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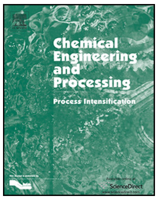

Aggregation and breakup of acrylic latex particles inside millimetric scale reactors

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ABSTRACT

Aggregation of acrylic latex is investigated inside tubular millireactors working under laminar hydrodynamic conditions. The size distribution and fractal dimension of aggregates are measured using light scattering. Results show that the equilibrium between rupture and aggregation is achieved quickly, allowing the study of cluster size distribution and shape at the aggregation/rupture steady state. Both laminar hydrodynamic conditions and high shear rate are suspected to promote the formation of aggregates with a high fractal dimension, which means that the particles are almost spherical, thereby offering an interesting alternative to conventional batch processes. These results can provide useful information for industries aiming at producing aggregates at specified size and quality.

1. Introduction

Colloidal aggregation (or coagulation) is a common practice in a wide range of industries. In wastewater treatment, the role of aggregation/flocculation processes is to assist the removal of the undesired organic matter by forming strong aggregates from colloidal matter before separation [1]. Indeed, this phenomenon is of primary importance for the success of the water treatment process. In the polymer industries, latex coagulation, which typically occurs just after batch polymer synthesis, is a key process. It defines the size and shape of the final agglomerates and thus the properties of the resulting product. However, conventional coagulation techniques, which are typically performed in stirred tanks, can lead to quality and safety issues related to the size and shape of the clusters [2]. Understanding the fundamentals of colloidal coagulation and proposing new processes to perform the operation is thus essential for these industries.

Colloidal suspensions are metastable. The equilibrium between the attractive Van der Waals forces and the repulsive electrostatic forces, which are induced by the surface charges of the particles, grants interesting stability properties to these suspensions. As a result, they can spend extended periods of time without deterioration or change in the particle size and associated properties. Due to the metastability of such suspensions, coagulation does not occur naturally for most cases and therefore must be triggered by a coagulant (acid or salt). When a salt is used, the coagulant lowers the repulsive forces by screening the charge effects. If the charged functions are pH sensitive, an acid can be used to change the pH of the medium and thus the charges at the surface of the colloidal particles.

The collision mode of the particles also plays an important role in coagulation. When the initial particles – or early clusters – are small enough (i.e. with diameters less than several hundred nanometers), Brownian motion causes the particles/clusters to move around their equilibrium position and temperature has an impact on the coagulation rate. In such cases, the term perikinetic coagulation is then used. When the colloidal entities are larger than several hundred nanometers, the shear rates created in the suspending fluid has more influence on the coagulation process than Brownian motion. When the coagulation process is entirely controlled by the shear rates in the flow, the term of orthokinetic (or shear) coagulation is used.

As mentioned by Owen et al. [3], coagulation/flocculation is frequently studied in batch vessels, and extensive experimental results in stirred tanks can easily be found [4–10]. However, in stirred tanks, dead volumes, inhomogeneous mixing and poor control of the local hydrodynamics can lead to unexpected coagulation issues such as fouling and broad cluster size distributions.

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Nomenclature

A_d	aggregate diameter (m)
C	floc or aggregate strength coefficient obtained using d_{max} (Eq. (8))
D_f	mass fractal dimension
D_{f1}	mass fractal dimension of the first class of clusters observed
D_{f2}	mass fractal dimension of the second class of clusters observed
d_{max}	maximum aggregate diameter (m)
d_{mixer}	internal diameter of the micromixer (m)
d_{tube}	internal diameter of the tube (m)
d_i	mean diameter of class i (m)
d_{50}	50% (resp. 10%, 90%) floc diameter (m)
$G(r)$	shear rate at a distance r from the axis (s^{-1})
G_{av}	average shear rate (s^{-1})
J_{ij}	collision frequency per unit volume ($m^{-3}\,s^{-1}$)
k_{ij}	coagulation kernel ($m^3\,s^{-1}$)
k'_{ij}	modified coagulation kernel taking efficiency into account ($m^3\,s^{-1}$)
L^e	entrance length (m)
m	optical contrast
N	concentration of particles with radius r (m^{-3})
N_0	initial particle concentration (m^{-3})
N_i	concentration of particle with radius r_i (m^{-3})
p	power-law scaling exponent
q	scattering vector (m^{-1})
r	radial distance from the tube axis (m)
R	coefficient of determination
r_0	mean primary particle radius (m)
r_{tube}	internal radius of the tube (m)
Re	Reynolds number inside the reactor $((4\cdot\rho\cdot Q)/(\mu\cdot\pi\cdot d_{tube}))$
Re_m	Reynolds number inside the mixer $((4\cdot\rho\cdot Q)/(\mu\cdot\pi\cdot d_{mixer}))$
t	residence time (s)
$v(r)$	velocity at a distance r from the axis ($m\,s^{-1}$)
v_{av}	average velocity inside the tube ($m\,s^{-1}$)
v_{max}	maximum velocity inside the tube ($m\,s^{-1}$)
V_i	volume fraction of class i particles
Greek Letters	
α_{ij}	collision efficiency
ϵ	dissipation rate per unit mass ($m^2\,s^{-3}$)
γ	floc or aggregate size exponent obtained using d_{max} (Eq. (8))
γ_{part}	surface energy of the particles ($J\,m^2$)
μ	dynamic viscosity (Pa s)
ν	kinematic fluid viscosity ($m^2\,s^{-1}$)
λ	incident light wavelength (m)
ϕ	volume fraction occupied by particles
ρ	density ($kg\,m^{-3}$)
θ	scattering angle
ζ	zeta potential (V)

An alternative to stirred tanks is the use of tubular reactors, where local hydrodynamics are well defined in both laminar and turbulent conditions. Concerning aggregation studies in pipes with laminar flow conditions, the first studies have mainly focused on the evolution of the particle concentration over time, as well as the aggregate size distributions [11,12]. More recent studies have used laminar flow tubular reactors to study the effects of shear flocculation processes [13] and the resulting shape of the flocs produced [14], with colloidal suspensions other than latexes.

Until now, few works have focused on the benefits of having a millimetric-scale tubular coagulator working in laminar flow conditions over both cluster size distribution and shape of the coagulated particles at aggregation equilibrium. The aim of this work is thus to further investigate coagulation of colloidal suspension inside millimetric tubes to highlight the advantages of using miniaturized equipments with laminar hydrodynamic conditions for controlled cluster size distributions (CSD) and floc shapes.

2. Theory

2.1. Shear coagulation theory

Colloidal aggregation is a long-time studied phenomenon. Almost a hundred years ago, Smoluchowski [15] theorized aggregation kinetics in analogy with chemical kinetics and proposed theoretical collision frequency expressions in the cases where particle motion is driven by Brownian motion and by laminar convection. This approach was later extended to turbulent conditions by other authors, as will be described below. In the most general case, the collision frequency per unit volume J_{ij} between two classes of particles i and j that differ by their radius r_i and r_j and present in solution at a concentration of N_i, N_j can be expressed as in Eq. (1). k_{ij} is called coagulation or aggregation kernel.

$$J_{ij} = k_{ij} \cdot N_i \cdot N_j \tag{1}$$

The expression of the coagulation kernel differs depending on the motion considered (i.e. diffusion or convection) and the hypothesis formulated by the authors.

2.1.1. Laminar coagulation

When considering shear coagulation under laminar flow, Smoluchowski [15] assumed that:

- All the collisions are efficient (i.e. there is no repulsion between the particles)
- The particles follow the fluid streamlines
- The particles are spherical

Under these assumptions, Smoluchowski [15] obtained the expression of the collision frequency per volume unit J_{ij} presented in Eq. (2), where G_{av} is the average shear rate.

$$J_{ij} = \frac{4}{3} \cdot G_{av} \cdot (r_i + r_j)^3 \cdot N_i \cdot N_j \tag{2}$$

This expression can then be implemented in a population balance to predict the evolution of the concentration of clusters of different sizes through aggregation. By considering an initially monodisperse suspension of spherical particles with a radius r_0 and concentration N, the decrease of the particle number at the very early stages is described by Eq. (3).

$$-\frac{dN}{dt} = \frac{16}{3} \cdot N^2 \cdot G_{av} \cdot r_0^3 \tag{3}$$

When the volume fraction ($\phi = 4/3 \cdot \pi \cdot r_0^3 \cdot N$) of the particles is constant through aggregation, Eq. (3) can be expressed as a pseudo first order equation (Eq. (4)).

$$-\frac{dN}{dt} = \frac{4}{\pi} \cdot \phi \cdot N \cdot G_{av} \tag{4}$$

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