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Spontaneous formation of bimodal particle size distributions: A novel one-step strategy for obtaining high solid content, low viscosity poly(vinyl acetate-*co*-ethylene) latexes

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ABSTRACT

A novel one-step semi-batch method was developed as a means of synthesizing vinyl acetate-*co*-ethylene (VAE) latexes with bimodal particle size distributions (PSDs). This technique allows high solid content while maintaining extremely low viscosity. In contrast to previous methods, the formation of a bimodal PSD based on the limited auto-aggregation of particles was found to occur spontaneously. The effects of the reaction temperature, initiator concentration, surfactant concentration, sodium dodecyl sulfate (SDS)/nonionic surfactant ratio and reaction time on the PSD and solid content of the latex were all investigated. A stable VAE latex consisting of 78.4 vol% large particles and 21.6 vol% small particles with a large-to-small particle diameter ratio of 4.51 was readily synthesized using this approach. The viscosity of one such latex with a 71.83 wt% solid content was below 300 mPa s at a constant shear rate of 20 s^{-1}. This synthesis method was also demonstrated to be highly reproducible.

1. Introduction

It is well known that a polymer latex having a high solid content (HSC; generally more than 60% by mass) will possess many advantageous properties, including reduced film-formation and drying times and better surface coverage. Additionally, the synthesis of a HSC latex can maximize the space-time yield of a reactor as well as reduce transportation and storage costs, all of which help to lower the expenses associated with industrial production [1–3].

An HSC latex cannot simply be obtained by increasing the monomer content in the reaction system. This is because the viscosity of the latex will increase sharply with slight increases in the solid content above a certain point (typically 55–60 wt%) at which the particles begin to interact strongly. This is deleterious because an overly viscous latex is difficult to apply [4]. In addition, the mass/heat transfer, mixing and stability of the reactant mixture will all be significantly affected [5]. HSC latexes have attracted considerable attention over the past three decades, and researchers have found that the particle size distribution (PSD) has a pronounced effect on the relationship between the solid content and the viscosity of the latex [6–11]. As such, the key to obtaining low viscosity HSC latexes is to optimize the PSD.

Bimodal PSD latexes appear to have more potential than monomodal versions. In theory, the maximum packing factor for a monomodal PSD latex is 0.74 (assuming perfectly monodisperse particles in a face centered cubic (fcc) arrangement). However, in reality, latex particles will not spontaneously arrange in this ideal manner because the particles cannot move with respect to one other in an fcc packing, resulting in an infinitely high viscosity. Therefore, a chaotic random arrangement with a maximum packing factor of 0.64 is used to evaluate the maximum solid content of a latex [12]. This is the primary reason why the solid content of a latex obtained from a conventional process typically has an upper limit of 55 wt%. In contrast, the maximum packing factor for a bimodal PSD latex will be higher, as the smaller particles can fit into the interstitial spaces between the larger particles. For this reason, bimodal PSD latexes with the same solid content as monomodal latexes will exhibit lower viscosity values. According to the available literature, the lowest viscosity can be obtained in the case of a latex containing 75–85 vol% large particles and 15–25 vol% small particles, and with a large-to-small particle diameter ratio in the range of 4–8 [1,4,13–15].

To date, significant effort has been devoted to preparing bimodal PSD latexes and to obtaining optimal PSDs, and many practical, feasible

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methods have been reported. The techniques for preparing bimodal PSD latexes can be largely divided into two categories: (i) physical blending of two populations of particles with different sizes followed by concentration or parallel growth [5,16–19], and (ii) *in situ* nucleation of the second population of particles [13,15,20–23].

The first approach is simple, direct, and produces well-controlled particles sizes, but is not suitable for industrial production because it is cumbersome based on the requirement to pre-prepare the seed particles. Greenwood et al. [16] investigated the effects of the large-to-small particle diameter ratio and the volume ratio on the viscosity of bimodal dispersions by producing monodisperse polystyrene or polymethyl methacrylate latexes containing varying particle sizes. The results showed that the lowest viscosities were obtained at a small particle volume fraction of 25% and a diameter ratio of 7.83. Leiza et al. [5,19] explored a two-step process to synthesize HSC latexes. In the first step, a polymer seed latex was introduced into a reactor and grown to a target particle size/solid content under starved conditions. Subsequently, a fraction of the same seed was added into the reactor and the blend was further polymerized until the desired PSD and solid content were achieved. An iterative strategy was applied to this process to obtain the optimal PSD, resulting in a bimodal latex with a maximum particle diameter below 350 nm and a solid content above 65 wt%.

The second approach is widely used in the preparation of bimodal or multimodal PSD latexes because it is highly efficient and relatively rapid. Typically, the generation of the second population of particles involves the *in situ* nucleation of smaller particles in the presence of larger particles. This can be accomplished by adding sufficient quantities of surfactant, monomer, seed, initiator and other components during the polymerization process [1,13,15,20,23,24]. Marinangelo et al. [23] were able to synthesize a bimodal poly(styrene-*co*-butyl acrylate) latex with a solid content of approximately 64 wt% and a reasonably low apparent viscosity using a semi-batch process in which the second population of (smaller) particles was generated via the instantaneous feeding of an additional charge of emulsifier. Although numerous studies have indicated that *in situ* nucleation is a very effective route to latexes with solid contents in the range of 65–70 wt% and relatively low viscosities, there are still some drawbacks associated with this approach. These include the requirement for a multi-step process, possible instability of the reaction system caused by the nucleation of new particles, and the sensitivity of the PSD to the amount and introduction point of the surfactant and the reaction conditions [13,15,25–27]. As an example, Boutti et al. [15,26,27] synthesized a bimodal HSC latex using a process consisting of four stages: creation of the first population batch polymerization initiated by H_2O_2/ascorbic acid (AsAc), growth of the first population to the target solid content of 60 wt% (semi-batch polymerization initiated by H_2O_2/AsAc), creation of the second population (semi-batch polymerization initiated by ammonium persulfate (APS)) and parallel growth of both populations to the desired solid content (semi-batch polymerization initiated by APS). This process resulted in a latex with a solid content of 74 wt% and a viscosity of approximately 1581 mPa s at a shear rate of $20\ s^{-1}$. Although latexes with satisfactory solid contents and relative low viscosities can be obtained by this strategy, the complex process involved and the varying additions of nonionic surfactants over time limit its industrialization.

Vinyl acetate-*co*-ethylene- (VAE) latex, a waterborne dispersion, is widely used in industrial adhesives and coatings, as well as in paints, wood processing, textiles, paper, packaging, civil engineering and other fields [28–30]. In the present work, a novel strategy based on the limited auto-aggregation of particles was applied to synthesize a bimodal PSD VAE latex having a HSC while exhibiting a low viscosity, using a one-step semi-batch reaction. The formation of the bimodal PSD and the effects of reaction temperature, initiator concentration, surfactant concentration, sodium dodecylsulfate (SDS)/nonionic surfactant ratio and reaction time on the PSD and the solid content of the final latex were investigated. We anticipate that the results presented herein will assist in the future investigation of low viscosity HSC latexes.

2. Experimental section

2.1. Materials

In this study, polyoxyethylene (20) sorbitan monolaurate (Tween 20, chemically pure), polyoxyethylene sorbitan monopalmitate (Tween 40, chemically pure), octylphenol ethoxylate (Triton X-100, chemically pure), sodium erythorbate (SoE, 98.0%), *tert*-butyl hydroperoxide (TBHP, analytical reagent), sodium dodecyl sulfate (SDS, analytical reagent), polyethylene glycol 400 (PEG-400, chemically pure), ferrous sulfate ($FeSO_4$, > 99.95%) and hydroquinone (analytical reagent) were purchased from Aladdin Reagent (Shanghai, China), Polyoxyethylated phenol (OP-10, chemically pure) was purchased from Macklin Biochemical Company (Shanghai, China). Ethylene (99.95%), vinyl acetate (VAc, chemically pure) and polyvinyl alcohol (PVA-0488, chemically pure) were purchased from the Guangxi Vinylon Co., Ltd. (China).

The VAc was distilled under vacuum at 40 °C before use to remove the polymerization inhibitor. All other chemicals were used as-received unless otherwise noted. Double-deionized (DDI) water was used throughout the work.

2.2. Apparatus

The latexes were synthesized in a 2 L high pressure stainless steel autoclave (maximum working pressure and temperature: 30.0 MPa and 300 °C) equipped with a stainless-steel anchor impeller, a gas inlet, a sample holder, a cooling coil, a heating jacket, a programmable logic controller and a feed inlet tube. The reactor temperature was regulated by a flow of a cooled ethanol/water mixture from a thermostatic bath through the cooling coil or by heating with the electric heating jacket. A constant flow pump was used to feed an aqueous solution of the oxidant into the reactor. Nitrogen and ethylene were supplied from a compressed nitrogen cylinder and an ethylene cylinder. The experimental apparatus is shown in Fig. 1.

2.3. Latex synthesis

The water-soluble redox initiator system TBHP/Fe^{2+}/SoE (in which the TBHP, Fe^{2+} and SoE function as oxidant, redox reaction catalyst and reductant, respectively) was investigated in our previous work [31] and was employed in this study. Scheme 1 shows the reaction for the synthesis of the VAE copolymer. All experimental trials were carried out using a semi-batch emulsion polymerization process. In this process, all the chemicals except the oxidant solution were batch charged into the polymerization reactor prior to the reaction. Table 1 provides the reagent amounts and the reaction conditions employed in the polymerization runs. The Tween 20, Tween 40, SDS, SoE, ferrous sulfate aqueous solution (0.03 mmol/L based on total VAc), VAc (600 g), protective colloidal aqueous solution (obtained by dissolving 10 wt% PVA-0488 and 10 wt% PEG-400 in DDI water at 80 °C, 150 g) and DDI water (85 g) were introduced into the reactor. This initial reactant mixture was purged once with nitrogen (1.0 MPa) and twice with ethylene (1.0 MPa) to remove dissolved oxygen. The reactor was subsequently pressurized to 3.0 MPa with ethylene and the blender started at 500 rpm while slowly heating the reactant mixture to 50 °C. These conditions were maintained for 30 min to pre-emulsify the VAc monomer and aqueous phase. Following this, the emulsified mixture was heated to the desired reaction temperature and an aqueous TBHP solution was added at a constant rate throughout the reaction time span. During the reaction, the chamber pressure was maintained at 3.0 MPa. The mixture was held at the reaction temperature for 20 min after the reaction and was then cooled to below 40 °C followed by release of the residual ethylene.