A New Model for the Shear Viscosity of Carbon Black–Polybutadiene, Styrene Suspensions

CHAO-CHENG CHEN and WEN-YEN CHIU*

Graduate Institute of Materials Engineering, National Taiwan University, Taipei, Taiwan, Republic of China 10764

SYNOPSIS

The shear viscosity of carbon black–polybutadiene, styrene suspensions is studied. The suspensions show strong shear thinning behavior. At very low shear rate, an extrapolated constant shear stress that is designated as the apparent yield stress can be obtained. A model is developed based on the kinetics and energy dissipation of the flocculation process in suspensions of Newtonian liquid. With a mixing rule, the model can also predict the viscosity of suspensions with particle-size distribution. The applicability of the model can be extended to suspensions of non-Newtonian liquid if the parameters in the model are regarded as functions of the viscosity of suspending liquid.

INTRODUCTION

Viscosity is an important physical property in processes where suspensions are involved. It tells us what the inner structure of suspension may be like and how easy the suspension can be handled. Therefore, viscosity of suspensions is worth studying for both theoretical research and practical application. As a matter of fact, a lot of models based on either theoretical or empirical consideration have been used to describe how the viscosity of suspension changes with process parameters like shear rate and particle concentration. Especially for those systems that consist of Newtonian liquids and noninteractive particles, we can find extensive research on their viscosity. In this work, by combining two approaches already adopted in many articles, we try to develop a model of viscosity as a function of shear rate for systems of strongly interactive particles and Newtonian liquid and then extend the model to systems of non-Newtonian liquid. The two approaches are briefly reviewed before the development of our model.

In concentrated suspensions or suspensions of interactive particles, particles are prone to aggregate and deaggregate in shear field. If the rates of these two processes are equal, the structural state of aggregates might reach a kinetic equilibrium that decides the viscosity of suspension. This is also the underlying cause for pseudoplasticity. Therefore, a kinetic approach is adopted by researchers to describe the structure changes of aggregates in shear field. Cross[1,2] assumed that the growth of aggregates was due to Brownian motion and aggregates were broken down by shear stress. Viscosity was made proportional to the sizes of aggregates. The following equation was obtained:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + b\dot{\gamma}^m} \tag{1}$$

where η_0 and η_∞ are the viscosity at zero shear rate and high shear rate, respectively, and b and m are constants.

Krieger and Dougherty[3] studied suspensions composed of Newtonian liquid and noninteractive particles of the same size. With similar approach the assumption, they attributed the pseudoplasticity to the creation and rupture of doublets of particles. Equation (2) was derived

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + b\tau} \tag{2}$$

where b is a constant.

The other approach makes use of the correlation between viscosity and dissipation energy. The nec-

* To whom correspondence should be addressed.

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essary energy to keep suspension flow includes various dissipation mechanisms like breakage or deformation of aggregates, additional viscous energy due to flow around particles, and so on. Since different combinations of dissipation mechanisms were chosen by researchers, different equations were derived. Michaels and Bolger[4] studied suspension of kaolin in water. They considered three mechanisms: energy stored in aggregates, energy needed to rupture linkage, and viscous energy. Firth and Hunter[5-7] proposed an elastic floc model to calculate dissipation energy with the same considerations as Michaels and Bolgers. In Van de Ven and Hunter's study,[8] the elastic floc model was still used. However, different mechanisms were considered. The main causes for energy dissipation were rupture of linkage, resistance to motion of particles in aggregates when aggregates were stretched, and the viscous energy inside aggregates.

In this work, we adopt the kinetic approach as the basic structural model to calculate the dissipation energy and then the viscosity for the system of Newtonian liquid and strongly interactive carbon black particles. In the case of non-Newtonian liquid and carbon black, we devise an algorithm based on the model for Newtonian liquid to calculate the viscosity.

THEORETICAL CONSIDERATION

In a previous paper,[9] we considered the kinetics of aggregation and degregation. For suspension of Newtonian liquid and monosize particles, the degregation rate was written as

$$\frac{dn_1}{dt} = k_1 n \dot{\gamma}^m \quad (3)$$

and the aggregation rate as

$$\frac{dn_c}{dt} = \frac{k_c}{\lambda^m}(n_0 - n) \quad (4)$$

where n is the current structural state or the number of links between particles; n_0 is the structural state at zero shear rate; k_1 and k_c are the loss and growth rate constants, respectively; λ is a characteristic time for growth of aggregates; and m is a parameter that is assumed to be related only to particle surface properties but irrelevant to particle size.[9] At steady state, we find the structural state at a given shear rate:

$$n = \frac{n_0}{1 + b\dot{\gamma}^m}; \quad b = \frac{k_1}{k_c}\lambda^m \quad (5), (6)$$

In the following section, we will use this model to calculate the dissipation energy for suspensions of Newtonian liquids.

I. VISCOSITY OF SUSPENSION OF NEWTONIAN LIQUID

Here, the total dissipation energy, E_t, is assumed to be the sum of network energy (E_n), creep energy (E_{cr}), and viscous energy (E_v), which will be explained individually later. It should be noted that the unit of the various energy terms is really energy per unit time per unit volume, not simply energy:

$$E_t = E_n + E_{cr} + E_v \quad (7)$$

and

$$\tau = E/\dot{\gamma}; \quad \eta = \tau/\dot{\gamma}$$
$$\tau = \tau_n + \tau_{cr} + \tau_v \quad (8)$$

(i) E_n

This is the energy stored in aggregates and proportional to the structural state of the aggregates:

$$\frac{E_n}{\dot{\gamma}} = \tau_n = \frac{Y}{1 + b\dot{\gamma}^m} \quad (9)$$

where Y is the apparent yield stress. Y is chosen as a parameter since in systems of strong interactive particles like carbon black, an apparent yield stress is always found.

(ii) E_{cr}

This is the energy needed to break the aggregates in unit time and volume. This term can be rewritten as follows:

E_{cr} = (the number of links ruptured per unit time per aggregate)

× (the number of aggregates

per unit volume)

× (the necessary energy to rupture a link)

$$= \frac{dn_1}{dt} \times \frac{\Phi_A}{\frac{\pi}{6} d_A^3} \times W$$

where Φ_A is the volume fraction of aggregates and d_A is the average diameter of aggregates. For simplicity, we assume

$$\frac{\Phi_A}{\frac{\pi}{6} d_A^3} = k'\dot{\gamma}^{m'}$$

therefore,

$$E_{cr} = \frac{k_1 n_0 \dot{\gamma}^m}{1 + b\dot{\gamma}^m} \times k'\dot{\gamma}^{m'} \times W = \frac{k\dot{\gamma}^{n+1}}{1 + b\dot{\gamma}^m} \quad (10)$$

$$k = k_1 n_0 k' W; \; n + 1 = m + m'$$

$$\tau_{cr} = \frac{k\dot{\gamma}^n}{1 + b\dot{\gamma}^m} \quad (11)$$

(iii) E_v

This is the additional energy dissipation around particles

$$E_v = \eta_\infty \dot{\gamma}^2 \quad (12)$$
$$\tau_v = \eta_\infty \dot{\gamma}$$

Now, we have the sum of eqs. (9), (11), and (12):

$$\tau = \frac{Y + k\dot{\gamma}^n}{1 + b\dot{\gamma}^m} + \eta_\infty \dot{\gamma} \quad (13)$$

Therefore, the viscosity can be found.

In the case of particles of bimodal size distribution, we will adopt the same approach in our previous paper[9] (but with the equation in this work) to test its validity.

II. VISCOSITY OF SUSPENSION OF NON-NEWTONIAN LIQUID

It is natural to expect strong non-Newtonian behavior from suspensions of non-Newtonian liquids. However, it would be difficult to follow the individual and cooperative structural changes of the two phases (liquid medium and solid particle). Furthermore, the theoretical approach in this field is still restricted by some assumptions on liquid properties and solid structure like power law fluid and cell model.[10] Therefore, to find the viscosity, we would try a simple and empirical calculation scheme in which the model for suspension of Newtonian liquid is still applicable only with some additional assumptions.

At a given shear rate, a non-Newtonian liquid attains its corresponding viscosity. At the same shear rate, the suspension of this liquid is assumed to be composed of a Newtonian liquid of the same viscosity. Then, the model derived above is applied with the proper parameters only if we know the relations between the parameters and the viscosity of the liquid phase. Thus, the viscosity of suspension of non-Newtonian liquid at various shear rates could be estimated easily with the equation for suspension of Newtonian liquid if other conditions are the same. We will show how this algorithm is carried out in the experimental section. Finally, it is worthwhile to mention that it is only an approximation to consider the non-Newtonian medium to behave as a Newtonian medium whose viscosity is that of the non-Newtonian medium at the same overall rate of shear, since local rates of shear near particles are often higher than is the overall rate of shear.

EXPERIMENTAL

Material and Sample Preparation

Two kinds of carbon black were chosen as the fillers, HI-Black 20L and HI-Black 40B, which will henceforth be called CB1 and CB2, respectively. They are both furnace black. CB2 has larger surface area (by nitrogen absorption, 153 m^2/g vs. 86 m^2/g), larger DBP absorption (130 cc/100 g vs. 55 cc/100 g), but smaller particle size (19 nm vs. 28 nm). Carbon black is demoistured for 24 h at 105°C before use. Mediums of different viscosity are prepared by dissolving different percent weights of polybutadiene (96% cis) in styrene: 4 wt % of polybutadiene in styrene is found to be Newtonian (0.53 poise) and 7 wt % non-Newtonian. (They will be denoted as 4% BR and 7% BR in the following context.) The polybutadiene has a $\bar{M}_n$ of about 1.6×10^5 and $\bar{M}_w$ 5.0×10^5. To prepare the suspension, the mixture of carbon black and BR solution is ground in a ball mill for 24 h.

Measurement

The measurement was carried out with a HAAKE viscometer. Suspension temperature was kept at 30°C for all measurements. The shear rates ranged from 10^{-1} to 10^{3} s^{-1}. For all measurements, the sample was first sheared at the highest shear rate possible; then the shear rate was shifted to the given value under which the viscosity was to be obtained. Besides, appropriate time was allowed between two consecutive measurements so that a steady and reproducible value was obtained.

Theoretical Prediction

In the model for suspensions of Newtonian liquids, the parameter Y (the apparent yield stress) and η_∞ (viscosity at high shear rates) were obtained by extrapolation of experimental data; other parameters, b, k, n, and m, were obtained by least-squares fitting.

To check our algorithm for calculating viscosity of suspensions of non-Newtonian liquids, the following procedures were taken.

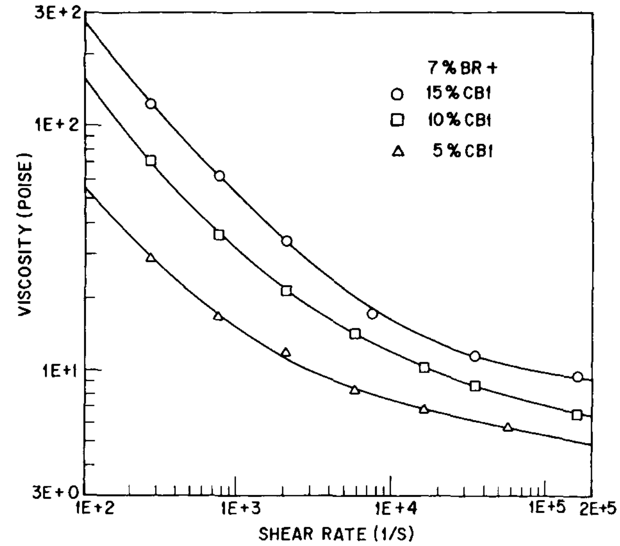

Figure 2 Effect of shear rate and particle concentration on the viscosity of suspension of non-Newtonian liquid (7% BR + CB2).

i. Three Newtonian liquids, 4% BR, 4.5% BR, and 5% BR, and the corresponding suspensions of 10 wt % CB1 were prepared. Then, the shear-dependent viscosity for these suspensions was measured. After the data was fitted, the parameters were obtained.
ii. 7% BR solution, which is non-Newtonian, was prepared. Its shear-dependent viscosity was also obtained.
iii. From (i), we assumed some empirical equations describing the relationships between the parameters obtained in (i) and the viscosity

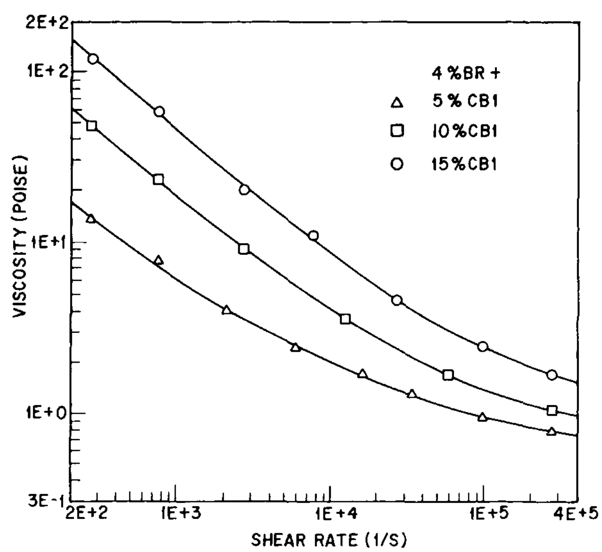

Figure 1 Effect of shear rate and particle concentration on the viscosity of suspension of Newtonian liquid (4% BR + CB1).

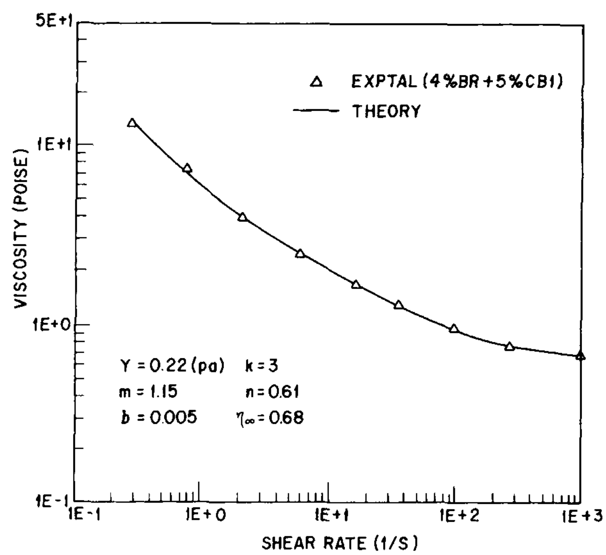

Figure 3 Comparison between experimental data and predicted values of the viscosity of suspension of Newtonian liquid (4% BR + 5% CB1).

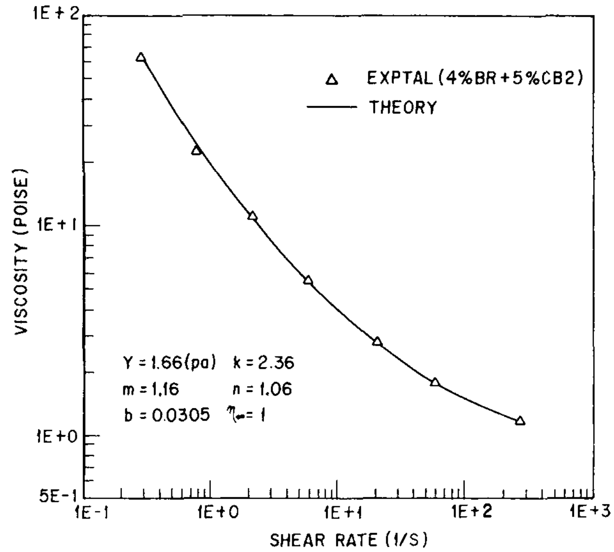

Figure 4 Comparison between experimental data and predicted values of the viscosity of suspension of Newtonian liquid (4% BR + 5% CB2).

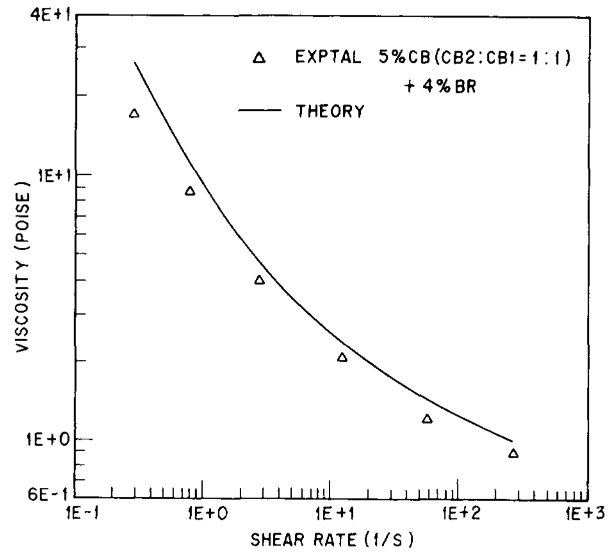

Figure 6 Comparison between experimental data and predicted values of the viscosity of suspension composed of Newtonian liquid (4% BR) and two kinds of particles CB1 and CB2, 50 wt % of the particles being CB2.

of the Newtonian liquids. We can calculate the parameters for suspension of 7% BR and 10 wt % CB1 at a given shear rate simply by substituting the viscosity of 7% BR at that shear rate [from (ii)] into those equations obtained above. The model is again applied with these parameters, and the shear-dependent viscosity of the suspension can be estimated.

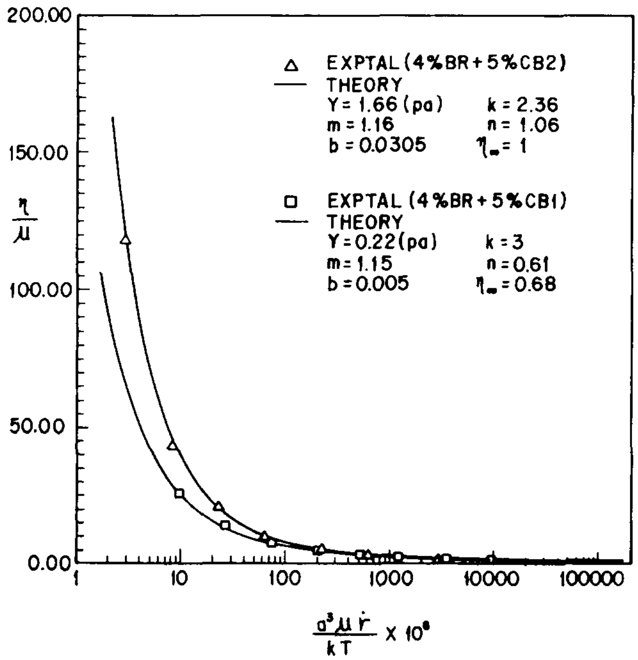

Figure 5 Comparison between data from Figures 3 and 4 in dimensionless forms [η/μ vs. $a^3\mu\dot{\gamma}/(kT)$].

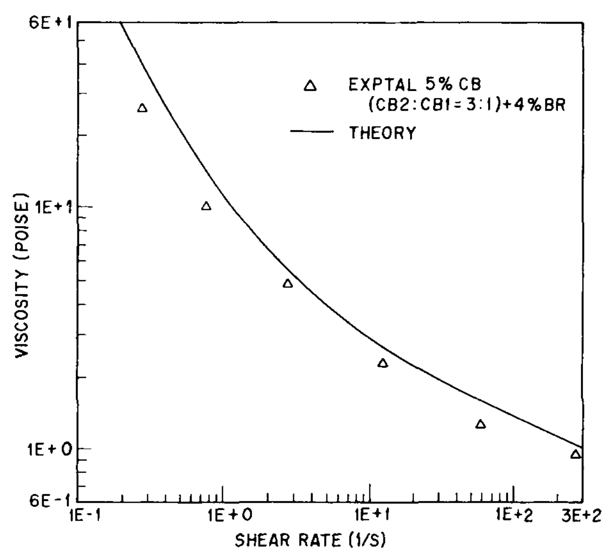

Figure 7 Comparison between experimental data and predicted values of the viscosity of suspension composed of Newtonian liquid (4% BR) and two kinds of particles, CB1 and CB2, 75 wt % of the particles being CB2.

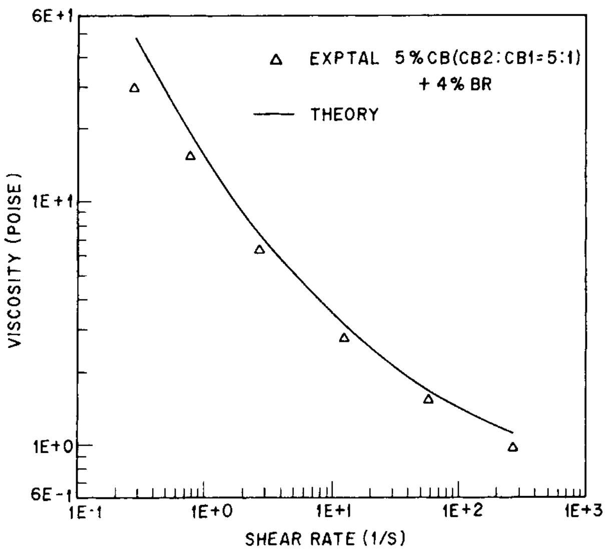

Figure 8 Comparison between experimental data and predicted values of the viscosity of suspension composed of Newtonian liquid (4% BR) and two kinds of particles, CB1 and CB2, 83.3 wt % of the particles being CB2.

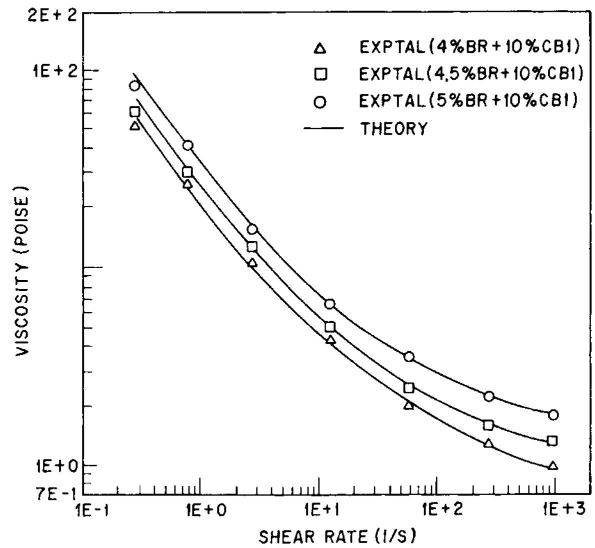

Figure 9 Experimental data and predicted values of the viscosity of three suspensions of Newtonian liquids (4%, 4.5% 5% BR + 10% CB1).

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate how shear rate and particle concentration affect the viscosity of suspension of Newtonian liquid and non-Newtonian liquid, respectively. Both show shear thinning behavior in the experimental range. Increase of carbon black concentration raises the viscosity evidently, especially at low shear rates. This is the reason that at low shear rates the interparticle forces are dominant. Contrarily, at high shear rates, hydrodynamic force prevades and differences in viscosity are due mainly to the voume effect of the particle.

We apply our model [eq. (13)] to predict the viscosity of suspensions of Newtonian liquid at different shear rates. The results are shown in Figures 3 and 4 (for systems of 4% BR + 5% CB1 and 4% BR + 5% CB2, respectively). The correlation is good. We also see that suspensions of smaller particles, all other conditions being set, have higher viscosity. This phenomenon may be contributed to the fact that CB2 has a larger surface area and a stronger tendency to aggregate or that there is more occluded liquid in the aggregates of CB2, which makes the effective particle concentration of CB2 even higher. To compare data in Figures 3 and 4, we plot η/μ (relative viscosity) vs. Péclet number $(a^3\mu\dot{\gamma}/(kT)$, where a is the radius of particle, k is the Boltzman constant, and T is absolute temperature), in Figure 5. As expected, the curves diverge at low shear rates and get closer with an increase of shear rate.

The parameters obtained in the model are also listed in Figures 3 and 4. The values of m's for the two systems with carbon black of different sizes are very close, as is in accord with our assumption in the Theoretical Prediction section. b^2 is found to be larger than $b1$ (1: CB1; 2: CB2; $b1$ = 0.005; $b2$ = 0.0305). By definition, b is proportional to λ^m, λ being the characteristic time of aggregation. Therefore, a smaller particle has larger b value since it aggregates more slowly because of smaller surface

Table I Parameters for the Three Suspensions of Newtonian Liquids

% BR	μ	b	k	Y	η_∞	n	m
4	0.53	0.03063	6.187	13.5	0.75	0.6953	0.6819
4.5	0.68	0.08675	10.05	16.0	1.04	0.6000	0.4415
5	0.95	0.24260	17.27	21.3	1.43	0.5660	0.2589

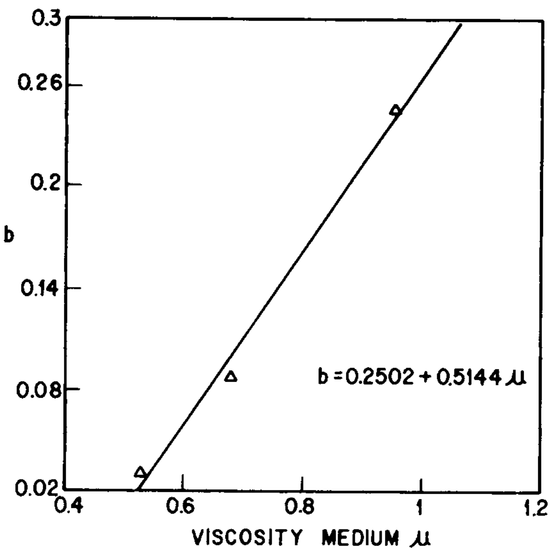

Figure 10 Effect of the viscosity of medium of parameter b.

area. We can also find that the values of m's are positive for both suspensions (by definition $m' = n - m + 1$). We assume in the theory that Φ_A/d_A^3 is proportional to $\dot{\gamma}^m$. When aggregates are ruptured with shear, both Φ_A and d_A^3 decrease with an increase of shear rate. The reduction in Φ_A comes from the occluded liquid given off, and d_A^3 diminishes simply because the size of aggregates are broken down. Therefore, that m's are positive means Φ_A is not as much affected by shear rate as is d_A^3.

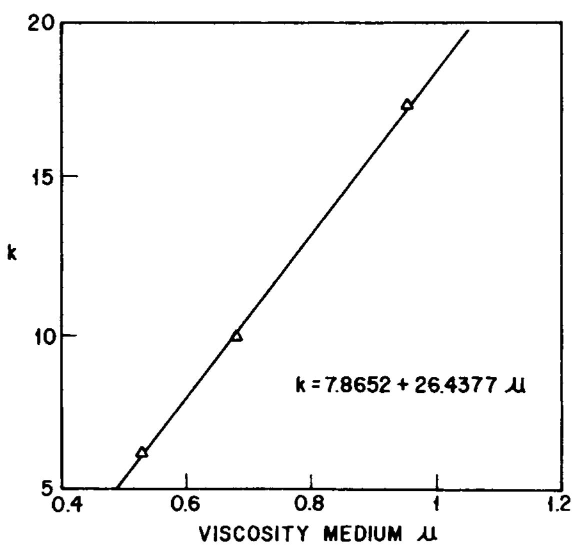

Figure 11 Effect of the viscosity of medium on parameter k.

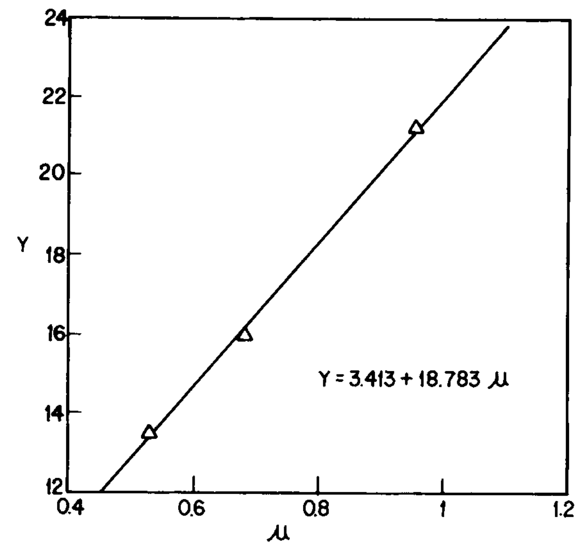

Figure 12 Effect of the viscosity of medium on Y.

Figures 6, 7, and 8 compare the viscosity obtained from the theoretical prediction [the same approach as in our previous paper[9] but using eq. (13)] and experimental data of suspensions composed of two kinds of carbon black (4% BR + CB1 + CB2). In all cases, prediction values are higher than are the experimental data. We mentioned in our previous paper[9] that the increase in maximum packing factor, Φ_m, after mixing particles of different sizes, would lower the viscosity. We do not take Φ_m into account in the theory, so we overestimate the viscosity.

According to our algorithm for predicting the vis-

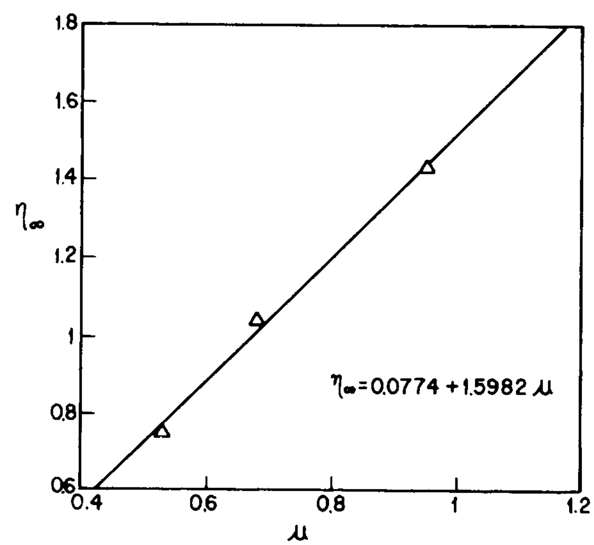

Figure 13 Effect of the viscosity of medium on η_∞.

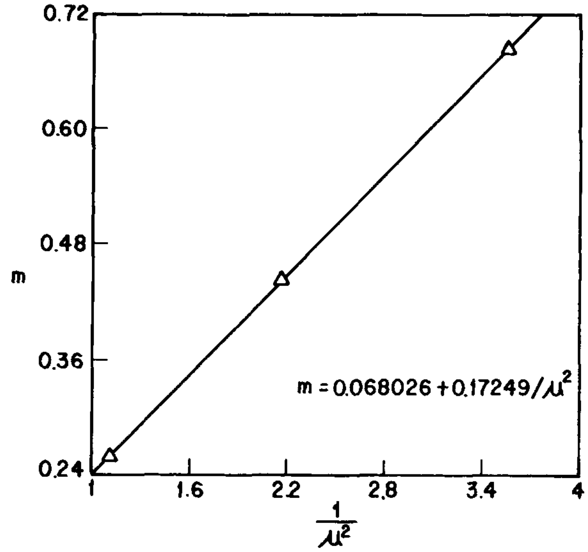

Figure 14 Effect of the viscosity of medium on parameter *m*.

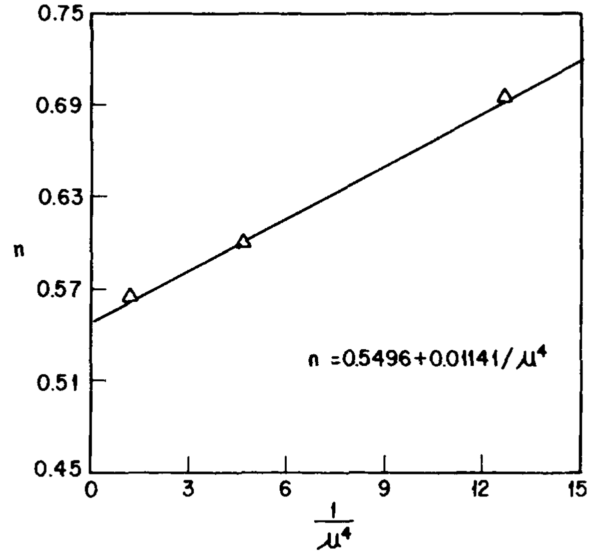

Figure 15 Effect of the viscosity of medium on parameter *n*.

cosity of suspensions of non-Newtonian liquids, the viscosity of three suspensions of Newtonian liquids (4%, 4.5%, 5% BR + 4% CB1, respectively) are first obtained experimentally and fitted with eq. (13). Figure 9 and Table I are the results of fitting. Then, the parameters obtained are shown in Figures 10–15 as functions of the viscosity of the Newtonian liquid (μ). The parameters b, k, Y, and η_∞ all increase linearly with μ: m with μ^{-2} and n with μ^{-4}. Next, the shear-dependent viscosity of non-Newtonian liquid, 7% BR, is obtained and the result is listed in Table II.

At a certain shear rate we have a value of viscosity, and it is substituted into those empirical equations to find the parameters for the suspension of 7% BR + 10% CB1. In the final step, we simply use the parameters to calculate the viscosity at the shear rate. The calculated values are compared with the experimental data in Figure 16. It can be seen that at low shear rates the prediction is satisfactory but the experimental data deviate upward in the high shear rate region.

As expected, b increases with increasing the viscosity of the liquid phase since particles aggregate more slowly in the thicker medium. As to the parameter η_∞, we may drop the minute constant of the empirical equation relating $\eta\infty$ to μ in Figure 13. Then, η_∞ becomes proportional to μ, as conforms to the form of the Einstein equation, though the coefficient is not the same. Also from Table II, as μ increases, m gets smaller and b gets larger (or λ becomes larger). In other words, the flocculation and deflocculation rates of aggregates are very slow in viscous liquid. This could be the reason why in Figure 16 the shear thinning behavior of suspension of non-Newtonian liquid is not as strong as that of Newtonian liquid. There is another way to explain the phenomenon in Figure 16. For the viscous liquid

Table II Parameters, Experimental Data, and Predicted Values of the Viscosity of the Suspension 7% BR + 10% CB1 at Various Shear Rates

$\dot{\gamma}$	μ	b	k	Y	η_∞	n	m	η_{expt}	η_{theory}
270.54	1.5	0.5214	31.8	31.6	2.32	0.5521	0.1447	6.72	3.57
58.05	2.0	0.7786	45.0	41.0	3.12	0.5505	0.1112	9.60	6.70
12.42	2.8	1.1901	66.2	56.0	4.40	0.5500	0.0900	15.2	14.8
2.7	3.4	1.4988	82.0	67.3	5.36	0.5500	0.0830	29.5	34.8
0.76	3.8	1.7251	93.6	75.5	6.06	0.5499	0.0797	71.3	82.8
0.27	3.8	1.7251	93.6	75.5	6.06	0.5499	0.0797	147.	176.

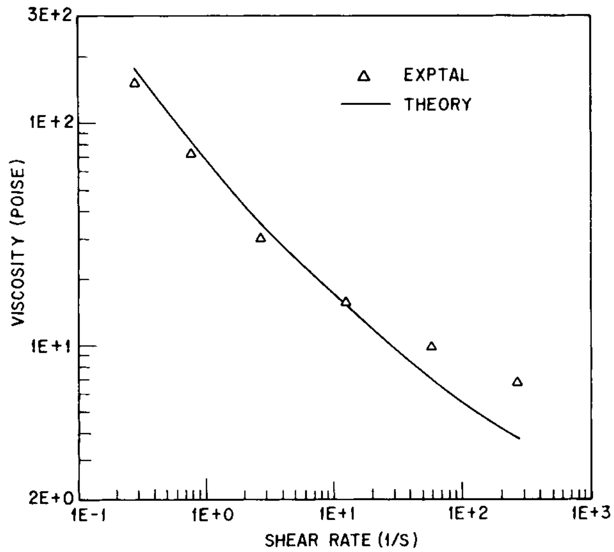

Figure 16 Comparison between experimental data and predicted values of the viscosity of suspension of non-Newtonian liquid (7% BR + 10% CB1).

phase (like polymer melt, viscosity > 10^3 poise), the hydrodynamic force exerted on particles cannot overcome the viscous force to form aggregates. Then, the suspension will not show strong shear thinning behavior.

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