Normal Stresses in Flow of Polyvinyl Chloride Plastisols

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ABSTRACT: In the steady state flow of many liquids, such as polymer solutions and melts, the first normal stress difference, $N_1 = \sigma_{11} - \sigma_{22}$, is positive. However, with liquid crystal systems and some colloidal suspensions, negative values of N_1 were reported in literature. In our past work with a commercial polyvinyl chloride plastisol, negative values were observed. During the steady state flow, the plastisol undergoes stress-induced phase separation into an immobilized layer and a mobile phase. The concentration difference between the two phases gives a rise to an osmotic pressure difference, $\Delta\pi$, which is countered by a normal stress, N, generated by the flow. Because N is balanced with $\Delta\pi$, N cannot be observed directly. In this work, N is identified as an isotropic and N_1, directional. The disturbance among rotating particles in the mobile phase produces two effects; one is an increase of pressure, which is N; the other, N_1 is associated with a small volume increase, which is directed towards the opening of the rheometer. The directional expansion is caused by the shear-stress gradient in the liquid between the rotating particles. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2769–2775, 2007

Key words: PVC plastisol; normal stresses; rheology

INTRODUCTION

Polyvinyl chloride (PVC) plastisol is a suspension of fine particles of PVC in a plasticizer. After shaping, e.g., coating, the material is heated in an oven to gel and fuse. The product is a flexible PVC. Because plastisol is a fluid at room temperature, it is relatively easy to process. Consequently, a variety of processing technique has been developed.[1] To meet the requirements of different processes and different properties of finished products, many types of PVC resins were developed.[2] For the same reason, many formulations were devised for plastisols.[3]

Therefore, for the purpose of examining the rheology of commercial grades of plastisol, representative samples needed to be selected.[3] The attractive and repulsive forces between particles were balanced in the commercial formulations to provide stable suspensions. Therefore, our studies on rheology exclude concern of the colloidal stability.

Like many suspensions, plastisol exhibits various phenomena such as thixotropy at low shear, pseudoplastic flow at the intermediate shear, and dilatancy and fracture at high shear. However, the rheology of PVC plastisol is entirely different from that of smaller particle (typically smaller than 100 nm) suspensions, where Brownian motion plays an important role. With the monodispersed and spherical particles of the latter, progress has been made in the basic understanding of the flow mechanisms.[4–6]

On the other hand, the particle size of PVC plastisol is, more or less, 1 μm and larger. The resins have broad particle size distribution up to the largest size of 15 μm. The particle of about 1 μm is a primary particle made during emulsion polymerization and the larger particles are agglomerates formed during the drying of the resin. The agglomerates are not necessarily spherical, and their shape and morphology were reported before.[7,8] In the microscopic views, a plastisol is shown to be very crowded with particles.[7,8]

There had never been an attempt to elucidate the flow mechanism of PVC plastisol, until Hoffman discovered an immobilized layer of PVC particles developed with the increase of shear rate.[9] His sample was a model plastisol containing uniform-size particles. We applied his discovery of the immobilized layer to the flow of commercial samples of PVC plastisol. Our interpretive model was a stress-induced phase separation into an immobilized layer and a mobile phase. Growth of the immobilized layer with the increase of shear rate or frequency accounted for the pseudoplastic flow.[10] Dilatation of the immobilized layer with the further increase of shear rate resulted in dilatant flow.[11] The concentration difference between the immobilized layer and the mobile phase gave rise to a difference of osmotic pressure. The normal stress generated in the mobile phase must have been counteracting the osmotic pressure difference.[12] The mode of failure at very high shear-rate was of two kinds, one was brittle fracture of the immobilized layer and the other ductile failure, which was preceded by yielding
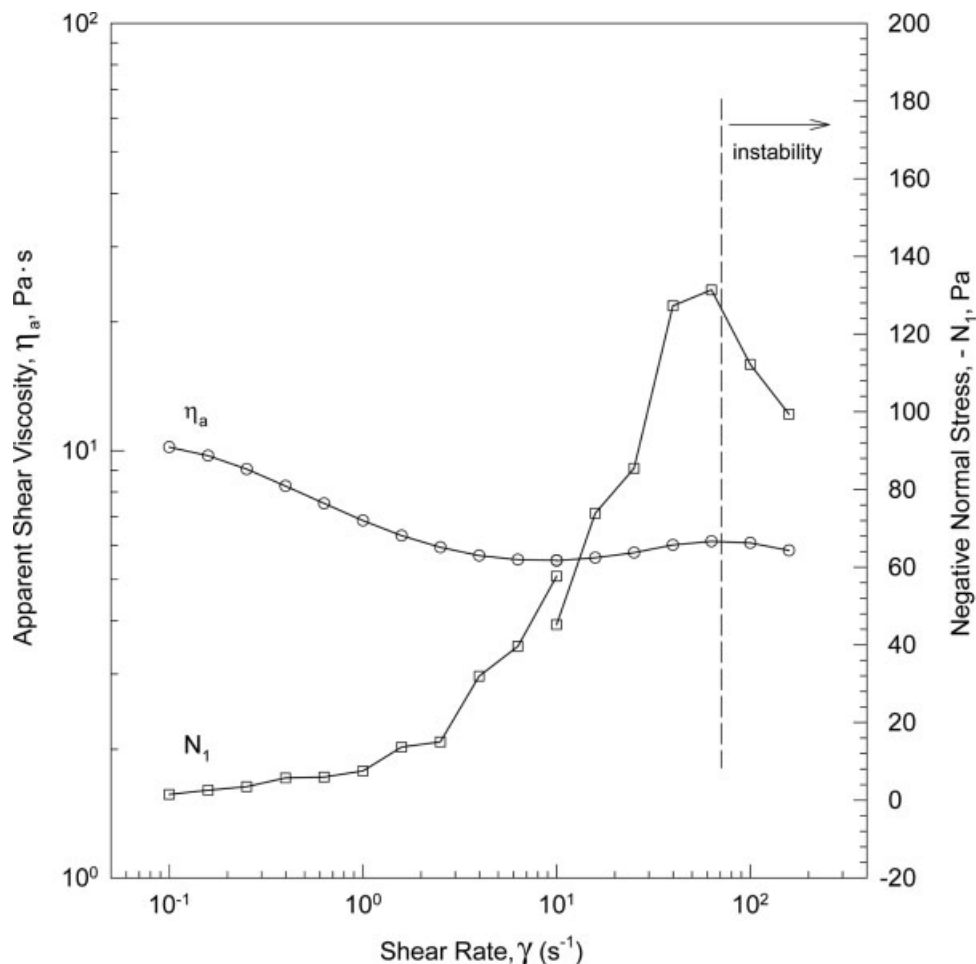
Figure 1   Apparent viscosity, η_a, and normal stress difference, $N_1 = \sigma_{11} - \sigma_{22}$, of PVC plastisol at 25°C as functions of shear rate.

of the layer.[13] In the dynamic measurements, the increase of amplitude of oscillation affected the flow very similarly to the increase of frequency. Viscosity decreased first and then increased, leading to fracture as the amplitude was increased. It was realized that the shear rate of oscillating flow was a product of frequency and amplitude. Subsequently, the flow behavior under increasing amplitude was explained with the growth, dilatation, and fracture of the immobilized layer.[14] Storage modulus of the mobile phase was explained as a momentary contact of particles, forming a temporary network.[15]

The remaining question is how the mobile phase gives a rise in normal stresses. In this work, we will describe our observation on steady state flow with respect to the normal stress difference, $N_1 = \sigma_{11} - \sigma_{22}$, (the subscript; 1, the direction of the force and 2, the direction of the velocity gradient). We will also consider the nature of the normal stress, N, which counteracts the osmotic-pressure difference, $\Delta\pi$. We will estimate the magnitude of volume expansion, which is assumed to accompany the negative N_1.

EXPERIMENTAL

Sample

The resin sample was polyvinyl chloride (PVC), Geon® 124A, (PolyOne, Avon Lake, OH). The plasticizer was diethylhexyl phthalate. The plastisol was a mixture of 0.50 volume fraction each of the resin and plasticizer. The plastisol was aged for 95 h until the increase of viscosity (viscosity aging) practically ceased.

Instrument

A rheometric mechanical spectrometer (Rheometrics, Piscataway, NJ) was used with a concentric rotor–stator arrangement; the diameter of cup and bob were 50.0 and 48.0 mm, respectively.

The length of the bob was 25.0 mm. The bottom part of the rheometer was a cone and plate, designed to give essentially the same shear rate as that within the concentric part. The cone and plate portion of the cup and bob geometry provided the ability to measure the normal stress difference, $N_1 = \sigma_{11} - \sigma_{22}$.
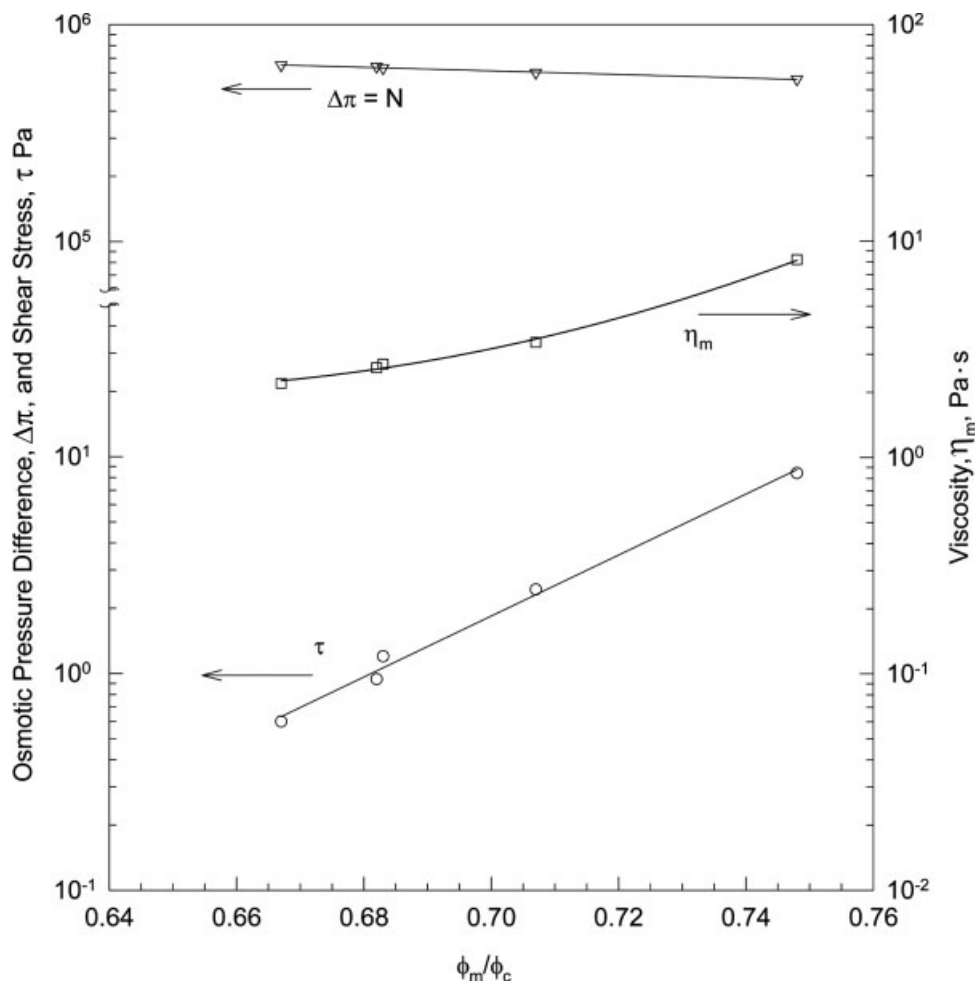
Figure 2 Osmotic pressure difference, $\Delta\pi = N$, viscosity of mobile phase, η_m, and shear stress, τ, as functions of particle volume-fraction of mobile phase, ϕ_m/ϕ_c at shear rate of $\dot{\gamma} = 0.2$ s^{-1}. The ϕ_c is the tightest packing volume fraction of particles. The data taken from reference.[12]

RESULTS

Figure 1 shows an example taken from many similar data of steady state flow.

The viscosity curve shows pseudoplastic flow between shear rate of 10^{-1} and 10^1 s^{-1}. Then, it becomes slightly dilatant between 10^{-1} and 10^0 s^{-1}. The negative normal stress difference, N_1, is present even at very low shear rate. Its magnitude is very small but increases at shear rate between 10^{-1} and 10^0 s^{-1}, where the viscosity data clearly indicate pseudoplastic flow. When the viscosity curve starts leveling towards a minimum, the negative normal stress begins to increase steeply and continues to increase in the region of dilatant flow.

At two points before the dashed line indicating instability, a slight distortion of the free surface of plastisol was observed at the opening of the concentric cylinders. After the viscosity maximum, flow instability sets in and the recordings of the viscosity and the normal stress show the decrease.

DISCUSSION

Formation of immobilized layer in pseudoplastic flow

The stress-induced phase separation occurs because it is effective in reducing flow resistance. When the immobilized layer is formed in plastisol, the flow channel becomes narrower. Consequently, shear rate is increased. The corresponding shear stress must increase if viscosity had remained the same. However, the viscosity of the mobile phase is decreased because particle concentration is decreased as a result of the phase separation. Whereas the increase of shear rate is linear with the narrowing of the channel, the concentration dependence of viscosity is logarithmic.[16] The net result is that the decrease of the particle concentration has an overwhelming effect on reducing flow resistance.

A question is, then, what makes the viscosity levels off to the minimum, instead of continuing to decrease with the growth of the immobilized layer. It appears that when the concentration of particles in the mobile
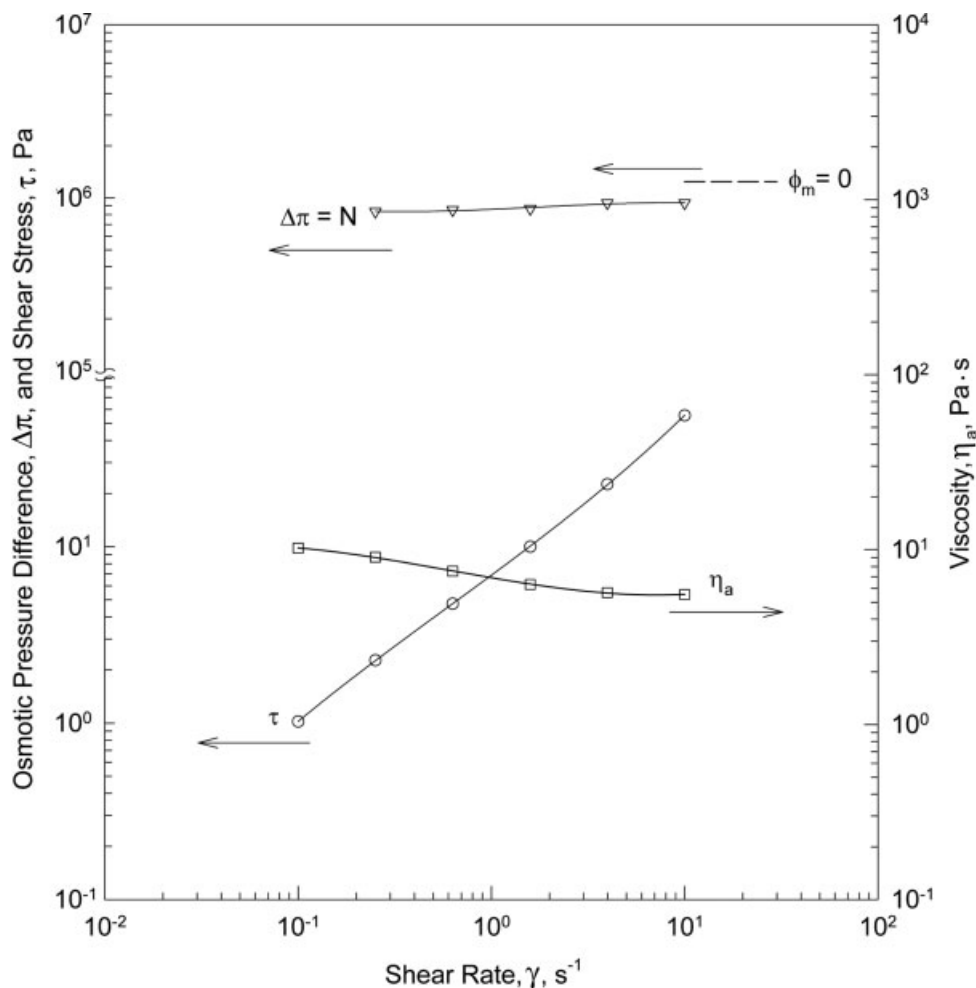
Figure 3 Osmotic pressure difference, $\Delta\pi = N$, apparent viscosity, η_a and shear stress, τ, as functions of shear rate, $\dot{\gamma}$, with particle volume-fraction of $\phi = 0.5$.

phase becomes below certain limit, the viscosity of the mobile phase becomes so low that the flow cannot produce high enough normal stress, N, to hold back the immobilized layer. Figure 2 illustrates that when the concentration is made to decrease at a fixed shear rate, viscosity and shear stress decrease sharply.

The above explanation is not completely satisfactory because it does not provide an explanation on how the normal stresses arise in the flow of the mobile phase.

Normal stress and shear stress in steady flow

Figure 3 shows the data of the normal stress, $N = \Delta\pi$, shear stress, τ, and viscosity, η_a, (the same η_a data as in Fig. 1) as a function of shear rate, $\dot{\gamma}$ in the region of pseudoplastic flow. With the increase of shear rate, the normal stress (N) increases, but gradually levels off towards a limiting value at assumed zero-particle concentration in the mobile phase. On the other hand, shear stress increases steeply. Also, it is noticed that shear stress is orders of magnitude smaller than normal stress. The normal stress, N, and shear stress, τ, do not seem to have a simple relation.

Normal stress and storage modulus in oscillating flow

In some systems, the primary normal stress difference in steady flow at low shear rate gives the same information as G' at low frequencies.[17] If this is applicable to the present system, then, contrasting N with G'_m (G' of the mobile phase) may provide some insight into the nature of N. Figure 4 shows such plots, where the data were taken from the previous publication.[14] The trends of both N and G'_m are very similar to respectively those of N and τ shown in Figure 3. That is, no simple relation is suggested by these data.

Interpretive model for N and N_1

We now assume that the normal stress consists of two terms, one being isotropic, N, and the other directional, N_1. In our model, with respect to the mobile phase, both pressure-increase and volume-increase are assumed to occur. These are caused by the disturbances between the neighboring particles, whose nearest surfaces are moving in opposite directions, Figure 5.
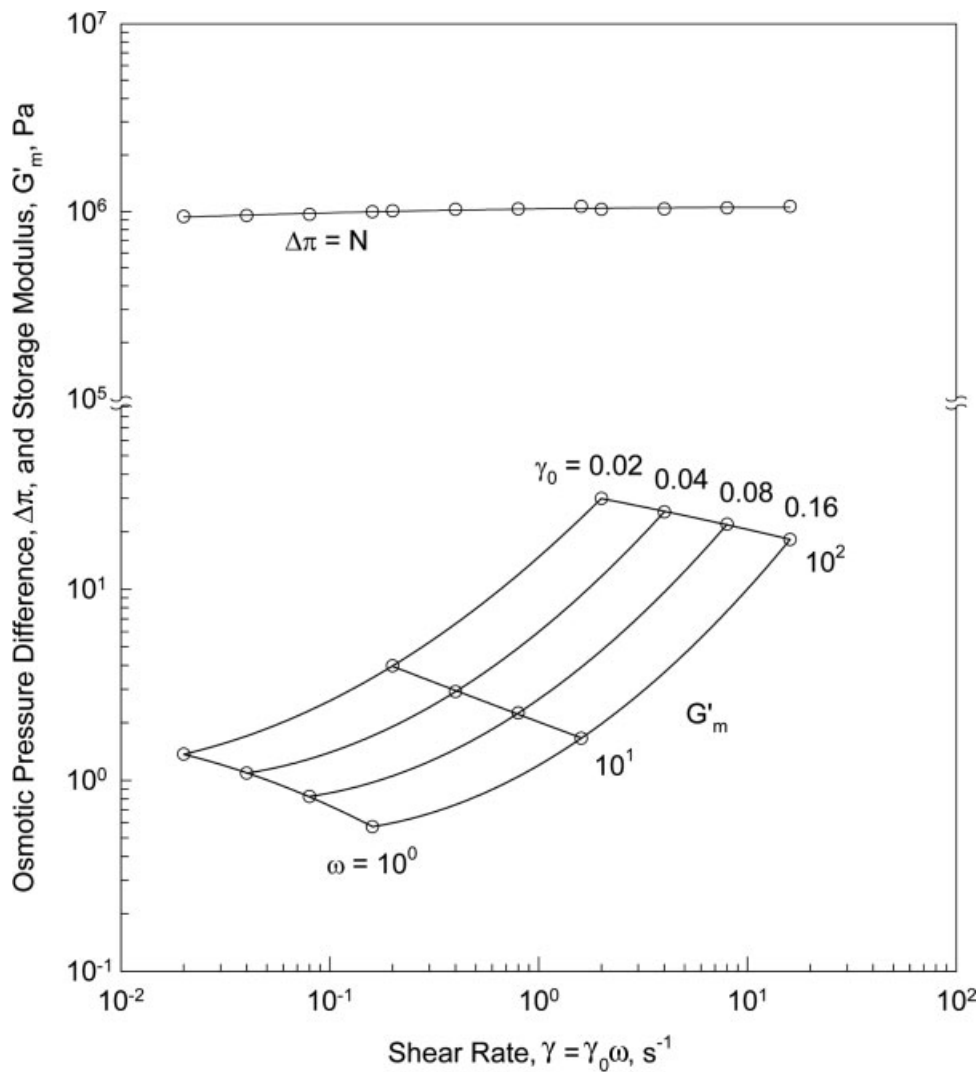
Figure 4 Osmotic pressure difference, $\Delta\pi = N$, and storage modulus of mobile phase, G'_m as functions of shear rate, $\dot{\gamma}$.

The system tries to minimize the disturbance. The first and major way to minimize the disturbance is the phase separation, which was described already. However, the growth of the immobilized layer has a limit as discussed earlier. After the phase separation, the mobile phase still contains rather high concentration of particles. With reference to the steady state viscosity data of Figure 1, the volume fraction of particle in the mobile phase is $\phi_m = 0.48$ at the viscosity minimum, Table I.

For a small change of volume, V, the term, N is identified with pressure, P. Then, for steady state and closed system, the mechanical energy, dU, imparted to the system by the rheometer may be written with expression of nonequilibrium thermodynamics[18]

$$dU = (\partial U/\partial V)_p \, dV + (\partial U/\partial P)_v \, dP + dU(\eta) \quad (1)$$

where $dU(\eta)$ is a term for the energy dissipation due to viscosity, η.

In applying equivalence of mechanical and thermal energy, eq. (1) may be transformed to

$$dT = (\partial T/\partial V)_p \, dV + (\partial T/\partial P)_v \, dP + dT(\eta) \quad (2)$$

where heat capacity is omitted, because it is a common factor for each term.

Relationship between internal pressure and thermal pressure coefficient

The following equation gives the relationship between internal pressure, P_i, and thermal pressure coefficient, $(\partial P/\partial T)_v$[19]

$$P_i = T(\partial P/\partial T)_v - P = T(\alpha/\beta_i) \quad (3)$$

where α is the coefficient of thermal expansion and β_i is the isothermal compressibility.

The value of P_i is given as $P_i^{1/2}$ in the unit of $(cal/cc)^{1/2}$ for diiso-octyl phthalate as 9.63 and for diiso-octyl sebacate as 9.34.[19] Because no value is listed for diethyl-
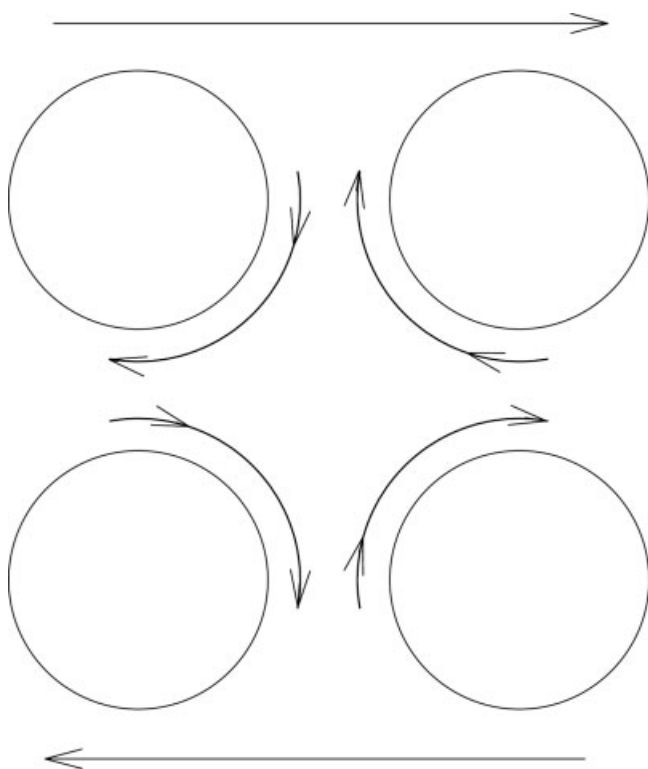
Figure 5 Disturbance created between rotating particles.

hexyl phthalate, we assume 9.5 to be a good estimate and P_i is calculated to be $P_i = (9.5)^2$ cal/cc = 378 MPa.

Thermal equivalent of mechanical energy

For the ambient condition of $T = 298$ K and $P = 1$ atm = 0.1013 MPa, the thermal pressure coefficient is calculated by using eq. (3) to be $(\partial P / \partial T)_v = 1.28$ MPa/K. If we assume that the coefficient is constant over the temperature and pressure range of our interest, then, $(\Delta P = 1.28 \, \Delta T)_v$. Subsequently, ΔP is identified with

$$\Delta P = \Delta \pi = N \quad (4)$$

The value of the osmotic pressure difference is ~1.0 MPa (Figs. 3 and 4).

Therefore, in terms of the thermal equivalence, ΔT = 1.0/1.28 = 0.78 K. Using this value of ΔT, the volume expansion, ΔV, may be estimated as

$$\Delta V = \alpha \Delta T \quad (5)$$

The value of thermal expansion coefficient is given[19] as $\alpha = 0.00,076$ (cc/cc)/°C at 20°C. The estimated ΔV = 0.0006 (0.06%). The volume expansion of the system in the pseudoplastic region is thus estimated to be very small. The volume expansion takes place towards the direction 3 because it is pointing towards the opening between the concentric cylinders at the top of the rheometer.

The volume expansion brings about the decrease of pressure. When the expansion is allowed only to the

direction 3, the opening of the rheometer, it may register the negative normal stress difference, N_1. However, we wish to explore further to see if there is another explanation.

Negative normal stress observed with liquid crystalline material

Negative value of the first normal stress difference has been observed with many liquid crystalline (LC) material. We have taken two recent articles on the subject to see if any hint may be available for interpreting the meaning of our finding. One article is on solutions of very stiff polymer chain of very high molecular weight, 500,000, lyotropic LC,[20] and the other is on the melt of a planar, low molecular weight, 1000, thermotropic LC.[21] In the former, negative N_1 was observed at high concentrations, 15.5% and 17.2%.

In spite of the large difference in the structure of molecule, their steady state flow follows similar pattern of shear-rate dependence, consisting of three regions. The first region is shear thinning at low shear rates. The second region is shear thickening with the lyotropic system and constant viscosity with thermotropic material. The third region is shear thinning. Both systems contain polydomains. The growth in negative value of N_1 occurs in the first region, where the system is isotropic. As soon as partial orientation starts in the second region, the negative N_1 reverses the trend, decreasing the negative value. With the increase of the shear rate and the increase of the orientation, N_1 goes through zero to positive. With respect to our system, we are interested in the first region, where N_1 increases in negative value. With LC systems, the growth of negative N_1 is attributed to the deformation of the domain without involving apparent orientation.

TABLE I
Growth of Immobilized Layer and Volume Fractions of Particle of Mobile Phase in Pseudoplastic Region

Shear rate (s⁻¹)	Fraction of immobilized layer[a]	Volume fraction of particles of mobile phase
$\dot{\gamma}$	$v_i + v_i^0$	ϕ_m
0.100	0.000	0.500
0.159	0.016	0.498
0.251	0.031	0.495
0.398	0.045	0.493
0.631	0.059	0.490
1.00	0.073	0.488
1.59	0.098	0.483
2.51	0.110	0.481
10.0[b]	0.122	0.478

[a] v_i, Volume fraction of particles and v_i^0, volume fraction of plasticizer in the immobilized phase and ϕ_m, volume fraction of particle in the mobile phase; the same data listed in Table XI of Ref. 14.
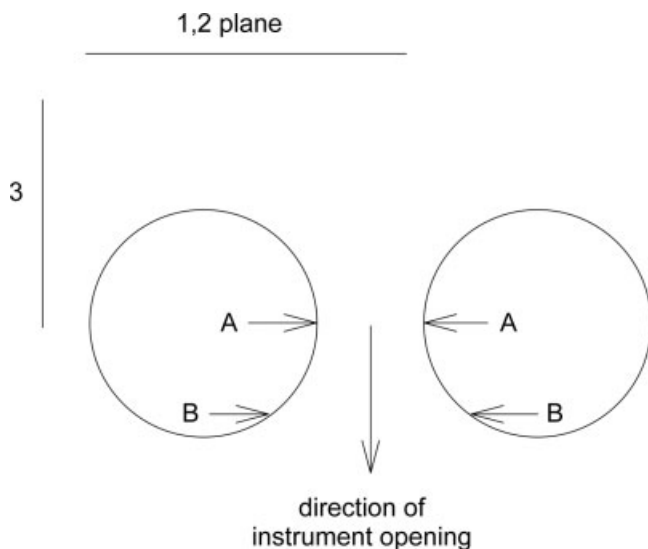[b] Shear rate at viscosity minimum.

Figure 6 Expansion of material towards direction 3, caused by the difference of stresses at sections $A-A$ and $B-B$.

In our system, the immobilized layer is deforming (dilating) under shear stress, and N_1 increases in negative value with the increase of deformation. The calculated value of the dilatational stress is about 60 kPa[14] at the shear rate where N_1 is -0.1 kPa. If the dilatation of the immobilized layer is responsible for the occurrence of the negative N_1, only a small part of the dilatational pressure affects it.

Nonisotropic volume expansion

Another possible explanation for the occurrence of negative N_1 is given below; Figure 6 illustrates our interpretation on the volume expansion, which is specifically directed towards the direction 3. At the cross section of 1,2 plane, $A–A$, the distance between two particles is shortest; it is shorter than that at the cross section, $B–B$, for example. Therefore, shear rate, $\dot{\gamma}_{12}$ $(A–A)$ is higher than $\dot{\gamma}_{12}$ $(B–B)$. Because the plasticizer is a Newtonian liquid, the corresponding shear stress, τ_{12} $(A-A)$ is higher than τ_{12} $(B-B)$. This gives a driving force to expand the material towards the direction 3, which is the direction of the opening at the top of the rheometer.

CONCLUSIONS

For concentrated suspension, the nature of the interparticle disturbance is very complex even with the uniform-size spheres; many kinds of the secondary flow are conceivable. With the present system, having size distribution, it is even more complicated. Therefore, we have treated the phenomenon with overall pressure-increase and volume-increase.

The highest value of negative N_1 observed in our system was about 0.1 kPa, which is very similar to those observed with LC.[20,21] The normal stress difference is very small when compared with, for example, atmospheric pressure of 0.1 MPa. Evidently, the phenomenon is a very subtle one, which is very difficult to pin down. The loading memory and erroneous zero setting of the rheometer were attributed to be a possible cause of the appearance of the negative value. However, in the above-mentioned works with LC as well as in our's, care was taken to prevent it from happening.

The normal stress difference, N_1, was assumed to be the result of flow within the cone-plate part of the rheometer because the flow within the concentric cylinder part is not likely to influence the N_1 measurement. However, at the point where the cone-plate and concentric cylinder meet, the geometry is neither cone-plate nor concentric cylinder. If a secondary flow is generated here, it may affect the measured value of N_1. This is a subject for the future investigation.

Another noteworthy feature is the observation of a smooth plastisol surface at the opening of the rheometer for much of the examined shear rate range. This suggests that the flow was not in the turbulent region.

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