Fusion of particles in a emulsion aggregation process

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Abstract

A latex when subjected to shear can exhibit Newtonian or a non-Newtonian flow and a yield stress depending on inter-particle forces. Under dynamic deformation, elastic modulus shows a plateau as the shearing frequency is decreased. Acrylic latex was made under varying processing conditions, which resulted in differences in yield stress, elastic modulus and non-Newtonian behavior. Coalescence and fusion results from interplay of inter particle forces (van der Waals, electrostatic and stearic forces) which are opposedby mechanical forces (hydrodynamic and Brownian) forces. Static and high frequency shear modulus are particle and concentration dependent. Experiments on latex colloids under dynamic oscillation are found to be consistent with the models.

Introduction

A chemical toner is prepared by a process of sequential steps of making a latex emulsion from resin, water and ionic surfactant. The latex is blended with dispersion of a colorant, coagulated and then heated to coalesce particles and accelerate their fusion to form toner by lowering pH.[1]. The toner is made from a latex which has a static yield stress and has viscosity which decreases with increase in shear rate as a power law [2]. In the past, a number of studies have been engaged elucidating the nature of the forces which could promote the deformation of the particles, and their evaluation leading to many mechanisms and theoretical models: dry sintering under the influence of polymer-air surface tension, wet sintering under the influence of polymer-water interfacial tension, sintering under the action of capillary forces originating from the water-air interfacial tension, theory of mechanical compression under the influence of osmotic pressure. Forces promoting coalescence are capillary force and London-van der Waals, forces. Force opposing the deformation of the particles to be taken into account is their mechanical resistance. The polymers constituting the particles are considered be incompressible and viscoelastic in nature. Considering the deformation undergone by the particles is sufficiently small, their mechanical behavior can be described by the theory of linear viscoelasticity.

Latex stability is dependent on inter particle surface forces and interplay of external forces. In the absence of external forces such as Brownian and hydrodynamic, colloidal stability in a latex is governed by electrostatic double layer repulsion or/and steric repulsion compensation van der Waals force of attraction between particles. Thickness of the double layer repulsion in electrostatic stabilization increases with decrease in electrolyte concentration and increase in zeta potential. Under Brownian forces, rate of fast flocculation in electrostatic stabilization increases with the decrease in viscosity, increase in particle size, increase in shear rate. In steric stabilization, grafting or adsorption of a polymer on the particle surface, thickness of the polymer layer and the solubility of the polymer are key controlling factors. When volume fraction of the solid is large, adsorbed polymer thickness is small (low molecular weight) or when concentration of non-adsorbing polymer is large, weak flocculation can occur while strong flocculation can occur when solvency of the medium for polymer is poor.

Calculating the *non-equilibrium* properties of colloidal suspensions is a highly nontrivial exercise because these depend both on the short-time thermal Brownian motion and the long-time hydrodynamic behavior of the solvent the effects of the solvent can be taken into account through Brownian dynamics (BD),which assumes that collisions with the solvent molecules induce a random displacement of the colloidal particle positions, as well as a local friction proportional to their velocity. Additionally, momentum transport through the solvent—as described by the Navier-Stokes equations—which leads to long-range hydrodynamic interactions (HI’s) between the suspended particles. Lattice- Boltzmann technique is used to solve Navier- Stokes equation for colloidal dynamics[3]. Using Molecular Dynamics electrostatic interaction between two of these particles can be described by an exponentially screened Coulomb potential[4],

$$V_{Coul} = \pi \varepsilon_r \varepsilon_0 \left[\frac{2+\kappa d}{1+\kappa d} . \frac{4k_B T}{Ze} \tanh\left(\frac{ze\varsigma}{4k_B T} \right) \right]^2 x \frac{d^2}{r} \exp(-\kappa[r-d]) \tag{1}$$

where d denotes the particle diameter and r is the distance between the particle centers. ε is the elementary charge, T the temperature, k is the Boltzmann constant, and z is the valency of the ions of added salt. The effective surface potential ζ is the electrostatic potential at the border between the diffuse layer and the compact layer, it may therefore be identified with the ζ -potential ε_0 is the permittivity of the vacuum, ε_r is the relative dielectric constant of the solvent., κ is the inverse Debye length

$$\kappa^2 = 8\pi l_B I$$

defined by with the ionic strength I and the Bjerrum length l_B .

The Coulomb term of the DLVO potential competes with the attractive van der Waals term

$$V_{VdW} = -\frac{A_H}{12}\left[\frac{d^2}{r^2-d^2}+\frac{d^2}{r^2}+2\ln\left(\frac{r^2-d^2}{r^2}\right)\right]$$

(2)

On shorter distances, a lubrication force has to be introduced explicitly in the molecular dynamics simulation. The most dominant mode, the so-called squeezing mode, is an additional force.

$$F_{\text{lub}} = -\left(v_{rel},\hat{r}\right)\hat{r}\,\frac{6\pi\eta {r_{rel}}^2}{r+r_1-r_2}$$

(3)

$$r_{red} = \frac{r_1 r_2}{r_1+r_2}$$

(4)

between two spheres with radii r_1, r_2 and the relative velocity v_{rel} ,η is the dynamic viscosity of the fluid.

To avoid that the particles penetrate each other, one needs a repulsive force depending on their overlap. We are using a Hertz force described by the potential

$$V_{Hertz} = K\left(d-r\right)^{5/2}$$

(5)

where K is expressed by the elastic modulus

Computer simulation methods are used for many-particle systems, for the inclusion of inertia effects (Reynolds numbers > 1) and Brownian motion (Peclet number of order 1). Two parts of the simulation, Molecular Dynamics, MD and Stochastic Rotation Dynamics method (SRD) are coupled, the simulations on the colloidal particles are used compute viscosity shear rate dependence.[4]

In another model, the equations of motion for *N* such particles immersed in a Newtonian fluid with viscosity thus express a quasistatic force balance [5].

$$F^H + F^P + F^B = 0$$

(6)

The 6*N* force/torque vectors are: 1) hydrodynamic forces F^H, exerted on the particles due to their relative motions in the presence of the solvent, 2) colloidal forces F^P, the sum of repulsive and attractive terms!, and 3) Brownian forces F^B. F^H is dominated by lubrication hydrodynamic terms between the close approaching surfaces of the colloidal particles. The colloid force term, **F***P*, contains both attractive—hence the term‘‘aggregated’’ colloids—and repulsive terms. The attractive force is identified as depletion force and has been modeled using Asakura–Oosawa potential; a short range repulsive force **f** rep is also included at the surface of the spheres. This takes on the form of a Hookean spring force mimicking the osmotic part of an attached/adsorbed polymer layer.

The microscopic viscous and elastic moduli have been determined from the mean-squared displacement by assuming t the Stokes-Einstein relation that is valid for Newtonian fluids can be generalized to viscoelastic fluids with frequency-dependent linear viscoelastic moduli and considering inertial effects on the motion of the probe particles to be negligible [6].

Magnitude of the shear modulus is calculated as

$$\left|G(\omega)\right| = \frac{k_B T}{\pi a\left(r^2(1/\omega)\right)\tau\left(1+\alpha(\omega)\right)}$$

(7)

Where k_B is the Boltzman constant, T is the temperature, a is the particle radius and τ the gamma function. The viscous modulus is given by

$$G''(\omega) = \left|G(\omega)\right|\sin\left(\frac{\pi\alpha(\omega)}{2}\right)$$

(8)

and the elastic modulus is

$$G'(\omega) = \left|G(\omega)\right|\cos\left(\frac{\pi\alpha(\omega)}{2}\right)$$

(9)

Shear stress shear rate *dependence* of colloids with yield stress is found to follow Herschel – Bulkley constitutive relation.

$$\sigma = \sigma_y + K\dot{\gamma}^n$$

(10)

where σ_y is the yield stress. K is the consistency and n is a power law index.

Methods and Materials

Latexes were prepared according to the methods described in references [1,2]. Steady shear viscosity as function of shear rate was calculated using Rheomterics Fluid Spectrometer in a Couette flow. Shear stress shear rate plots were fitted into Herschel-Bulkley constitutive equation and yield stress and power law indices were obtained. Using oscillatory sinusoidal deformation, torque was resolved into real and imaginary components. Elastic and viscous modulus was calculated as function of shearing frequency. Relaxation modulus as function of time was obtained by using transformation functions and numerical approximations.

Results and Discussion

Viscosity of eight latexes show that there is a shear rate dependence as result of Brownian and hydrodynamic forces on shearing colloidal particles subject to inter-particle forces, electrostatic, van der Waal and steric forces. As the shear rate is increased, colloidal particles aggregate and break-down. As given in Figure 1, higher shear rates result in diminishing differences between latexes.

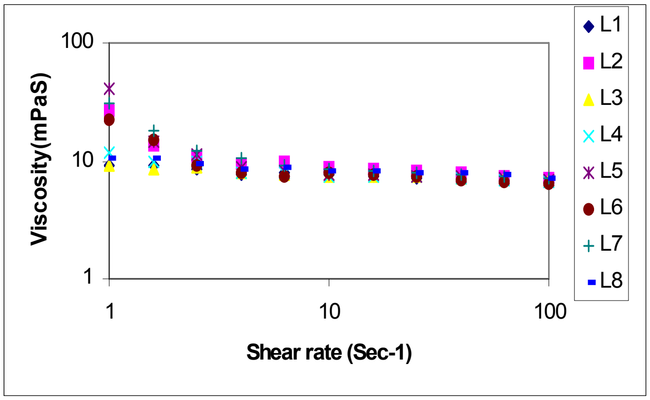

Figure 1 Viscosity shear rate dependence of latex L1 to L8 is shown

On taking viscosity at shear rate of 1sec-1 and 100sec-1 and plotting them against particle size, there is a good correlation between viscosity and particle size at shear rate of 1sec-1 but no such dependence exist at 100sec-1.

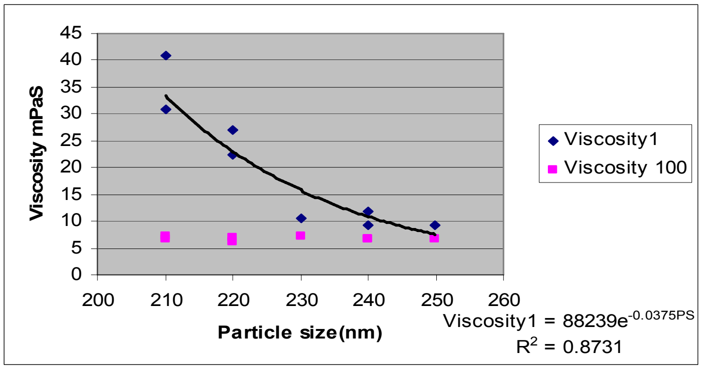

Figure 2 shows the dependence of viscosity on particle size at shear rates of 1sec-1 and 100sec-1

In Brownian Aggregation and shear induced aggregation, the particle aggregation rate with increasing shear rate, decreasing viscosity and increasing particle concentration.

Yield stress computed using Herschel-Bulkley constitutive equation is determined for all eight latexes and is plotted against particle size. The equation showing dependence of yield stress on particle size is given by $\sigma_Y = 142563e^{-0.0393PS}$ $R^2 = 0.9286$

where PS is the particle size and σ_y is the yield stress

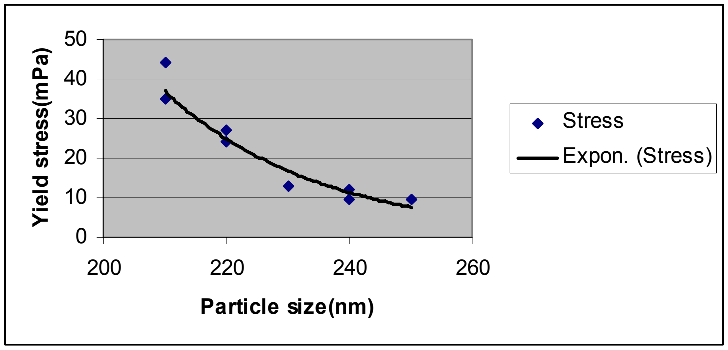

Figure 3 shows dependence of yield stress on particle size of latex

Nonlinear rheology in colloidal systems is a consequence of external deformation that reduces barriers, accelerate relaxation and flow, and ultimately drive yielding. Increasing stress modifies the nonequilibrium free energy resulting in a reduction of the degree of transient localization, softening of the elastic shear modulus, a reduction of the entropic barrier, and viscosity thinning. At a critical value of strain or stress, the system is predicted to undergo an absolute yield transition, i.e, the solidlike mechanical response is lost since particles are no longer transiently trapped by the surrounding cage.

Relaxation modulus of the latexes was obtained from dynamic modulus as function of time. Depending on the particle size, differences in relaxation modulus. In general higher particle size leads to a lower relaxation modulus. The latex L5 and L7 have the same particle size but L5 has higher relaxation modulus. Dependence of relaxation modulus on time shows an exponential dependence.

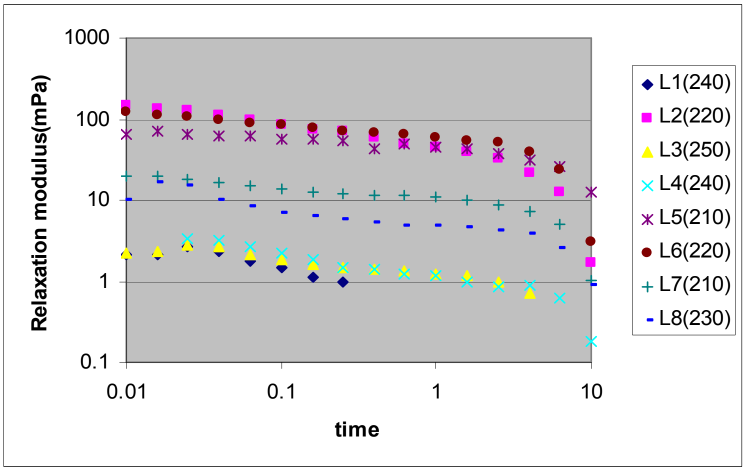

Figure 4 gives dependence of relaxation modulus on time for latexes of different particle nanometer size

The force required to push together two viscoelastic balls is given by [8]

$$F(t) = \frac{16}{3R}\int_0^t G(t-\theta)\frac{da^3}{d\theta}\,d\theta \qquad (11)$$

The model suggests that combination (fusion) of two viscoelastic particles depend on radius of the particle, R and relaxation modulus G(t).

Conclusion

Models on soft matter like colloidal dispersions of latex were analyzed. Effect of Brownian and hydrodynamic forces result in concentrated. Emulsion Aggregation dispersions being shear thinning, exhibiting yield stress and giving relaxation modulus that are particle size dependent.

References

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Author Biography

Suresh Ahuja received his BS in physics and chemistry from the Punjab University (1959), his MS in Soil Physics from Indian Research Institute (1961) and his PhD in Polymer Physics from Polytechnic Institute of Brooklyn (1967). After working over 37 years at Xerox with several years as Principal Scientist he retired. He hasover twenty(20) patents.. He has published over 50 publications and presentations at international conferences. He is a member of APS, ASME, SOR and IST.