Mechanical Coagulation in Emulsion Polymerizations

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Synópsis

Coagulum formation for different emulsion polymerizations was correlated to various agitation parameters. For low Reynolds numbers, rotational speed was shown to be important, whereas, for high Reynolds numbers, power consumption was the important parameter. These results were theoretically tied to first-order coagulation kinetics by incorporating shear rate relationships for flow in an agitated tank. For low Reynolds numbers, the average shear rate was assumed to be proportional to the rotational speed of the impeller. And for high Reynolds numbers, Kolmogorov's theory of locally isotropic flow was employed to relate the average shear rate to the power consumption.

INTRODUCTION

The formation of coagulum during an emulsion polymerization is an important industrial problem. Coagulum can result in a costly waste of raw materials as well as process inefficiencies. The primary raw material for emulsion polymerizations is the monomer, and most monomers are petroleum-based products. Therefore, as the cost of petroleum continues to rise, so does the cost of coagulum formation. Also, coagulum can collect on reactor surfaces such as the impeller blades and heat transfer surfaces, altering the desired characteristics of these surfaces. As a result, these surfaces need to be cleaned periodically, requiring costly cleaning equipment along with a costly expenditure of time. Product quality is also affected by coagulum formation, both on a macroscopic and microscopic level. Large flocs of coagulum are not a useful product due to the uncontrolled and varied composition of the polymer. In addition, small flocs of coagulum (particle doublets, triplets, etc.) can change the desired properties of the latex by altering the particle-size distribution. Hence, coagulum can cause product problems as well as process difficulties.

Even though coagulation has been studied extensively, for ideal dilute systems it has not been studied extensively in complex environments such as stirred tank reactors (STR), or under reaction conditions. Furthermore, agitation in an STR is achieved by rotation of an impeller blade, which causes fluid motion, consequently causing velocity gradients (shear rate) to develop throughout the reactor. The shear rate is not constant throughout the system, thus complicating the environment observed by the latex particles. To understand the role of agitation in coagulum formation, a way of quantifying the shear rate in an STR must be accomplished since the shear

rate has been shown to affect coagulation. The purpose of this paper is to discuss methods which have been used to estimate the shear rate in an STR and to present data obtained from the literature to show how these estimates can be employed in emulsion polymerizations.

THEORY

Colloid Stability

In general, colloid stability is governed by electrostatic and steric repulsion. Colloidal particles can develop a surface charge by many different mechanisms.[1-6] The surface charge of the particles causes ions of opposite charge (counterions) to distribute themselves near the surface of the particle. This associated layer of ions is called the diffuse double layer. The thickness of the double layer is given by the Debye length $(1/\kappa)$ according to the following equation:

$$\kappa = (8\pi n z^2 e^2/dkT)^{1/2} \tag{1}$$

where n is the number of ionized groups, z the valency, e the elementary charge, d the dielectric constant, k the Boltzmann constant, and T the absolute temperature.

Also, owing to the surface charge, an electrostatic potential (Ψ) exists. This potential is a result of the charge density difference between the particle surface and the bulk of the fluid. Consequently, when two particles of the same charge approach each other, a repulsive force develops, owing to the potential energy interactions.

The energy of interaction of two charged particles can be mathematically quantified using the DLVO theory.[7,8] The energy of repulsion can be represented by several different equations. However, for low surface potential,[9] the potential energy of repulsion between two particles is

$$V_r = \frac{1}{2}da\Psi_0^2 \ln[1 + \exp(-\kappa H_0)] \tag{2}$$

where H_0 is the distance of separation between the surfaces of the two particles, a the particle radius, and Ψ_0 the surface potential.

Also, an energy of attraction is developed between two interacting colloidal particles, and this attraction is mainly due to van der Waals forces. An equation depicting attractive energy between two particles is

$$V_A = A^*a/12H_0 \tag{3}$$

where A^* is the effective Hamaker constant.

The addition of attractive and repulsive energy provides the total energy of interaction, which is shown for a stable colloid in Figure 1. The potential energy of interaction is plotted against the separation distance of two colloidal particles. A positive energy of interaction at a certain separation distance indicates that repulsive forces are predominant, whereas a negative
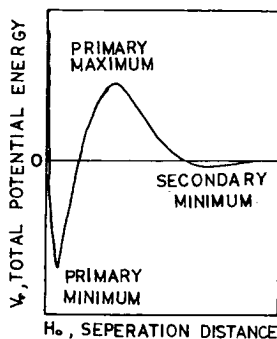
Fig. 1. The total energy of interaction between two particles, as a function of interparticle distance (H_0).

potential indicates attractive force dominates. If the colloidal particles collide with enough energy to surmount the potential energy maximum separating them, they coagulate.

Electrostatic stabilization is not the only means of stabilizing colloid dispersions. Steric stabilization[10-14] also play a role in the stabilization of many colloidal systems. Primarily, steric stabilization is achieved by the addition of long chain nonionic polymer molecules. Since these polymers have no electric charge, electrostatic repulsion cannot be the mechanism of stabilization. The long chain polymers hinder the approach of colloidal particles due to thermodynamic reasons. Only a few segments of the long chain molecules are adsorbed on the particle surface, whereas the rest of the molecule is in the aqueous phase. The stability is a result of a change in free energy of mixing of polymer segments with solvent. Both entropic and enthalpic interactions can make a positive contribution to the free energy of the system, and this can be considered as an energy barrier to coagulation. Although steric stabilization operates by a different mechanism from electrostatic stabilization, a potential energy barrier still needs to be overcome if the particles are to coagulate. However, in some cases, steric stabilization may eliminate the primary minimum shown in Figure 1, consequently preventing agglomeration of colloid particles.

Coagulation Kinetics

In general, colloidal particles can be forced together with enough energy to surmount the potential energy barrier separating them by two different mechanisms: Brownian coagulation and shear coagulation. Brownian coagulation is induced by the thermal energy content of the colloidal particles. All colloidal particles display a certain amount of Brownian motion, where the intensity of motion is directly proportional to the temperature and inversely proportional to the particle size. Then, if two particles collide with an energy of collision sufficiently greater than the potential energy barrier, they will coagulate. Or, if the energy of collision is smaller than the potential energy barrier, no coagulation will occur.

von Smoluchowski[15] has shown that Brownian coagulation is governed by a second-order rate equation:

$$dN_t/dt = -(4kT/3\mu W)N_t^2 \tag{4}$$

where k is the Boltzmann constant, T the temperature, μ the viscosity, W the stability factor, t the time, and N_t the number of particle per unit volume.

If the fluid is not at rest, but is being moved by some form of agitation, fluid velocity gradients will develop, which have a twofold effect on coagulation. A velocity gradient can increase the force of collision as well as the frequency of collisions. Shear coagulation has also been mathematically quantified[16,17]:

$$dN_t/dt = -(4S\phi/\pi W)N_t \tag{5}$$

$$N_t = N_0(1 - c) \tag{6}$$

where ϕ is the volume fraction, S the shear rate, W the stability factor, N_t the number of particles per unit volume, N_0 the initial particle concentration, and c the fraction of particles coagulated. Then, if eq. (5) is solved with initial condition $N_t = N_0$ at $t = 0$, and eq. (6) is substituted into eq. (5), the following equation is obtained:

$$-\ln(1 - c) = (4/\pi W)\phi St \tag{7}$$

Equation (7) can be used to see if coagulation proceeds according to a first-order process by plotting the $\ln(1 - c)$ vs. time.

It has been shown[18] that the type of flow can also effect shear coagulation; i.e., compressional and extensional flow will have a different effect than simple shear flow. Primarily, this effect accounts for a difference in collision surface, which directly effects collision frequency. Generally, the form of eq. 5 will not be altered and can adequately be used, at least, as a first approximation of the shear coagulation process in an STR.

Surface coagulation has also been shown to be an important mechanism of coagulation.[19-24] Latexes or other colloid particles are adsorbed at the air–liquid interface according to Langmuir adsorption isotherm. At the surface, the latex particles coagulate according to second-order kinetics, i.e., Brownian coagulation. Surface renewal is accomplished by agitation of the colloidal system. If there is no fluid motion, coagulation will stop once a surface film if formed. The theoretical equation describing surface coagulation[22] is as follows:

$$dC/dt = -(A/V)k_0C^2/(K_1 + K_2C)^2 \tag{8}$$

C is the concentration of colloidal particles, A/V the surface area to volume ratio, K_0 the surface reaction rate constant, and K_1, K_2 the Langmuir adsorption constants. An interesting point is that at high concentration ($K_2C >> K_1$), eq. (8) becomes independent of concentration. Consequently, the reaction would proceed as a zeroth-order reaction.

Heller and Peters[22] have shown that, for a few iron oxide sols, surface coagulation is a major factor in mechanical coagulation. Equation (8) held up to approximately 90% coagulation. Heller[23] also employed two latex

samples: polychlorostyrene and polystyrene. When these latexes were subjected to stirring, it was found that they would not coagulate unless potassium chloride was added. Then, if enough salt was added to cause the latexes to be sensitive to stirring but not to Brownian coagulation, they found that the agreement with eq. (8) was not as good as for the iron oxides. Deviation from eq. (8) was observed between 25 and 45% coagulation. This deviation was explained by the increase in stability of the latexes which was caused by desorption of surfactant from coagulated latex particles and readsorption on uncoagulated surfaces. Consequently, Heller suggests that mechanical coagulation is due to surface coagulation.

One major problem with Heller's work is that the solids of the colloidal systems employed were very dilute (0.02–0.04% w/w). Consequently, one should be careful in applying this theory to industrial latexes where the solid contents may be as high as 50% w/w. This 2500-fold increase in solid fraction could affect the rate of shear coagulation by the same magnitude [see eq. (5)], whereas the rate of surface coagulation should not be greatly affected since, as the concentration increases, this rate becomes zeroth order, i.e., concentration-independent.

Shear Rate in an STR

It is believed that shear coagulation plays an important role in the mechanism of coagulation of latexes during an emulsion polymerization. Consequently, a way of estimating the shear rate in an STR must be accomplished. The shear rate in an agitated vessel is not a constant value, owing to the velocity gradients generated by the impeller. For most practical purposes, however, an average value can be used. For relatively low Reynolds numbers, the shear rate S has been shown to be directly proportional to the rotational speed of the impeller N[25]:

$$S = KN \qquad (9)$$

where the proportionality constant K is independent of impeller diameter and a function only of the impeller type:

Impeller type	K value
Flat blade turbine	11.5 ± 1.4
Fan blade turbine	13.0 ± 2.0
Marine propeller	10.0 ± 0.9

Thus, the shear rate in an STR can easily be estimated for relatively low Reynolds numbers.

For relatively high Reynolds numbers, eq. (9) does not apply. For highly turbulent flow, the primary shear phenomena occur in the microstructure of the turbulence. Therefore, an expression for shear rate must be obtained for what is commonly characterized as random chaotic motion. However, if the flow is observed on a small enough scale, Kolmogorov's theory of locally isotropic flow can be applied. There are several references[26-31] on

this subject; therefore, the theory will only be briefly summarized in the following paragraphs with particular attention to its applicability to STRs.

Turbulent flow consists of an array of fluid domains, commonly referred to as eddies. The size of the eddies are generally distributed and vary in size from the dimensions of the system, L, to the dimension of the microstructure of the turbulence. Kolmogorov has shown that the smallest eddies of the system along with their associated velocity can be expressed as a function of kinematic viscosity ν and energy dissipation rate ϵ. Kolmogorov's length scale η and velocity scale v are:

$$\eta = (\nu^3/\epsilon)^{1/4} \tag{10}$$

$$v = (\nu\epsilon)^{1/4} \tag{11}$$

In a turbulent system, most of the energy is contained in the macroscopic fluid domains as kinematic energy. Very little of this energy is dissipated internally, and most of it is transferred to the smaller eddies where it is eventually dissipated. An understanding of why the bulk of energy is dissipated in the small scale can be obtained by observing the Reynolds number based both on the microscopic and macroscopic scale. The Reynolds number represents the ratio between inertial and viscous forces, and the basic form is given as follows:

$$\text{Re} = VL/\nu \tag{12}$$

where V is the characteristic velocity, L the characteristic length, and ν the kinematic viscosity. For highly turbulent flow, the Reynolds number based on the overall dimension of the system is very large. Consequently, the viscous forces are small, and little energy will be lost due to viscous effects. However, for the Reynolds number based on the small scale structure, the viscous forces are much more important:

$$\text{Re} = v\eta/\nu = (\nu^3/\epsilon)^{1/4}(\nu\epsilon)^{1/4}/\nu = 1 \tag{13}$$

Kolmogorov also postulated that for large Reynolds numbers and $L >> \eta$, the microstructure of turbulence becomes statistically independent of the main flow and loses its directional awareness. Therefore, on a small scale, the flow becomes isotropic, i.e., the root mean square average velocities are independent of axial direction. For locally isotropic flow, the local energy dissipation rate ϵ_i can be expressed as a function of local shear rate S_i:

$$\epsilon_i = (15/2)\nu(S_i)^2 \tag{14}$$

The theory of locally isotropic flow can be applied to turbulence in an agitated system provided Kolmogorov's assumptions are met. Therefore, the Reynolds number needs to be large (10^4), a condition easily met in most industrial STRs. Also, the characteristic length of the system, normally given by the impeller width, must be significantly greater than the microstructure of the system. In general, L is of the order of centimeters and η can be calculated using eq. (10). Table I presents an idea of the average

TABLE I
Kolmogorov's Length Scale as a Function of Power Input for $\nu = 1.0 \times 10^{-6}$ m²/s

hp/100 gal	W/kg	(μm)
25.0	49.29	11.9
2.0	3.94	22.4
1.0	1.97	26.7
0.5	0.99	35.1
0.25	0.50	37.6

magnitude of η as a function of power input into an agitated system, and it can be seen that $L >> \eta$. As a result, Kolmogorov's theory should apply to agitated systems in which the Reynolds numbers are high and the power input is sufficiently high.

In summary, Kolmogorov's theory of locally isotropic flow provides a means to estimate the average shear rate in an STR. Basically, the shear rate is a function of energy dissipation, and, in an STR, the energy dissipation rate is a function of position. Some experimentally determined shear rate distributions have been presented in the literature[32]; however, the distributions are not easily applied to STRs. In general, the average energy dissipation rate, which is equal to the power input into the system, can be used to estimate the average shear rate in an STR:

$$S_{avg} = (2\epsilon_{avg}/15\nu)^{1/2}; \text{ where } \epsilon_{avg} = P/\rho V_r \qquad (15)$$

and P is the power consumption, V_r the reactor volume, and ρ the fluid density. If the maximum energy dissipation rate is assumed to be proportional to the average energy dissipation rate,[29,31] a relationship for maximum shear rate can be obtained and is as follows:

$$S_{max} = (2\theta P/\rho\nu V_r 15)^{1/2} \qquad (16)$$

where θ is the turbulent intensity factor.

RESULTS AND DISCUSSION

Two methods have been presented to estimate the shear rate in an STR, one for relatively low Reynolds numbers and the other for relatively high Reynolds numbers. Neither of these methods have been applied to emulsion polymerizations. However, there is some indication that the expressions for the shear rate are applicable to the phenomenon of shear-induced coagulation. A plot of $\ln(1-c)$ vs. S with all other parameters constant should provide a straight line [see eq. (7)]. For low Reynolds numbers, the shear rate is directly proportional to rotational speed of the impeller, so the variation of $\ln(1-c)$ on N should be linear. For high Reynolds numbers, the shear rate is directly proportional to the square root of power consumption, so the variation of $\ln(1-c)$ with $P^{1/2}$ should also be linear. In the following paragraphs, two experimental situations are analyzed with respect to eq. (7) in order to show the applicability of eqs. (9) and (16).

For low Reynolds numbers, some data were obtained at Lehigh,[33] in which the following reaction conditions were observed:

(1) emulsion polymerization of styrene;

(2) 500-mL reactor;

(3) 1.5-in. pitch blade impeller;

(4) 70°C;

(5) ca. 30% solids;

(6) $500 \leqslant Re \leqslant 3000$;

(7) time of reaction = 5 h.

The results obtained can be seen in Figure 2. As one can see, a plot of $\ln(1-c)$ vs. N provides a straight line as would be expected if $S \propto N$. However, only three data points are provided, which indicates that more work must be done to confirm that eq. (9) is applicable to shear coagulation.

For high Reynolds numbers, some data[34] were reanalyzed with respect to Kolmogorov's theory of locally isotropic flow. In Ruben's experiments, he observed the effect of agitation on the emulsion polymerization of vinyl chloride–ethyl acrylate comonomer systems. The reactor employed was approximately 2 gal, and three different-size flat blade impellers were used. The experimental formulation and conditions can be observed in Table II. If the experimental data is analyzed with respect to eqs. (7) and (16) by plotting $\ln(1 - c)$ vs. $P^{\frac{1}{2}}$, three linear relationships are obtained (see Fig. 3). Each solid content is represented by a linear function where the 50% case proves to be the most sensitive to shear as would be expected. However, the lines do not intercept the origin as predicted, but this could possibly be due to a minimum shear requirement necessary for initiation of coagulation. In other words, as Figure 3 indicates, the higher the solid content of the latex in the reactor, the lower the critical shear requirement of initiation of coagulation. This finding could be related to the minimum forces of interaction between latex particles, in a concentrated system, which is required to maintain stability against shear coagulation. In summary, shear coagulation during an emulsion polymerization can be represented by a linear relationship which is independent of impeller diameter.
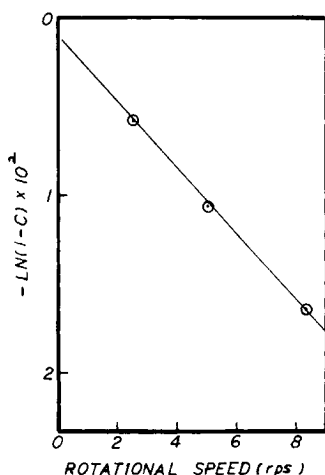

Fig. 2. Coagulum formation as a function of rotational speed for low Reynolds numbers.

TABLE II

Vinyl Chloride/Ethyl Acrylate Latex Formulation for the 45% Solids Polymerization

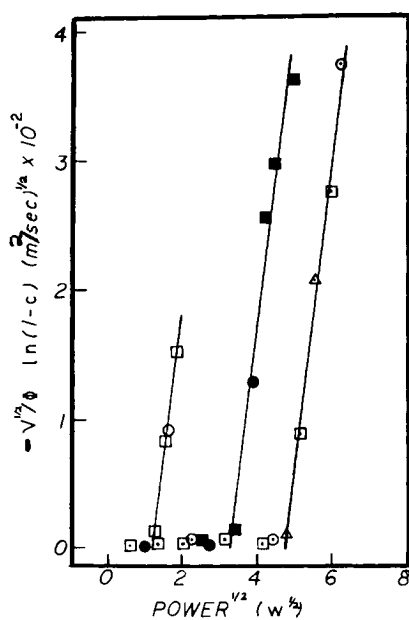| Ingredients	Parts by weight
Distilled water	123.5
Hydrocarbon sulfonate	11.4
Polyoxyethylated phenol	2.8
Sodium acetate	0.5
Ammonium persulfate	0.7
Ethyl acrylate	35.0
Vinyl chloride	65.0
Reactor—2-gal. jacketed SS—batch	
Temperature—4 h at 125°F	
2 h at 130°F	
3 h at 140°F	
Pressure—less than 110 Psi	

Fig. 3. Coagulum formation as a function of power consumption based on Kolmogorov's theory:

Impeller diameter (cm)	% Solids		
	40	45	50
5.1	△	▲	△
7.6	⊡	■	□
10.2	⊙	●	○

SUMMARY

Shear coagulation in an STR can be important in high solids industrial applications such as emulsion polymerizations. In an STR, the shear rate can be estimated theoretically, using the theory of locally isotropic flow if the Reynolds number is large. If the Reynolds number is low, the shear rate can be assumed to be proportional to the rotational speed of the impeller. These two shear rate estimates have been correlated with coagulation data of different emulsion polymerizations.

At high solid concentrations, surface coagulation should play a subordinate role in total coagulation. And since the data of Figures 2 and 3 adequately correlates to shear rate, this would indicate that shear coagulation is the predominant mechanism, at least for these colloidal systems. However, no coagulation mechanism should be ruled out for a particular system without sufficient evidence.

References

1. H. A. Abramson, *Electrokinetic Phenomena,* The Chemical Catalog Co., New York, 1934.

2. R. K. Iler, *The Colloid Chemistry of Silica and Silicates,* Cornell University Press, Ithaca, NY, 1955.

3. A. A. Kamel, C. M. Ma, M. S. El-Aasser, F. J. Micale, and J. W. Vanderhoff, *J. Disp. Sci. Tech.,* **2**, 215 (1981).

4. H. R. Kruyt, *Colloid Science,* Elsevier, New York, 1952, Vol. I.

5. J. W. Vanderhoff and H. J. van den Hul, *J. Macromol. Sci. Chem.,* **A7**, 677 (1973).

6. H. van Olphen, *An Introduction to Clay Colloid Chemistry,* Interscience, New York, 1963.

7. B. V. Deryaguin and L. D. Landau, *Acta Physicochim. USSR,* **14**, 633, 1941.

8. E. J. W. Verway and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids,* Elsevier, New York, 1948.

9. R. H. Ottewill, *Polymer Colloids,* NATO/ASI Tech. Univ. of Trondheim, 1975.

10. J. Lyklema, *Adv. Coll. Interface Sci.,* **2**, 65 (1968).

11. D. H. Napper and R. J. Hunter, *MTI, Int. Rev. Sci.,* M. Kerker, Ed., Butterworths, London, 1972, pp. 225, Series I, Vol. 7.

12. D. H. Napper and R. J. Hunter, *MTI, Int. Rev. Sci.,* M. Kerker, Ed., Butterworths, London, 1973, Series II, Vol. 7, Chap. 3, p. 161.

13. R. H. Ottewill, *Non-Ionic Surfactants,* M. J. Schick, Ed., Dekker, New York, 1967, Chap. 19, p. 627.

14. B. Vincent, *Adv. Coll. Interface Sci.,* **4**, 193 (1974).

15. M. von Smoluchowski, *Physik,* **A17**, 557, 585 (1916); *Z. Physik. Chem.,* **92**, 129 (1917).

16. J. Th. G. Overbeek, *Colloid Science,* H. R. Kruyt, Ed., Elsevier, New York, 1952, Vol. 2, p. 290.

17. M. von Smoluchowski, *Z. Physik. Chem.,* **92**, 155 (1917); P. Tuorila, *Kolloidchem. Beihefte,* **24**, 1 (1927); H. Mueller, *Kolloidchem. Beihefte,* **27**, 223 (1928).

18. G. R. Zeichner and J. Schowalter, *J. Coll. Interface Sci.,* **71**, 237 (1979).

19. W. B. DeLauder and W. Heller, *J. Coll. Interface Sci.,* **35**, 308 (1971).

20. S. Diep, W. Heller, and S. Kalousdian, *J. Coll. Interface Sci.,* **70**, 328 (1979).

21. W. Heller and J. Peters, *J. Coll. Interface Sci.,* **35**, 300 (1971).

22. W. Heller and J. Peters, *J. Coll. Interface Sci.,* **32**, 592 (1970).

23. W. Heller and W. B. DeLauder, *J. Coll. Interface Sci.,* **35**, 60 (1971).

24. J. Peters and W. Heller, *J. Coll. Interface Sci.,* **33**, 578 (1970).

25. A. B. Metzner, *AIChE J.,* **7**(1), 3 (1961).

26. G. K. Batchelor, *The Theory of Homogeneous Turbulence,* MIT Press, Cambridge, MA, 1953.

27. D. M. Levins and J. W. Glastonbury, *Chem. Eng. Sci.,* **27**, 537 (1972).

28. R. Shinnar and J. M. Church, *Ind. Eng. Chem.,* **52**, 3 (1966).

29. R. Shinnar, *J. Fluid Mech.,* **10**, 259 (1960).

30. H. Tennekes and J. L. Lumley, *A First Course in Turbulence,* MIT Press, Cambridge, MA, 1972.

31. D. T. Tomi and D. F. Bagster, *Trans. IChemE.,* **49**, 1 (1978).

32. L. A. Cutter, *AIChE J.,* **12**(1), 35 (1966).

33. T. L. Minick, unpublished research, Lehigh University, 1981.

34. R. W. Rubens, MS. thesis, Newark College of Engineering, 1958.