

Extensional Viscosity of Silica Dispersions

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Synopsis

The rheological behavior in extensional flow was investigated for silica dispersions in polymer solutions using the tubeless syphon technique. The flow field of tubeless syphon is unsteady in the Lagrangian sense; hence the data are taken under transient stress conditions. Due to the insensitive nature of the extensional rate to flow rate, the extensional viscosities at different flow rates lie very close to a single curve, once they are plotted against strain. Two important points are noted with regard to the behavior of the dispersions. First, the extensional viscosity decreases with increasing particle concentration. Second, the viscosity growth curves of the dispersions can be superimposed by a vertical shift, but the curve shape differs from that of the medium. This implies a change in the relaxation time.

INTRODUCTION

The rheological behavior in extensional flow for dispersions in polymer solutions is very important because this type of flow takes place in many manufacturing processes. However, relatively little effort is devoted to the extensional viscosity measurement for dispersions, whereas the behavior in shearing flow has been extensively studied by many authors.¹⁻⁴ This is related to the practical difficulties involved in the measurement, especially in the case of low viscosity fluids. Actually, one cannot grab and pull uniformly those whose shear viscosities are less than 10^2 Pa-s. In recent years, a tubeless syphon has been employed by various authors⁵⁻⁸ to investigate the extensional viscosity for polymer solutions. In the tubeless syphon apparatus the liquid is continuously drawn into a nozzle which is above the free level of liquid. The technique of forming a vertical free boundary column of liquid using a vacuum source was first described by Fano⁹ in 1908. The efficacy of this technique for the extensional viscosity measurement was rediscovered by Astarita and Nicodemo.¹⁰ The tubeless syphon enables us to evaluate the extensional viscosity for elastic liquids of relatively low viscosity. Therefore, it is also suitable for dispersions in dilute polymer solutions.

Nicodemo et al.¹¹ seem to have been the first to investigate experimentally the extensional viscosity of dispersions by the tubeless syphon. They used the dispersions of glass beads having diameters between $40\ \mu\text{m}$ and $50\ \mu\text{m}$ in polymer solutions and found that, while the shear viscosity increased, the extensional viscosity of dispersions decreased very sharply with increasing particle concentration. As a simplified approach, the results were explained by assuming that the cross-sectional area on which the tensile stress must be related is that occupied by the polymer solution alone. In this paper, silica, about $20\ \text{nm}$ in diameter, has been used to study the effect of the presence of fine particles on the extensional viscosity of polymer solution. The data are taken under transient stress

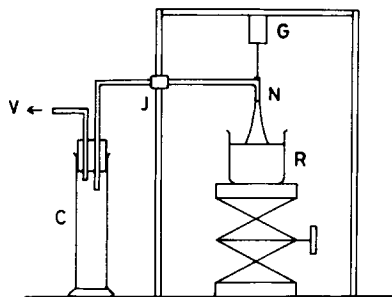


Fig. 1. Tubeless syphon apparatus: (C) graduated cylinder; (G) strain gauge; (J) joint; (N) nozzle; (R) reservoir; (V) vacuum pump.

fields. The dependence of the transient extensional viscosity on particle concentration will be discussed.

EXPERIMENTAL

A sketch of the tubeless syphon apparatus is shown in Figure 1. Sample liquid is sucked up into the nozzle at flow rate Q by a vacuum pump. The liquid is contained in a reservoir with a diameter of 9.0 cm. The internal radius of the nozzle, R_n , is 0.09 cm. The nozzle is initially immersed in the liquid, and, after the pump starts sucking, the reservoir is slowly lowered until a stable flow is obtained between the nozzle tip and the free level of liquid. When an oscillating bead of excess liquid at the nozzle entrance disappears, the flow is regarded as stable. Slight changes in total height result either in regenerating an oscillating bead or in cutting off the column because air will be sucked into the nozzle. Thus careful determination of the proper height is essential. The flow rate Q is obtained by measuring the time required for the liquid to fill a given volume of cylinder after stable operation is achieved. The force F_n exerted by the liquid on the nozzle entrance is measured directly by the use of a strain gauge (Shinkoh Co., Ltd., UT-100-120). Together with these measurements, a photograph of the syphon is taken, a schematic of which is shown in Figure 2. The horizontal and vertical coordinates of surface of each profile were read to 0.01 cm.

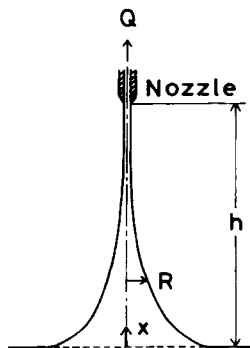


Fig. 2. Schematic of tubeless syphon.

The continuity and momentum balances over a length dx of the syphon can be written as

$$v = Q/\pi R^2 \quad (1)$$

and

$$\frac{d\sigma}{dx} = \rho g - \frac{2\sigma}{R} \frac{dR}{dx} + \rho v \frac{dv}{dx} \quad (2)$$

where R is the syphon radius, v the axial velocity, ρ the liquid density, g the acceleration of gravity, and σ the normal stress, defined as $F/\pi R^2$, where F is the total internal force. In eq. (2), it is assumed that both the axial velocity and the normal stress are constant through the cross section and that the surface tension and the force associated with aerodynamic drag are negligible. Also the inertial term $\rho v dv/dx$ is generally very small compared to the others. Therefore, it is possible to integrate eq. (2) by the finite-difference method and then to calculate the value of σ in each section.

Experiments were carried out on silica dispersions at concentrations of 1, 2, and 3 wt %. The silica was Aerosil (Degussa Co.). The medium used for dispersions was a solution of Separan NP10 (a polyacrylamide from Dow Chemical Co.) in glycerol at a concentration of 1 wt %. After mixing, the dispersions were stored for 1 day and were sufficiently degassed before measurements. The temperature for all runs was 22°C.

RESULTS AND DISCUSSION

Figure 3 shows the variation of total height h with flow rate Q for the dispersions at different particle concentrations. The total height of each dispersion increases with increasing flow rate. At a fixed flow rate, it rapidly decreases with increasing particle concentration.

Figure 4 shows the total-height dependence of the tensile force F_n required to maintain a given column. The plots for each dispersion become linear, showing that the total height is proportional to the tensile force. The total height at a fixed tensile force decreases with increasing particle concentration.

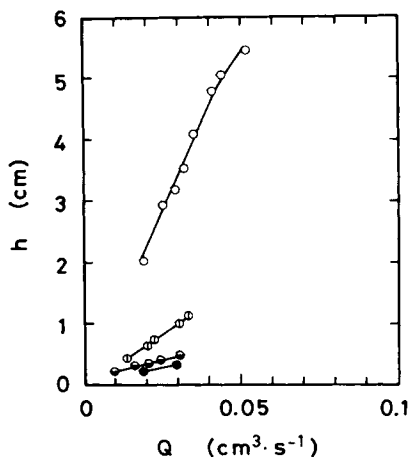


Fig. 3. Variation of total height h with flow rate Q . Aerosil concn (wt %): (○) 0; (◐) 1; (◑) 2; (●) 3.

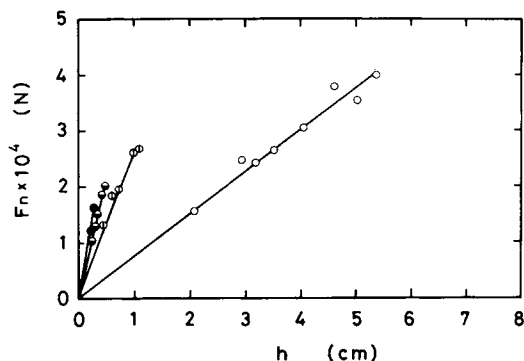


Fig. 4. Variation of vertical force F_n with total height h . Aerosil concn (wt %): (○) 0; (◻) 1; (◐) 2; (●) 3.

Figure 5 shows the column profiles at a flow rate of $0.03 \text{ cm}^3 \cdot \text{s}^{-1}$ for the dispersions at different particle concentrations. R and h are the radius at free level of liquid and the total height, respectively. The particle concentration is indicated by subscript. R_n is the internal radius of nozzle. The radius at free level shows a slight decrease, while the total height decreases extremely with increasing particle concentration. It is noted that the addition of fine particles to elastic liquid leads to a decrease in total height of syphon and, hence, makes it difficult to evaluate the extensional viscosity of concentrated dispersions. A pressure drop of more than 1 atm will be required to generate a syphon available for measurements.

The photographic analysis gives the geometrical function $R(x)$. Thus the average velocity as a function of distance along the column can be obtained from continuity. Figure 6 shows the dependence of velocity v on position x along the column at a flow rate of $0.03 \text{ cm}^3 \cdot \text{s}^{-1}$. The plots for the polymer solution are well correlated by a straight line, the slope of which gives the extensional rate G :

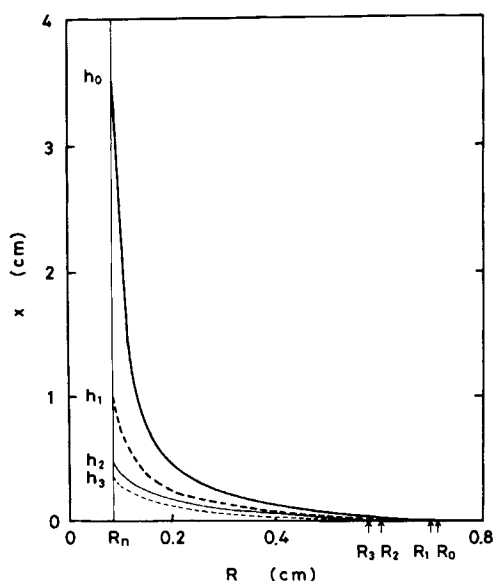


Fig. 5. Column profiles at a flow rate of $Q = 0.03 \text{ cm}^3 \cdot \text{s}^{-1}$. Aerosil concn (wt %): (—) 0; (---) 1; (— · —) 2; (- - -) 3.

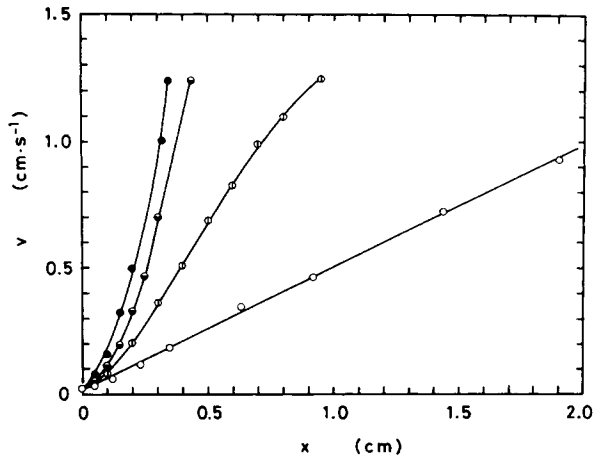


Fig. 6. Dependence of velocity v on position x along the column at a flow rate of $Q = 0.03 \text{ cm}^3\text{-s}^{-1}$. Aerosil concn (wt %): (O) 0; (◐) 1; (●) 2; (●) 3.

$$G = dv/dx \quad (3)$$

This clearly shows that the extensional rate is constant along the flow direction. On the other hand, the data for the dispersions are curved, especially near the column base and nozzle entrance. The extensional rate is not constant along the column for the dispersions. This is because of the fact that the tubeless syphon method is noncontrollable. Actually, operating the flow rate is all that is required in the setting of the variables. Since the column profile depends strongly on the flow properties of liquid, the extensional rate is not necessarily constant along the column, showing that the Fano column does not always have the same profile as the Coleman and Noll cylinder.¹² It must be realized that there are inherent difficulties in using the tubeless syphon for determination of extensional viscosity. Although complicated problems arise in analysis of flow of dispersions, the experiments can be expected to yield qualitative measures of resistance to extensional deformation.

In the tubeless syphon experiments, the flow fields are steady in the Eulerian sense, but unsteady in the Lagrangian sense. Careful attention must therefore be paid to the analysis of flows. Figure 7 shows the dependence of the normal stress σ on the time t for the dispersions at different particle concentrations. The t represents the time necessary to a fluid element to go from the free level to the position x , and is calculated by the following equation:

$$t = \int_0^x dx/v \quad (4)$$

The integral on the right-hand side of eq. (4) always exists in the sense that v approaches zero less rapidly than x . In our experiments, the maximum value of t for the polymer solution is of the order of 10 s. It decreases with increasing particle concentration. It is found that the higher the particle concentration, the more markedly does the normal stress increase with time.

Figure 8 shows the effect of flow rate on the normal stress growth for 1 wt % dispersion. The normal stress rapidly increases with time at higher flow rate. Because the velocity increases with increasing flow rate, it seems likely that the time scale is chiefly affected by flow rate. The time t was found to be sensitive to the flow rate.

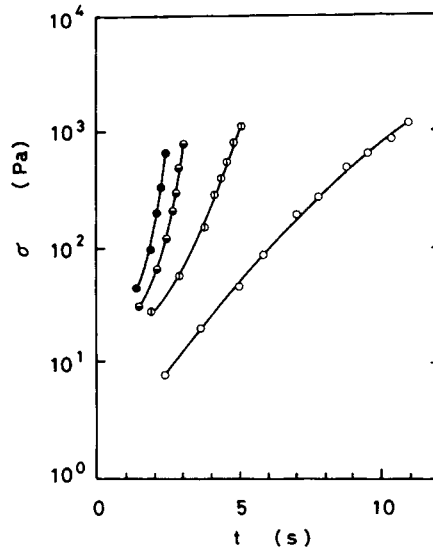


Fig. 7. Dependence of normal stress σ on time t at a flow rate of $Q = 0.03 \text{ cm}^3\text{s}^{-1}$. Aerosil concn (wt %): (○) 0; (⊙) 1; (◐) 2; (●) 3.

Let us now consider the relation between the transient extensional viscosity and the deformation history. Prior workers have discussed the results in terms of the extensional viscosity η_{el} and the dimensionless time s .¹¹ η_{el} has been defined by σ/G and s by Gt . Their treatment will be accepted on condition that the extensional rate is constant along the whole liquid column. However, in our experiments, the extensional rate for the dispersions varied along the column. Since both the normal stress and the extensional rate are transient, the problem

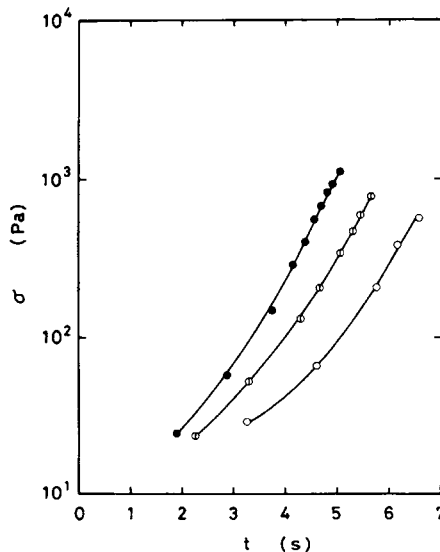


Fig. 8. Dependence of normal stress σ on time t at different flow rates (cm^3s^{-1}) for 1 wt % (Aerosil) dispersion: (○) 0.011; (⊙) 0.020; (●) 0.030.

arises of how to treat the results. We employed the rheological parameters defined by the following equations for further discussion:

$$\eta_{el} = \frac{\sigma}{G(x)} = \frac{\sigma}{dv/dx} \quad (5)$$

$$\epsilon = 2 \ln [R(0)/R(x)] \quad (6)$$

where $G(x)$ is the extensional rate at x and the change along the column is not large except near the column base. ϵ is a strain which is experienced by a fluid element drawn up from the free level to the position x . It has been shown by Hudson and Ferguson¹³ that the data obtained at different flow rates for polymer solutions can be correlated by using the total strain in extension.

Figure 9 shows the extensional viscosity η_{el} plotted against strain ϵ for 1 wt % dispersion. It can be seen that all the plots lie very close to a single curve. According to the results by Nicodemo et al.,¹¹ the values of the extensional rate are not very sensitive to the flow rate; hence curves of η_{el} vs. t at different flow rates are satisfactorily superimposed, once plotted in the form of η_{el} vs. Gt . In our case, the values of G (although not constant along the column, the variation was very slight) were from 1.31 to 1.54 s⁻¹ for 1 wt % dispersion. It is very interesting to note that the extensional viscosity as a function of strain can be obtained, owing to insensitive nature of extensional rate to flow rate.

The analysis was repeated for data obtained using different particle concentrations, and the master curve for each is shown Figure 10. For both the medium and the dispersions, the extensional viscosity increases markedly with strain.

Two important points are noted with regard to the behavior of the dispersions. First, the extensional viscosity decreases with increasing particle concentration. This is in contrast to shear viscosity, which is strikingly increased by the presence of particles in a liquid medium. The increase in shear viscosity has been explained to a considerable extent on the basis of the hydrodynamic principle and structural theory. However, up to date, there has been no acceptable interpretation of the relation between the extensional viscosity and the particle concentration. Considering that the extensional viscosity may be a manifestation

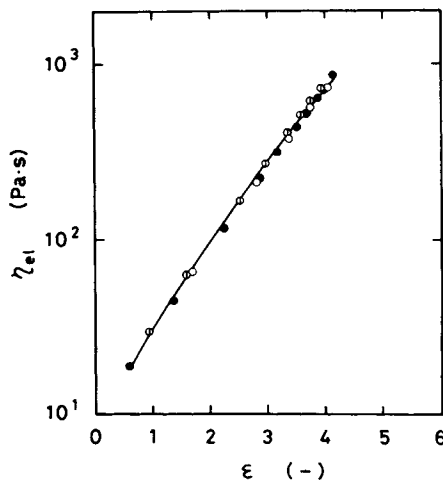


Fig. 9. Extensional viscosity η_{el} plotted against strain ϵ for 1 wt % (Aerosil) dispersion. Flow rates (cm³·s⁻¹): (○) 0.011; (◇) 0.020; (●) 0.030.

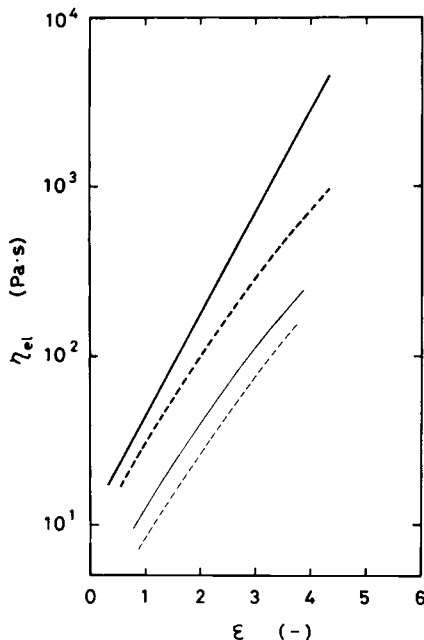


Fig. 10. Dependence of extensional viscosity as a function of strain on particle concentration. Aerosil concn (wt %): (—) 0; (---) 1; (—) 2; (- - -) 3.

of combined response of viscous and elastic effects, it is difficult to understand the mechanism of the reduced extensional viscosity. Moreover, it must be stressed that the extensional viscosity presented here is transient. We do not know whether the steady extensional viscosity decreases with increasing particle concentration or not. The measurements for discerning this point will meet with difficulties, because a very small force induces large extensional rates and such a flow is generally of short duration. Although the experimental results were obtained under transient conditions, the decrease in the extensional viscosity of the dispersions may be important observations.

The second point to note is that the curves of the dispersions can be superimposed by a vertical shift, but its shape differs from that of the medium. Experiments of viscosity growth in extensional flow published¹¹ so far have indicated that the data for both the polymer solution and the dispersions could be drawn together by a shift procedure. This disagreement may arise from the differences in the particles used. The silica particles used in this study are somewhat smaller than glass beads used by prior workers and have an extremely large specific surface (130 m²/g). In addition, under ordinary conditions the surface of silica is covered with silanol groups which give the adsorption sites for the polymer. In the case of nonionic polymer, the adsorption occurs usually in the form of loops, so that a large amount of polymer may be adsorbed on silica particles whose size is comparable to molecular dimension of the polymer chain. The adsorption experiments show that the adsorption curve is saturated at 1.6 mg/m². Silica is considered to have a strong effect on the molecular flow. Although the extensional viscosity may be observed as a combined effect of dissipation and storage of free energy, the latter seems to play a much more dominant role. Elastic response of the polymer solution is attributed to the orientation

and extension of the polymer chain in the flow direction. Since the adsorbed polymer chain extending as loops into the solution hardly accumulates the energy, the adsorption of polymer leads to a decrease of the elastic component in response. On the other hand, an apparent increase in particle concentration by the adsorbed polymer contributes to the dissipation of energy. As a result, the relaxation time of the polymer solution is decreased by silica particles. It is concluded that the decrease in relaxation time is primarily responsible for the change in curve shape of viscosity growth.

CONCLUSIONS

The rheological behavior in extensional flow was investigated for silica dispersions in polymer solution using the tubeless syphon technique. Some of the significant conclusions are as follows.

1. The extensional rate is constant along the column for polymer solution, but not for the dispersions.
2. Due to insensitive nature of extensional rate to flow rate, irrespective of flow rate, the extensional viscosity plotted against strain lies on a single curve.
3. The extensional viscosity decreases with increasing particle concentration.
4. The behavior of viscosity growth of the dispersions differs from that of the medium. This may be attributed to the change in relaxation time.

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