α is very small, particles will remain randomly oriented during flow. Conversely, if α is large, orientation will be high.

Dispersions of Iron Oxide

From an observation of γ -Fe₂O₃ electron micrographs, it is estimated that the acicular primary particles are 0.40 μm long, and have a ~ 6 – 7 axial ratio. Though dispersions in three polymers were investigated, discussion here will be confined mainly to the results for an epoxy resin solution.

According to eq. (7), the rotary diffusion constant θ for an isolated iron oxide particle in an epoxy resin solution is 3.77, i.e., near values in other polymer solution, as shown in Table II. As intrinsic viscosities were evaluated at shear rates of from 19.2 to 384 sec^{-1} in this study, the smallest and largest values are 5.1 and 102, respectively. When $P = 7$, Scheraga's calculation shows that $[\eta] = 7.1$ at $\alpha = 5.1$, and that $[\eta] = 3.90$ at $\alpha \geq 60$.

To explain the observed $[\eta] = 46$ at $D = 19.2 \text{ sec}^{-1}$ in terms of a uniform ellipsoid dispersion, it would be necessary to assume that $P = 26$, an unrealistic value for iron oxide particles. Furthermore, the $[\eta]$ value in this solution should

be identical with that in the other two polymer solutions on account of almost the same α , if the shear rate dependence results from the orientation of highly elongated particles. These observations provide convincing evidence, solely from the rheological viewpoint, that flocs exist even in very dilute dispersions.

If essentially all particles reside in flocs, the $[\eta] = 46$ observed at 19.2 sec^{-1} , gives $\phi_{ppf} = 0.05$ according to eq. (6). That is, the floc contains 95% by volume of immobilized liquid. This value is considered realistic. Also, it is in the same range as values derived from sedimentation rate data obtained by Michaels and others.¹⁰

Floc size can be reduced by increasing the shear rate, thus reducing the immobilized liquid fraction and hence, intrinsic viscosity. At a sufficiently high shear rate, some primary particles and clusters of several particles probably exist along with flocs.

The intrinsic viscosity at infinite shear rate appears to be about 9.0 as shown in Figure 6. If it is assumed that no flocs or clusters of several particles are present, it may be concluded that $[\eta]_{\infty} = 9$ signifies $P = 16$.

Although this value is about twice that of the most probable axial ratio of the $\gamma\text{-Fe}_2\text{O}_3$ particles, rodlike units could quite probably be formed from several primary particles. This is primarily due to magnetic forces between the $\gamma\text{-Fe}_2\text{O}_3$ particles.

On the other hand, if $[\eta]_{\infty} = 9$ is interpreted in terms of eq. (6), it follows that $\phi_{ppf} = 0.28$, a value which could readily be characteristic of a small particle cluster.

Of the three polymers, the lowest $[\eta]$ value is obtained in the dispersion of the phenol resin solution. This dispersion seems to be superior for practical application. For the other properties, almost identical results were obtained as shown in Table II.

CONCLUSIONS

The principal results of the present study may be summarized as:

(1) The concentration dependence of viscosity can be represented by the Mooney equation. Intrinsic viscosity $[\eta]$, as a function of shear rate, was obtained by fitting data to this equation. It was found to decrease from about 46 at 19.2 sec^{-1} to 14 at 384 sec^{-1} for an epoxy resin solution.

(2) Intrinsic viscosity $[\eta]$ was lowest of three polymer solutions in dispersion of phenol resin. This dispersion seems to be superior for practical application.

(3) The large $[\eta]$ value indicates that flocs containing immobilized liquid exist. Also, the decrease in $[\eta]$ with increasing shear rate results in a decrease of average floc size.

(4) Intrinsic viscosities at infinite shear rate, are 9, 3, 14, in epoxy resin, phenol resin, and PVB, respectively. Intrinsic viscosity at infinite shear rate indicates that possibly hydrodynamic units are the acicular iron oxide particles. However, they consist of either several primary particles linked together or very small flocs of tightly bound particles.

These results should open the way for high quality disks and tapes without significant increases in cost.

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