Mechanically Stirred Single-Stage Column for Continuous Gelation of Colloidal Systems

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A continuous and fast gelation unit, referred to as a single-stage mechanically agitated gelation column has been proposed to perform gelation of colloidal systems. A fluorinated polymer latex, MFA®, has been used. The column is initially filled with a coagulant solution at a concentration that fully destabilizes the colloid. Under agitation, the colloid is fed continuously to the discharging region of the agitator blades where it forms flocs of gel by mixing with the coagulant. If the density of the colloidal particles is larger than that of water, the flocs settle downward to the bottom of the column and flow out of the unit for further treatment or direct applications. Timescale analysis of the phenomena involved in the column has been carried out to understand the complex interplay between gelation and mixing. Various gelation regimes have been identified, which can interpret the observed gelation behavior in the column.
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Introduction

Gelation of colloidal particles is an important process for a variety of industrial applications ranging from food technology to polymer and pharmaceutical industries. Gelation systems are also model systems for fundamental studies of non-equilibrium statistical mechanics and dynamics of structural arrest.[1,2]

Any gel consists of at least two components: a macromolecular or colloidal network and a liquid (inorganic or organic). The latter has generally dominant volume fraction in gels. It is difficult to give a general definition of a gel, because gels formed from different systems can differ substantially when one looks at different (molecular or microstructural) length scales.[3,4] Gels are typical soft materials sharing properties of both solids and liquids (i.e., gels are structurally disordered and contain dominant liquid phase, but they have typically a non-zero shear modulus, a mechanical property of solids). Such properties lead to many potential applications of gels such as absorbents and membranes for separation, intermediate states for polymer purification, ion exchange and filtration, etc. Colloidal gels may be used as precursors for the synthesis of porous materials for catalysis, biosynthesis, and drug delivery.

Aggregation of colloidal systems at relatively large particle volume fractions can end up with a gel through interconnections among the aggregates.[2,5] Such an aggregation-gelation process can be realized simply by mixing a colloidal dispersion with an electrolyte (coagulant) solution, which is generally carried out in batch operation mode. In industrial practice, however, it is often required to operate the process in continuous mode so as to maximize the productivity. To this aim, in this work we propose a new operation unit, referred to as a mechanically agitated single-stage column, to perform continuous, fast gelation of colloidal systems. The principle of the operation is to continuously drop a colloidal dispersion

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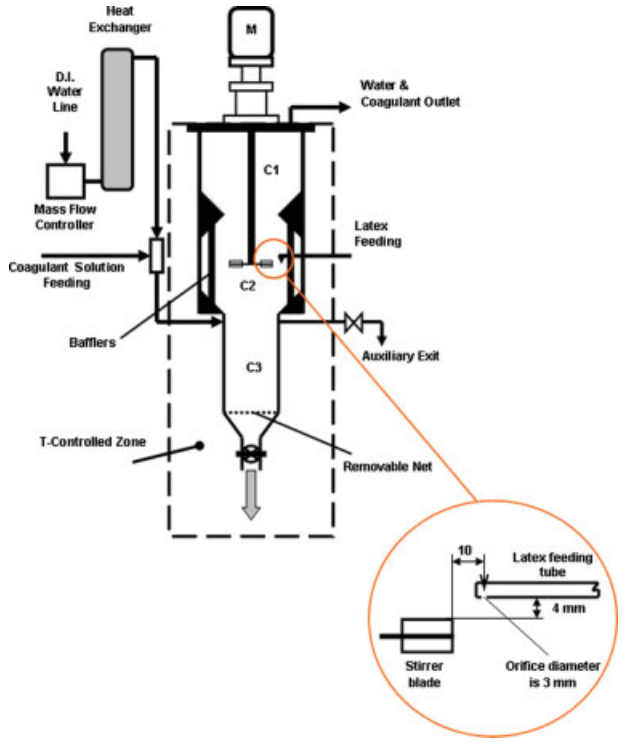

Figure 1. Schematic diagram of the mechanically agitated single-stage gelation column.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

into a chosen electrolyte solution under agitation to form gel flocs in the fast gelation regime, which separate from the liquid phase by gravitation. The main advantages of this unit are that it can operate either continuously or batchwise, and the gel structure can be tuned by varying operating conditions such as particle volume fraction, agitation intensity, temperature, and electrolyte concentration. The feasibility of the unit has been verified using fluorinated polymer (MFA®) colloids.

Gelation Experiments

The single-stage gelation column

A mechanically agitated single-stage gelation column has been constructed, as shown schematically in Figure 1. The body of the column is made of Plexiglas for ease of observation, and it is constituted by three chambers, C1, C2, and C3. The prerequisite for the applications of the gelation column is that the density of the colloidal particles must be significantly larger than that of the dispersing medium such that the formed gel flocs can move downward by gravity.

Chamber C2 in the center has the internal diameter of 150 mm and height-to-diameter ratio of 1. It is equipped with a six-blade disk turbine (D = 80 mm, L = 20 mm, and W = 13 mm) located in the middle of the chamber. The main purpose of the turbine is more to induce a flow of certain intensity around the latex feeding orifice (see Figure 1) rather than to make intense mixing of gel flocs and liquid phase in C2. The turbine, though similar to the Rushton disk turbine, has relatively small blades width (W) in order to reduce the global pumping efficiency. Too high pumping efficiency may lead to difficulties for gel flocs to settle down. Chamber C2 is also equipped with four cylindrical bafflers of 10 mm in diameter, which obviously leads to a partially baffled system. The clearance between the column wall and bafflers is 15 mm.

Chamber C1 is used to create a calm region that gives the possibility for some gel flocs dragged by the fluid from C2 to separate from the liquid phase and come back to C2 and then to C3. Chamber C3 is a cylinder of 80 mm in diameter and 200 mm in height with the function of separating the gel flocs, as products, from the liquid phase by sedimentation. When the gelation column operates continuously, the formed gel flocs flow continuously out of the column from the bottom after separating from water in C3. The stainless-steel net near the bottom of C3 is optional. It is used in this study to accumulate the gel flocs with the purpose of gel structure analysis, to be described in Section "Theoretical Background." The opening of the net is 50 μm.

The entire gelation column is placed inside a box of Plexiglas, where the temperature is controlled at a desired value by an air-conditioner. Moreover, the ambient temperature inside the box is set to be equal to that of the water inside the column.

Gelation of MFA® latexes

A fluorinated polymer latex (copoly-tetrafluoroethylene and perfluoromethylvinyl-ether, Hyflon® MFA620) with very narrow particle size distribution, supplied by Solvay Solexis (Italy), has been used for the gelation studies. The mean radius of the primary particles, determined by dynamic light scattering, is a = 37.5 nm, and the density of the MFA polymer is ρ = 2150 kg/m^3. The particle volume fractions used for the gelation experiments are in the range $\phi_o \in [0.03, 0.1]$ and obtained by direct dilution of the original latex with demineralized water prior to entering the column.

The column is first filled with water at a coagulant concentration larger than the critical coagulant concentration (CCC) for fast gelation, i.e., the gelation is carried out in the diffusion-limited cluster aggregation (DLCA) regime. The MFA particles are stabilized by carboxylic charge groups, and protonation is the most effective way to destabilize the latex. Thus, nitric acid is used as the coagulant in the present study. After agitation starts, the latex is fed continuously through a tube to the discharging region of the agitator blades (see insert in Figure 1), where the latex encounters the coagulant and immediately forms small pieces of gel flocs. Because the MFA polymer has a density larger than water, the formed gel flocs settle downward by gravitation and flow out of the column for further treatment or direct applications. To maintain the DLCA condition in the column during the process, the coagulant and water are fed continuously into the column from the lower part of C2 and exit from the top as indicated in Figure 1. This generates a slight upward flow, counter-current with respect to the settling of the gel flocs.

A membrane pump (RF 408.1, Seybert & Rahier) is used for feeding the latex to the column. The demineralized water comes from the main supply line and its flow rate is controlled by a mass flow meter (MAG 5000, Danfoss). The

water first passes through a heat exchanger, where it reaches the same temperature as in the column. Then, it mixes with the acid stream before entering the column. The acid is fed using a small piston pump (L7100 LaChrom, Merck-Hitachi). Concentration of the source acid is 32.5% wt, obtained by dilution of 65% wt commercial HNO_3 (analytical, Merck). The acid feeding rate guarantees a constant pH value in the column.

CCC for fast gelation

Before carrying out the gelation experiments in the column, it is important to determine the CCC for fast or diffusion-limited gelation under stagnant (Brownian) aggregation conditions, which is used as reference for determining the acid concentration in the gelation column. This was done by adding 0.4 ml of the MFA latex at ϕ_o=0.1 into each of a series of HNO_3 solutions of different concentrations and observing visually the time for the appearance of the gel flocs.[6,7] Figure 2 shows the measured gelation time as a function of pH. It is seen that when pH is small, i.e., at high HNO_3 concentrations, the gelation time is practically zero, indicating a fast or instantaneous gelation. In these cases, as soon as the latex droplet falls in the solution, a gel floc is observed instantaneously. From the data in Figure 2, it can be concluded that the fast gelation occurs for pH smaller than 1.9. For pH $>$ 1.9, the gelation time increases sharply with increasing pH, leading to slow or reaction-limited gelation. Thus, pH = 1.9 can be regarded as a good estimation of the CCC value.

Gel characterization

As mentioned in the Introduction, a colloidal gel prepared by DLCA is a network of interconnected clusters each of which exhibits a typical fractal structure.[8] In principle, by measuring the fractal dimension d_f of the clusters, one may quantify the structure of a gel. There are various techniques available to analyze the d_f value in aggregates or gels. These measure physical quantities related to the distribution of mass in space and can rely on rheology, microscopy, scattering, turbidity, etc. The most commonly used techniques are probably those based on light scattering[9] and rheological properties.[5,10] Some difficulties have been encountered recently both with Monte Carlo simulations[11–13] and with light scattering experiments,[6,7,13,14] which give evidence of the fact that the d_f value in colloidal gels estimated from the structure factor $S(q)$ decreases with increasing the particle volume fraction ϕ_o. The reason for this phenomenon is found[13] to be the perturbation induced by the nonfractal regime of the density correlation function of gels, which leads to a reduction in the slope of the linear part of $S(q)$ in the log-log plane and consequently to a reduced apparent fractal dimension. This indicates that $S(q)$ from light scattering experiments cannot give the correct estimation of the fractal dimension in gels. Although measuring the rheological properties of a gel is indeed a feasible approach to quantify the gel structure, the gel has to be formed in situ, which is difficult to realize at least with the present gelation process.

On the other hand, the volume of the gel formed from a given amount of particles provides very direct, although very macroscopic, information about the structure of the gel. In this work, we propose to use the specific gel volume, V_g, as an effective quantity to characterize the gel structure, which is defined as:

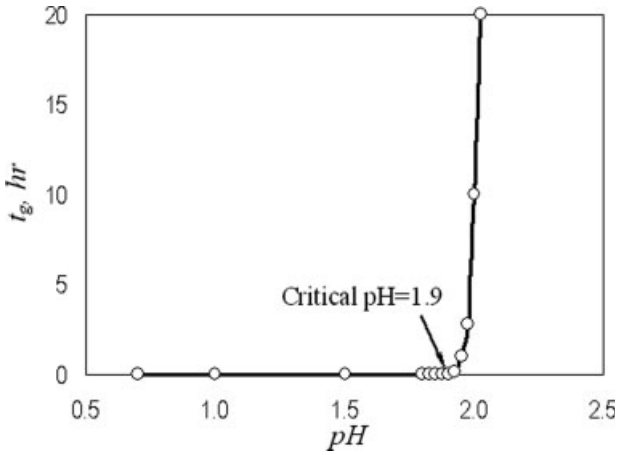

Figure 2. Gelation time, t_g of the fluorinated polymer MFA latex at stagnant (Brownian) aggregation conditions as a function of pH, measured experimentally by adding 0.4 ml of the latex at ϕ_o = 0.1 into HNO_3 solutions at various concentrations.

$$V_g = \frac{\text{Measured volume of gel } (m^3)}{\text{Fed mass of polymer particles } (kg)}. \quad (1)$$

It is evident that for a given mass of polymer particles, the smaller the formed specific gel volume (i.e., V_g) is, the more compact (or denser) the obtained gel structure.

To measure V_g, we have added the stainless-steel net between Chamber C3 and the conical part of the bottom to keep all the gel flocs within C3, as shown in Figure 1. During the experiments, the valve on the bottom is closed. After a suitable amount of gels is formed and accumulated in C3, we stop the experiment and register the amount of latex that has been fed to the column. In principle, one can directly read the volume of gels in C3, because all the gel flocs after a short time are generally collapsed to form a gel block. However, the formed gel block often has some irregular shape on the top, leading to difficulties to estimate the gel volume. Thus, in practice, we first discharge all the water over C3 through the auxiliary exit as indicated in Figure 1. The remaining total volume in C3 is registered, which includes all the gel flocs and some small amount of free water. Then, we open slightly the valve on the bottom to quickly discharge the remaining small amount of free water, whose volume is measured, and the difference between the total volume in C3 and that of the discharged free water gives the total volume of the gel.

Theoretical background

It is clear from the abovementioned description that as soon as the latex enters the column through the feeding pipe, gelation proceeds through a strong interplay among various simpler processes such as aggregation of colloidal particles,

mixing induced by agitation, diffusion of coagulant into latex droplets, etc. Thus, in order to better understand the gelation process, it is necessary to perform a proper timescale analysis for each such process so as to identify the most important ones in determining the evolution of gelation.

Gelation timescale

It is well known that the cluster mass distribution generated in a DLCA process is rather narrow.[1,15,16] This arises because under DLCA conditions the aggregation rate between clusters of different sizes increases as the difference in the size of the two clusters increases. Thus, the aggregation kinetics in this case can be well described by simply considering the number concentration of the average aggregates, $N_{\overline{k}}$, where $\overline{k}$ is the average number of primary particles in a cluster, and assuming a constant aggregation kernel.[15,17] In the case of a stagnant system, this corresponds to solving the following second-order aggregation kinetics:

$$\frac{\mathrm{d}N_{\overline{k}}}{\mathrm{d}t} = -\frac{8k_{\mathrm{B}}T}{3\pi\mu}N_{\overline{k}}^2(t), \tag{2}$$

where k_{B} is the Boltzmann constant, μ is the viscosity of the dispersion, and T is the absolute temperature. Because the dispersion is rather dilute, its viscosity can be regarded as that of water and constant during the process. On the basis of this second-order kinetics, the corresponding characteristic timescale of the aggregation, τ_{A}, can be expressed as[18]:

$$\tau_{\mathrm{A}} = \left(\frac{2k_{\mathrm{B}}T}{\pi\mu a^3}\phi_o\right)^{-1}. \tag{3}$$

ϕ_{o} is the particle volume fraction in the feed stream and it is assumed that in the early stage of the process aggregation takes place at the same particle volume fraction as in the feed stream.[17] When the contribution from the turbulence-induced collisions is also included, we have[17,19]:

$$\tau_{\mathrm{A}} = \left(\frac{2k_{\mathrm{B}}T}{\pi\mu a^3}\phi_{\mathrm{o}} + \frac{6}{\pi}\sqrt{\frac{8}{15}\pi}\sqrt{\frac{\varepsilon}{v}}\phi_{\mathrm{o}}\right)^{-1} \tag{4}$$

where ε is the turbulent kinetic energy dissipation rate and v is the kinematic viscosity. It should be pointed out that for typical colloidal systems of small particles (i.e., having radius smaller that 100 nm) the contribution of the turbulent energy to the overall timescale of aggregation is practically negligible. It becomes significant only when the particles or aggregates have reached a size at which their interactions with turbulent eddies become important.

To estimate the characteristic gelation timescale τ_{G}, one can compute the volume occupied by the clusters using the solution of Eq. 2, and define the gelation time as the time when the fraction of volume occupied by the aggregates is of the order of one as follows[17]:

$$\begin{aligned}\tau_{\mathrm{G}} &\approx \tau_{\mathrm{A}}(\phi_{\mathrm{o}}^{-[d_{\mathrm{f}}/(3-d_{\mathrm{f}})]}-1)\\ &= \left(\frac{2k_{\mathrm{B}}T}{\pi\mu a^3} + \frac{6}{\pi}\sqrt{\frac{8}{15}\pi}\sqrt{\frac{\varepsilon}{v}}\right)^{-1}\left(\frac{1-\phi_{\mathrm{o}}^{d_{\mathrm{f}}/(3-d_{\mathrm{f}})}}{\phi_{\mathrm{o}}^{3/(3-d_{\mathrm{f}})}}\right).\end{aligned} \tag{5}$$

where a typical value for the fractal dimension d_{f} under fully destabilized conditions is about 1.8.[15] The corresponding characteristic size of the clusters at the gel point, ξ, based on the fractal scaling, is given as a function of the particle volume fraction as[5]:

$$\xi/a \propto \phi^{1/(d_{\mathrm{f}}-3)}. \tag{6}$$

Mesomixing timescale

In general, mesomixing is considered as the portion of the mixing process that disintegrates large eddies, which belong to the inertial scale of turbulence, to form the smaller eddies in the Kolmogorov microscale. Because the gel flocs formed in the column are typically of macroscopic sizes, this suggests that the mesoscale mixing (i.e., at scales larger than the Kolmogorov microscale) could play a role in the gelation process. The characteristic time of mesomixing is given by[20]:

$$\tau_{\mathrm{meso}} = 2\Lambda_{\mathrm{c}}^{2/3}\varepsilon^{-1/3}, \tag{7}$$

where Λ_{c} is the characteristic length scale of the feed stream. Depending on the ratio of the fluid velocity in the feeding pipe, u_{p}, to the average velocity in the column near the feed point, $\overline{u}$, jet flow conditions may be defined as the situation when $u_{\mathrm{p}}/\overline{u} \gg 1$, whereas non-jet flow conditions correspond to the case with $u_{\mathrm{p}}/\overline{u} \ll 1$. In the jet flow conditions, Eq. 7 becomes[17]:

$$\tau_{\mathrm{meso}}^{j} = 2^{1/3}\frac{d_{\mathrm{p}}}{u_{\mathrm{p}}}, \tag{8}$$

whereas in the non-jet flow conditions we have[17]:

$$\tau_{\mathrm{meso}}^{nj} = 2\left(\frac{Q_{\mathrm{L}}}{\pi\overline{u}}\right)^{1/3}\varepsilon^{-1/3} \tag{9}$$

where d_{p} is the diameter of the feeding pipe and Q_{L} is the feeding rate of the latex. In the following analysis, $\overline{u}$ has been replaced by the value of the impeller tip velocity, u_{t}, which provides an upper bound of the $\overline{u}$ values.

Micromixing timescale

One of the most successful description of mixing at the microscale is provided by the Engulfment Deformation Diffusion (EDD) model.[20,21] According to this model, the small vortices (having size slightly above the Kolmogorov length) are responsible for deforming the contaminant phase (latex in our case) and for incorporating fluid in it from the environment (engulfment). This leads to the formation of partially segregated laminae, which are further stretched and elongated by the flow field. At the same time, chemical species move into the laminae due to diffusive transport, thus allowing for reaction. When engulfment is the limiting process with respect to diffusive transport, the characteristic micromixing timescale, τ_{M}, is on the order of the smallest time scale of the turbulent flow,[22]

$$\tau_{\mathrm{M}} \approx 17\tau_{\eta} = 17\sqrt{\frac{v}{\varepsilon}}, \tag{10}$$

τ_η being the Kolmogorov time scale. When the diffusive transport becomes limiting, which is particularly true for the colloidal particles, the micromixing timescale is characterized by the diffusion time of species into a shrinking lamina:

$$\tau_{DS} = 2\left(\frac{\nu}{\varepsilon}\right)^{1/2} \operatorname{arcsinh}(0.05Sc) \tag{11}$$

where $Sc \equiv \mu/\rho D$ is the Schmidt number, D is the diffusion coefficient of species, and μ and ρ are the viscosity and density of the dispersion, respectively. As we will see in the following, the diffusion times of both the acid (coagulant), $\tau_{DS,a}$, and the particles, $\tau_{DS,p}$, have to be taken into account in our analysis.

Figure 3 shows the values of various mixing timescales calculated from the above mentioned expressions for our gelation system as a function of the agitator tip velocity. It is seen that the turbulent micromixing timescale, τ_M, and the diffusion timescale of the colloidal particles, $\tau_{DS,p}$, are comparable and have the largest values. The mesomixing timescale in non-jet flow conditions, τ^{nj}_{meso}, is on the same order of the diffusion timescale of the acid, $\tau_{DS,a}$, whereas the mesomixing timescale in jet flow conditions, τ^{j}_{meso}, is the shortest one.

It is worth noting that under the operative conditions of our experiments, we have estimated the ratio of the fluid velocity in the feeding pipe to the average velocity in the column near the feed point, $u_p/\overline{u}$, to be in the range $0.72 < u_p/\overline{u} < 3.12$. Here one should also consider that because the membrane pump operates pulsatively, the u_p value used in this estimation is twice as large as the average velocity calculated from the latex feeding rate. From the computed range of the $u_p/\overline{u}$ values, we can then conclude that our gelation systems are in the transition regime between jet and non-jet flow conditions. However, we should expect that the low stirring speed experiments are dominated by the jet flow conditions, especially when one considers that the $u_p/\overline{u}$ values might be higher because $\overline{u}$ has been replaced by the agitator tip velocity u_t in the computations.

Results and Discussion

Effect of the agitator stirring speed

As mentioned earlier, the main purpose of using a turbine in Chamber C2 is to induce a flow of certain intensity around the latex feeding orifice (see Figure 1) rather than to make intense mixing between gel flocs and water. Because the latter can result in difficulties for gel flocs to settle downwards to the bottom of the column, it is first necessary to identify the range of the stirring speed values where the effect of agitation on the settling of gel flocs is negligible. To this aim, we have performed the gelation experiments in the column by varying the stirring speed at fixed values of all the other parameters. The obtained values of the specific gel volume, V_g, for a particle volume fraction in the feed equal to 0.07, are shown in Figure 4a as a function of the agitator tip velocity, u_t. The vertical broken line represents the agitator tip velocity u_t below which there is no difficulty for the formed gel flocs to settle downwards to the bottom of the column. For larger u_t values, V_g starts to decrease and increasing amounts of small gel flocs are detected at the water outlet.

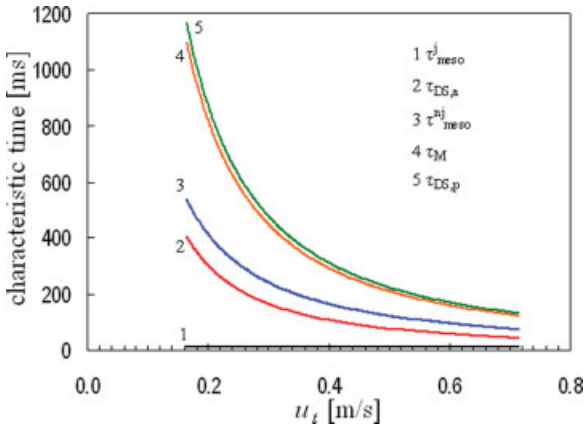

Figure 3. Characteristic times of the relevant mixing phenomena evaluated for the flow conditions in the column as a function of the agitator tip velocity.

1, mesomixing in jet flow conditions; 2, diffusion of coagulant into a shrinking slab; 3, mesomixing in non-jet flow conditions; 4, micromixing (engulfment controlled); 5, particle diffusion across a shrinking slab. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

This means that in the region on the right-hand side of the broken line, the agitator stirring speed is too high, thus preventing gel flocs from settling, and these are instead dragged out by the fluid moving upwards to the water outlet. Moreover, the fluid motion induced by a stronger agitation leads to gel flocs breakage which makes their settling even more difficult. Consequently, all the experiments discussed in the following were performed for agitator tip velocity values smaller than the one indicated by the broken line in Figure 4a.

To better understand the gelation process in the column, values of the ratio between the volumes of the formed gels and the fed latex,

$$R_V = \frac{\text{Volume of formed gels}}{\text{Corresponding volume of fed latex}}, \tag{12}$$

have been computed from the measured gel volumes in Figure 4a, and the results are shown in Figure 4b. It is seen that, in all the cases, the R_V values are larger than unity. This indicates that due to various mixing effects, the latex has reached, upon gelation in the column, a volume that is larger than that occupied initially by the system prior to feeding into the column. To explain these findings, we have run a series of experiments at a fixed stirring speed ($u_t = 0.528$ m/s) but at different particle volume fractions, i.e., keeping fixed the mixing rate and varying the gelation rate, to investigate the competition between gelation and mixing.

Competition between gelation and mixing

In Figures 5a,b, the V_g and R_V values measured experimentally are shown as a function of the particle volume fraction in the latex, ϕ_o, at a fixed pH (=1.3), stirring speed ($u_t = 0.528$ m/s) and constant values of all the other relevant parameters. In the figures, the same quantities computed for the same gelation systems but under stagnant conditions are

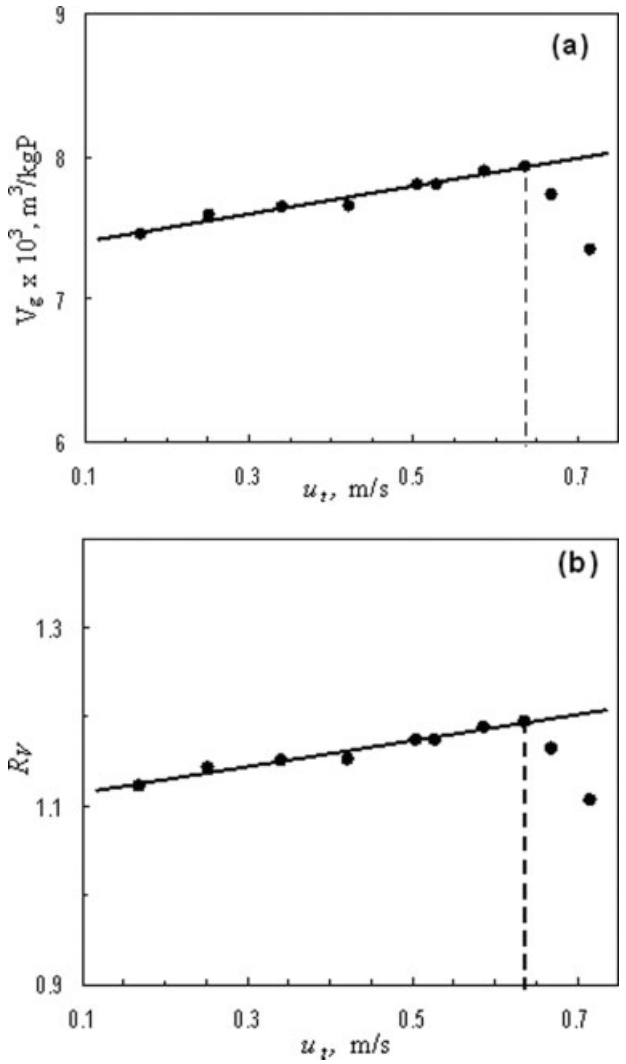

Figure 4. Values of (a) the specific gel volume, V_g, and (b) the gel-to-latex volume ratio, R_V, as a function of the agitator tip velocity, u_t, for gels formed in the column.

In the region on the right hand side of the broken line, very small gel flocs were detected at the water outlet. pH = 1.3; $Q_{latex} = 9.0 \times 10^{-7}$ m^3/s; $\phi_o = 0.07$; $Q_{water} = 5.0 \times 10^{-6}$ m^3/s; $T = 37.5$°C. Continuous lines are guides to the eye.

also shown. These have been computed by assuming that the final gels have the same volumes as the initial volumes of the latex, as it would be the case in the absence of flow. In the latter case we have: $V_g = (\rho\phi_o)^{-1}$. Such comparison gives evidence of a substantial difference between gelation processes under stagnant conditions and those occurring within a turbulent flow field. It is seen from Figure 5a that as ϕ_o increases, in both cases the specific gel volume V_g decreases, i.e., more compact gel structures are obtained. For the gelation under stagnant conditions, this is obvious because the gel volume corresponds to the filling space, which is given by the initial latex volume; thus, the V_g value decreases as the polymer mass (i.e., ϕ_o) in the latex increases. For the gelation in the column, however, it is interesting to note that, although the measured V_g value also decreases as ϕ_o increases, for $\phi_o < 0.05$ the V_g values are significantly smaller than those computed under stagnant conditions, i.e., the clusters exhibit a more compact structure, whereas for $\phi_o > 0.05$ they become larger, thus leading to less compact clusters. Such a difference in the gel structure produced in the column or under stagnant conditions becomes evident when the ratios of the gel volume to the initial latex volume, R_V, are compared in Figure 5b. It is seen that the R_V value, instead of being equal to one as in the case of stagnant gelation, increases monotonically as the particle volume fraction ϕ_o in latex feed increases. It is remarkable that the R_V value at $\phi_o = 0.07$ is almost twice as large as that at $\phi_o = 0.03$.

To understand these findings and to get more insight into the complex gelation mechanism under stirred conditions, let us analyze and compare the characteristic times of the mesomixing computed as discussed earlier and shown in Figure 6 as a function of the latex volume fraction. Note that the mesomixing characteristic times are just horizontal lines because

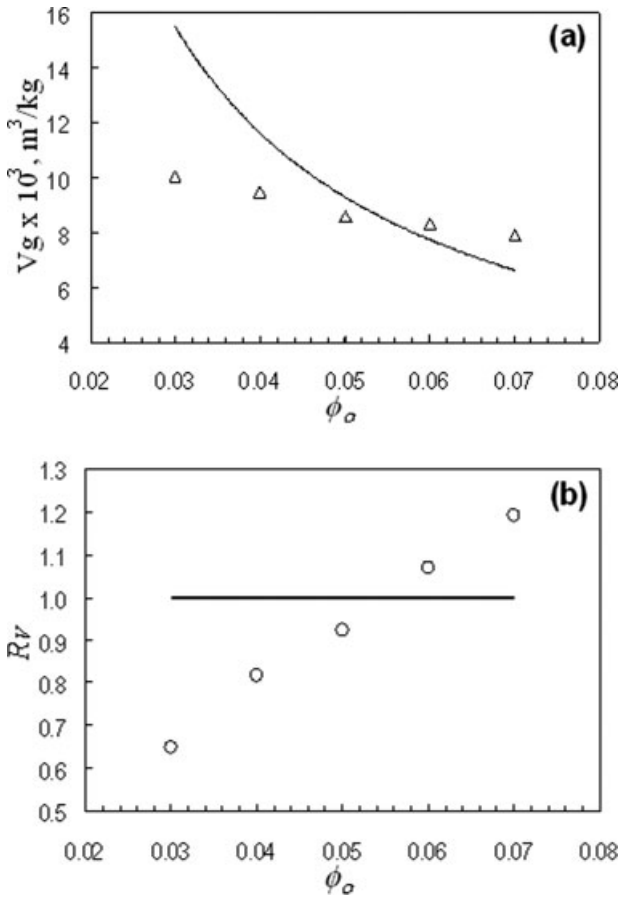

Figure 5. Experimental values of the specific gel volume, V_g (△), and the gel-to-latex volume ratio, R_V (○), as a function of the particle volume fraction in latex, ϕ_o, for gels produced in the continuous column.

Continuous lines refer to the theoretical $V_g = (\rho\phi_o)^{-1}$ and R_V values for gelation under stagnant conditions. $Q_{latex} = 9.0 \times 10^{-7}$ m^3/s; $u_t = 0.528$ m/s; $Q_{water} = 5.0 \times 10^{-6}$ m^3/s; $T = 37.5$ °C; pH = 1.3.

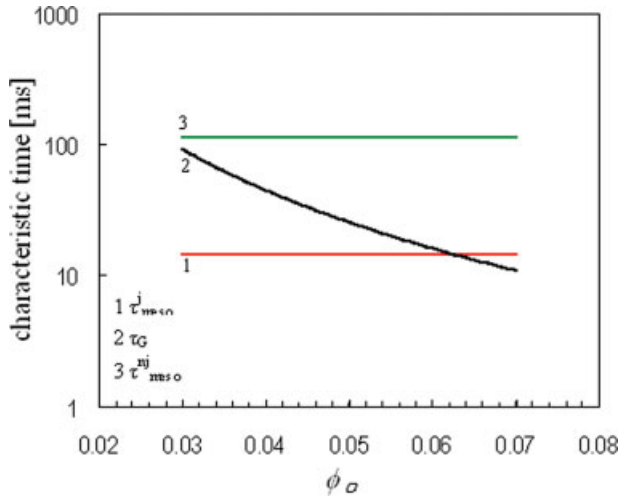

Figure 6. Comparison of characteristic times of mesomixing in jet flow conditions τ^{j}_{meso} (1), gelation τ_G (2), mesomixing in non-jet flow conditions τ^{nj}_{meso} (3), as a function of the latex volume fraction ϕ_o. u_t = 0.528 m/s.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

they are independent of ϕ_o. Moreover, because $u_p/\bar{u} = 0.482$, the mesomixing is in the transition regime between jet flow and non-jet flow conditions. Thus, it is expected that the mesomixing time should fall between those under jet flow and non-jet flow conditions. As ϕ_o increases, the gelation characteristic time τ_G decreases, but in the given range of ϕ_o, it always lies in between the τ^{j}_{meso} and τ^{nj}_{meso} lines. This implies that for small ϕ_o values (e.g. $\phi_o < 0.05$), the gelation time is most probably larger than the mesomixing time. In this case, the latex entering the column is subject to the action of eddies in the inertial regime before undergoing gelation, and the flow field acts as to restructure the growing clusters leading to more compact gel flocs than those under stagnant conditions. On the other hand, for large ϕ_o values (e.g. $\phi_o > 0.05$), the gelation time is shorter than the mesomixing time. Then, the aggregation–gelation process in the column can be sufficiently fast so that the latex enters the column and quickly freezes in the gel flocs, which are able to better withstand the strain action of the flow field, thus preventing the restructuring. In this case, the gelation process in the column is similar to that under stagnant conditions. This is consistent with the results in Figure 5a, where the measured specific gel volumes V_g in the column are closer to those under stagnant conditions for large ϕ_o values than for small ϕ_o values.

On the other hand, the V_g or R_V values for $\phi_o > 0.05$ in Figure 5 are significantly larger than those under stagnant conditions, i.e., the gels are less compact and exhibit apparent expanding behavior. This can be explained by comparing the gelation timescale with the micromixing timescales, as shown in Figure 7. The turbulent micromixing time τ_M and the diffusion time of the particles $\tau_{DS,p}$ are substantially larger than the gelation time in the entire range of ϕ_o, indicating that when the latex enters the column, gelation can be completed before it is altered by the two micromixing processes. This is in agreement with the fact that no primary particles or aggregates have been detected at the water outlet of the column. Thus, τ_M and $\tau_{DS,p}$ are not responsible for the expanding of the latex. However, in order for gelation to occur we need the acid to be transported (through diffusion) inside the latex, and the timescale of this transport is given by $\tau_{DS,a}$. As shown in Figure 7, for low ϕ_o values, the acid diffusion time, $\tau_{DS,a}$, is comparable with the gelation time, τ_G, but as ϕ_o increases, it becomes substantially larger than τ_G. This means that for large ϕ_o values, the acid diffusion into the latex stream is the time controlling step. Further, deformation of the latex slab in the quasi-elongated flow must be taken into account. This implies lateral shrinking of the slab and increased interfacial area between the latter and the acid solution. These phenomena accelerate the consumption of hydrogen ions (due to protonation occurring inside the slab where pH = 2.5–3, as in the original latex, i.e. orders of magnitude smaller than in the acid solution), which clearly increases with increasing ϕ_o. This, in turn, may cause a reduced gelation kinetics resulting in a partial expansion due to faster diffusion of the particles prior to gelation which becomes more pronounced with increasing ϕ_o. Again, this is a consequence of the action of the flow and thus peculiar of gelation processes in stirring devices. Knowledge and physical understanding of these phenomena are important for successful modeling and industrial realization of continuous gelation of colloids.

Effect of pH on gelation

The main effect of pH on the gelation process is that of varying the gelation rate. To investigate the influence of pH on the gelation process, we have performed two sets of gelation experiments by varying the pH in the column, at

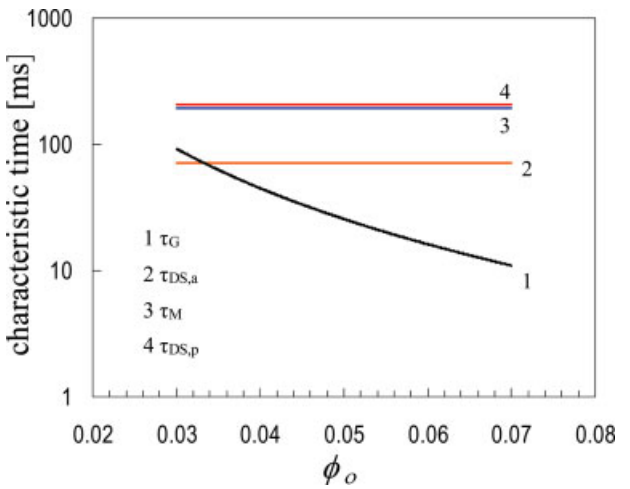

Figure 7. Comparison of characteristic times of gelation τ_G (1), micromixing of acid diffusion $\tau_{DS,a}$ (2), micromixing (engulfment controlled) τ_M (3), and micromixing of particle diffusion $\tau_{DS,p}$ (4), as a function of latex particle volume fraction ϕ_o; u_t = 0.528 m/s.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

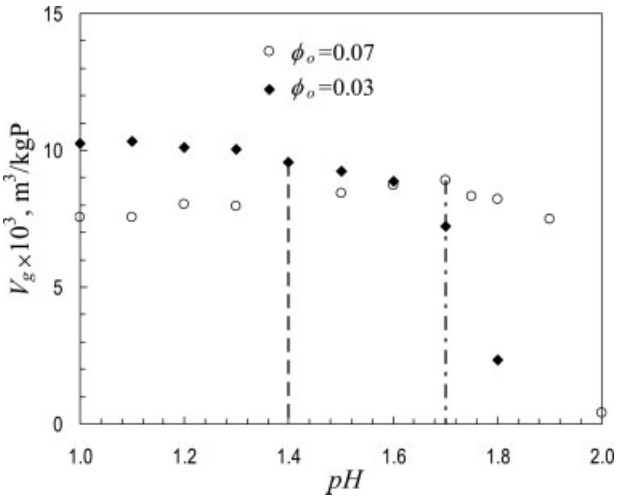

Figure 8. Values of the specific gel volume, V_g, as a function of pH, for gels formed in the column at ϕ_o = 0.03 and 0.07.

The broken and broken dotted vertical lines indicate the critical pH values above which small aggregates and primary particles were detected at the water outlet for ϕ_{o_x} = 0.03 and 0.07, respectively. Q_{latex} = 9.0 × 10^{-7} m^3/s; u_t = 0.528 m/s; Q_{water} = 5.0 × 10^{-6} m^3/s; T = 37.5°C.

two latex particle volume fractions, i.e. ϕ_o = 0.03 and 0.07, respectively. The obtained V_g values are shown in Figure 8 as a function of pH. In each case, the vertical lines separate two regions: on the right-hand side significant amount of small gel flocs and primary particles have been detected at the water outlet and increase as pH increases, whereas on the left-hand side gel flocs and primary particles in the water outlet are negligible. Although the final outcome is similar to what observed in the contest of Figure 4, the underlying phenomena are quite different. In the case of Figure 4a, the presence of small gel flocs at the water outlet is due to excessively high agitator stirring speed, which breaks and prevents the gel flocs to settle. In the case of Figure 8, although the acid concentration on the right-hand side of the vertical line is still larger than the CCC (pH = 1.9 see Figure 2), one could argue that the driving force for the acid to diffuse into the latex stream would decrease as pH increases. However, the acid diffusion time is independent of the driving force (see Eq. 11), and inhibited or delayed gelation is most likely due to deficit of hydrogen ions for reasons similar to those discussed in the previous subsection. This leads to a longer gelation time of the latex stream. Then, both the micro- and mesomixing processes in the column start playing a role, dispersing the latex particles into the vast amount of water. Because aggregation is a second-order process with respect to the particle concentration, once the particles are dispersed in the column, their gelation time becomes too long so that gelation cannot be completed before the particles and small aggregates are dragged out of the column.

Therefore, the vertical lines in Figure 8 actually define a sort of critical coagulant concentration under flow conditions below which gelation does not achieve completeness. It appears that at the given fluid motion conditions (u_t in this case), this critical concentration (pH) is smaller (larger) for ϕ_o = 0.07 than for ϕ_o = 0.03. This is again due to competition between gelation and mixing times. Because the gelation time is shorter at larger ϕ_o values than at a smaller ϕ_o value, this compensates partially the effect of reduction of the acid concentration on the gelation process, leading to the critical coagulant concentration under fluid motion being smaller for ϕ_o = 0.07 than for ϕ_o = 0.03. These results indicate that gelation in the proposed column requires not only to operate at fully destabilized conditions but also at high gelation rates, which can be achieved at sufficiently large particle volume fractions and/or coagulant concentrations.

On the left-hand side of the vertical line in Figure 8, the V_g values are larger for ϕ_o = 0.03 than for ϕ_o = 0.07. This has been discussed in the previous subsection. However, the trend in the variation of the V_g value with pH is significantly different between the two cases. For ϕ_o = 0.03, V_g decreases slightly as pH increases, whereas for ϕ_o = 0.07, it progressively increases with increasing pH. In light of the discussion in the previous subsection, for ϕ_o = 0.03 the mesomixing time is smaller than the gelation time, and the growing clusters during gelation undergo restructuring induced by strain of the flow field. Because the gelation time increases as pH increases, the growing clusters undergo a more pronounced restructuring, leading to more compact gel flocs, and as a result, the V_g value decreases slightly as pH increases. In the case of ϕ_o = 0.07, instead, the controlling step for the gelation is the (micromixing) time for the acid diffusion from the bulk fluid into the latex stream, which increases as pH increases. Thus, further expansion of the latex stream occurs at a larger pH, reflected in the V_g value increasing as pH increases.

Effect of temperature on gelation

Temperature in the column is expected to affect the gelation process in various aspects. First of all, increase in the system temperature brings about an increase in the diffusion coefficients of both coagulant and particles, and a decrease in the system viscosity, all of which promote the gelation process. Furthermore, increase in temperature may decrease the amount of surfactant adsorbed on the particle surface, leading to a decrease in the colloidal stability, thus accelerating the gelation process. Therefore, we expect a rise in temperature to decrease the gelation time.

We have performed the gelation experiments in the column in the range of temperatures between 293 and 333 K, at fixed values of the other parameters. Two sets of experiments at pH = 1.3 and 1.7, respectively, have been carried out. The obtained V_g values are shown in Figure 9 as a function of temperature. Let us first consider the case of pH = 1.7. Because the particle volume fraction of the latex is ϕ_o = 0.07, as discussed in the context of Figure 7, the gelation process is controlled by the diffusion rate of acid into the latex stream. Thus, because increasing temperature promotes the diffusion of the acid by increasing its diffusion coefficient, the gelation time decreases as temperature increases. Then, the extent of expansion of the latex stream before gelation becomes less with increasing temperature, leading to a slight decrease in the specific gel volume V_g (i.e. more compact gel) as temperature increases (Figure 9).

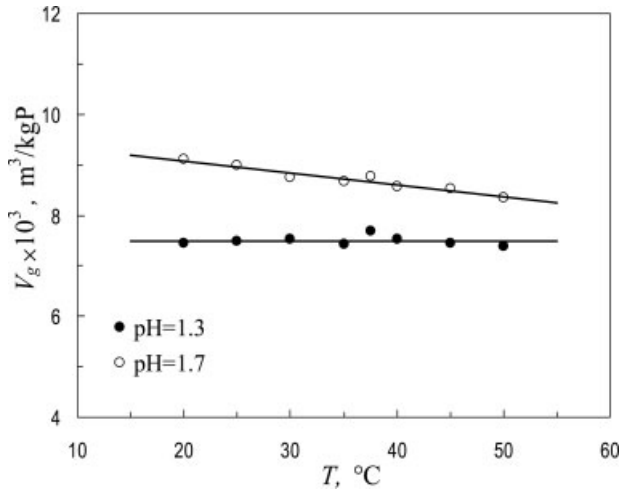

Figure 9. Values of the specific gel volume, V_g, as a function of temperature in the column, for gels formed at pH = 1.3 and 1.7.

$Q_{latex} = 9.0 \times 10^{-7}$ m^3/s; $u_t = 0.528$ m/s; $Q_{water} = 5.0 \times 10^{-6}$ m^3/s; $\phi_o = 0.07$. Continuous lines are guides to the eye.

In the case of pH = 1.3, however, the V_g value is insensitive to the variations in the system temperature. This arises most probably because at pH = 1.3 the gelation time is already very small and its further decrease due to the temperature increase is practically negligible. The expansion of the latex stream before complete gelation is in fact very small, with the ratio of the gel volume to the latex feed volume equal to about 1.1.

Concluding Remarks

Fast gelation of colloidal systems in a single-stage, mechanically agitated column has been proposed, as shown schematically in Figure 1, and investigated experimentally. This gelation column can operate either continuously or batchwise. The column is filled with water at a coagulant concentration that fully destabilizes the colloid, i.e. clearly above CCC. Under agitation, the colloid at a given particle volume fraction is fed through a tube to the discharging region of the agitator blades, where it encounters the coagulant (acid or salt) and forms small pieces of gel flocs under the effect of fluid motion. During gelation, the coagulant solution is fed continuously to the column from its bottom in order to keep a constant coagulant concentration in the column. If the density of the colloidal particles is larger than that of water, the formed gel flocs will settle downward to the bottom of the column due to gravitation and flow out of the column for further treatment or direct applications.

To verify the feasibility of the continuous gelation unit, we have carried out fast gelation in the column under various operative conditions, using fluorinated polymer (MFA®) latexes with particle size and density of 75 nm and 2150 kg/m^3, respectively. The nitric acid is used as the coagulant. The experimental results show that the constructed column can be well used to perform fast gelation. By tuning the complex interactions between gelation and various mixing processes by changing operative parameters such as agitator stirring speed, particle concentration in the latex, coagulant concentration, temperature, etc., one can control the size and structure of the formed gel flocs in the column.

Timescale analysis of the various involved processes has also been carried out in order to understand the competition between gelation and mixing. There exist two regimes, depending on the particle concentration in the latex and coagulant concentration. In the regime of very high particle and coagulant concentrations, the gelation time is very short such that the effect of perturbation of the flow field on the gelation process is less direct, and the effect of mixing is mainly confined to swelling the volume of the colloid slightly, resulting in gel volumes (structure) slightly larger (less compact) than those obtainable under stagnant conditions. Swelling or expansion of the gel may be enhanced by increased consumption of hydrogen ions promoted by deformation of the latex slab (due to the flow), a phenomenon which is more significant at higher latex volume fraction. In the regime of low particle and coagulant concentrations (but still under fully destabilized conditions), the mesomixing time can be smaller than the gelation time, and the effect of the strain induced by flow motion on gelation is substantial, leading to structures of the gel flocs more compact than under stagnant conditions. Our arguments and interpretation are further supported by the experimental results on the effects of pH and temperature on the gelation process in the column.

Acknowledgments

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Notation

a = radius of the primary particle, nm
D = diffusion coefficient
d_f = fractal dimension
k = Boltzmann constant
$N_{\bar{k}}$ = number concentration of the average aggregates
Q = flow rate, m^3/s
R_V = ratio of volumes between formed gel flocs and fed latex, defined by Eq. 12
T = absolute temperature, K
t = time, s
$\bar{u}$ = average velocity near the feed point, m/s
u_p = velocity in the feed tube, m/s
u_t = agitator tip velocity, m/s
V_g = specific gel volume, defined by Eq. 1, m^3/kg polymer

Greek letters

ε = turbulent kinetic energy dissipation rate
μ = viscosity, Pa s
ν = kinematic viscosity, m^2/s
ξ = characteristic size of the clusters in a gel defined by Eq. 6, nm
τ_A = characteristic time of aggregation defined by Eq. 4, ms
τ_{DS} = characteristic time of species diffusion defined by Eq. 11, ms
τ_G = characteristic time of gelation defined by Eq. 5, ms
τ_{meso} = characteristic time of mesomixing defined by Eq. 7, ms
τ_M = characteristic time of micromixing induced by turbulence defined by Eq. 10, ms
τ_η = Kolmogorov time scale, ms
ϕ = particle volume fraction in a gel
ϕ_o = particle volume fraction in a latex

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