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Short communication

Electrochemical agglomeration of polystyrene latex

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1. Introduction

The preparation of colloidal particles through aggregation and coalescence processes could have a great impact on various branches of applied science including polymer chemistry [1], semiconductor technology [2] and environmental chemistry [3]. Accordingly, a significant number of studies in these fields have been performed during the last few decades. However, problems are still posed by the discrepancies between theory [4] and experiment [5–9] as well as the control of excessive agglomeration. For example, with rubber toughened plastics, the average particle size and distribution of the dispersed phase greatly affect the physical properties of polymers [10]. However, it is not cost efficient to obtain optimal rubber particles via synthesis due to long reaction times. Thus, considerable attention has been given to the enlargement of various rubber colloidal particles of small sizes prepared in a relatively short period of time [11, 12]. Various methods based on chemical or physical destabilization of electrostatically stabilized polymer colloids have been suggested, but the formation of substantial amounts of coagulum still remains problematic, due to difficulties in controlling the rate of particle growth [13]. Moreover, addition of chemical substances such as electrolytes, weak acids and surface-modified colloids, necessarily result in dilution of the latex [14–16]. However, addition of concentrated solutions may lead to localized and excessive agglomeration. Physical methods [17, 18] such as freeze–thaw, shear force, and mechanical agitation also require additional facilities and large energy consumption.

In this communication, we first describe an electrochemical method for the agglomeration of a polystyrene (PS) latex. Destabilization of negatively charged PS colloidal particles was induced by lowering the solution pH electrochemically. It is believed that the electrochemical oxidation of water molecules lowers the pH in the vicinity of the positive electrode and suppresses the ionization of acidic groups at the colloidal surface. According to the DLVO theory [19, 20], reduction of electrostatic repulsion between PS particles allows the particles to reach a primary energy minimum and the irreversible coalescence is triggered.

The agglomeration via electrochemical methods is distinguishable from other chemical means reported to date. Since no agglomerating solutions are introduced, the total solid content of the latex remains invariant throughout the agglomeration reaction. Facile termination of the reaction is also possible simply by switching off the electric circuit. Continuous agglomeration due to residual pH perturbation near the electrode surface is negligible. In contrast, other chemical methods may require additional stabilizing agents to completely stop the reaction.

2. Experimental details

Emulsifier-free polystyrene latex, of average particle diameter (d) about 171.8 nm, was synthesized in a single step (ammonium persulfate: 26.7 mM, styrene: 550 mM) [21]. The solid content determined by a gravimetric method was 6.3%, indicative of 98.2% conversion. PS was dialysed to remove unreacted monomer and initiator using membrane tubing for 6000 to 8000 molecular weight cut-off. The surface charge density of dialysed PS, determined by a conductometric titration [22], was 0.98 μC cm^{-2}. For the electrochemical agglomeration, 30 ml of dialysed PS was introduced into a cell equipped with two 5 cm apart stainless steel foils (AISI316). The electrode area exposed to PS was 7.5 cm^2. Agglomeration was carried out by applying various a.c. potentials (60 Hz) between two electrodes. PS was stirred mildly during the reaction, although the quiescent condition gave identical results.

To immediately compare the change of particle size during agglomeration, the relative turbidities at two wavelengths were monitored as suggested by Jeffrey et al. [23]. A new function T, defined as $\tau_1\lambda_1/\tau_2\lambda_2$ was utilized, in which τ_1 and τ_2 are turbidities at different wavelengths λ_1 and λ_2. Since T is not sensitive to the extent of dilution, each PS sample was diluted about 50 times for turbidity measurements. T values obtained at 400 nm (λ_1) and 600 nm (λ_2), were compared with average particle diameters (d) measured by dynamic light scattering (Nicomp, Submicron Particle Sizer). All T values were converted to d, using a relation

d (nm)=725.5 − 212.8 T as T linearly decreased with increase in d.

3. Results and discussion

For the electrochemical aggregation to occur, the pH near the positive electrode should be so low as to reduce the surface charges and allow close contact of colloidal particles. Figure 1 shows that this condition can be easily attained by controlling the potential applied between two electrodes. Although no agglomeration reaction occurs at 2.0 V within 90 min, the onset time for particle size increase becomes shorter at higher potentials. It should be pointed out that lengthening the reaction time can trigger the particle growth at 2.0 V as well, since the applied potential markedly affects the onset time. Assuming that most of the current results from redox reactions of water molecules, one can speculate as to the effects of the potential on the onset. For example, the current densities of 0.33 and 0.43 mA cm^{-2} under 2.5 and 3.0 V at 54 °C, respectively, were utilized to determine the charge passed until d began to increase. Although 11.6 C were required at 2.5 V for the onset, 7.74 C were consumed at 3.0 V. The influence of the current density on the onset, rather than the total charge, indicates that the pH near the electrode is not completely neutralized immediately after a polarity reversal. Instead, low and high pH layers are present due to the higher mobility of H^+ relative to OH^-. This pH modulation will be more distinct at higher potentials, leading to the faster onset. Note that rapid pH modulation through polarity changes alleviates the formation of coagulum. Application of d.c. potentials resulted in the production of macroscopic precipitates on the positive electrode surface due to localized and excessive agglomeration. The effect of the current density on the onset can be more clearly seen by decreasing the reaction temperature. When 3.0 V was applied at 44 °C, the lower current density of 0.26 mA cm^{-2} gave the considerably prolonged onset of 150 min, although the total charge of 17.6 C is significantly higher than the value at 54 °C.

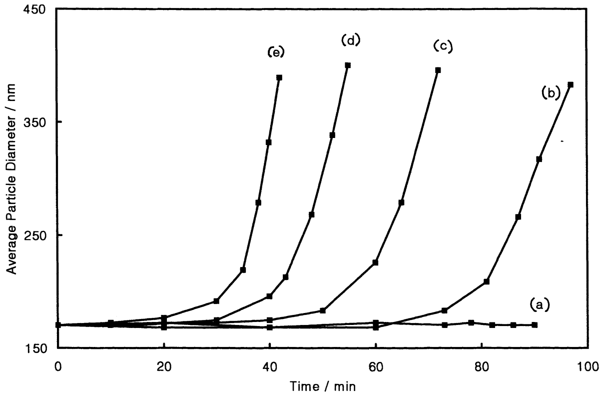

Fig. 1. Effects of a.c. potentials on the aggregation of PS. Various potentials of (a) 2.0, (b) 2.5, (c) 2.75, (d) 3.0 and (e) 3.25 V were applied between two electrodes at 54 °C.

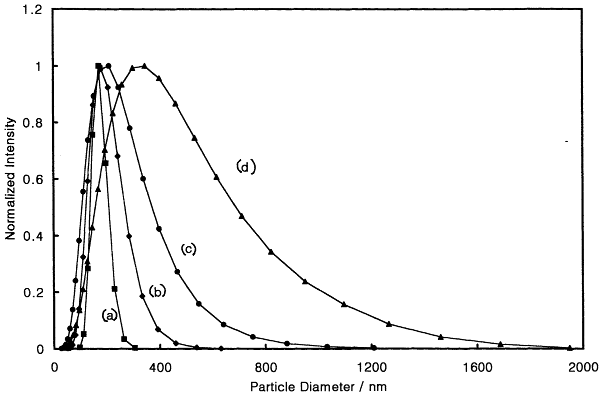

Fig. 2. Particle size distributions of PS after agglomeration at a.c. 3.0 V for (a) 0, (b) 38, (c) 44 and (d) 55 min. d and σ of PS were (a) 171.8, 29.5, (b) 191.6, 63.8, (c) 228.2, 120.4 and (d) 400.1, 249.2 nm.

Figure 1 also illustrates that once the agglomeration is triggered, d increases faster at higher potentials and linearly with time. The latter, which indicates that the reaction rate is increasing with time, is interesting since the increase in d should reduce the number density of particles and also the agglomeration rate. Although we found that for aggregated PS ($d = 400$ nm), the surface charge density decreased slightly from 0.98 to 0.75 $\mu C\ cm^{-2}$, it is unlikely that the increase in the rate results from a decrease in surface charge density. We investigated this by slowly adding a surfactant to maintain a constant surface charge density throughout the agglomeration and no significant decrease in rate was observed.

The electrochemical agglomeration also affects the particle size distribution. Figure 2 demonstrates the change in distribution with time when 3.0 V a.c. is applied. It is obvious that the electrochemical agglomeration causes the distribution to be broad and unsymmetrical. As the particles grew, the standard deviation (σ) of PS increased from 17.2% to 62.3% of the corresponding d. The broad and non-Gaussian distribution indicates that the rate of particle growth was not homogeneous, although most PS particles were subject to agglomeration after 55 min, as shown in Figure 2(d). Control of applied potential, reaction temperature and mechanical stirring does not change this behaviour. It should also be pointed out that attempts to obtain PS particles of d greater than 500 nm produced substantial amounts of coagulums, due to the broad and non-Gaussian distribution. When d is less than 500 nm, however, the formation of coagulum is minimized and the amount produced is less than 0.1 wt %.

Electrochemical agglomeration is a new method which allows latex of large particle size to be obtained without chemical additions. We are now investigating the effect of a.c. frequency on the particle size distribution.

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