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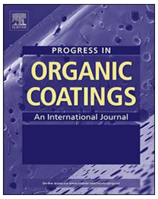

Preparation of high solids content waterborne acrylic coatings using polymerizable surfactants to improve water sensitivity

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ABSTRACT

High solids content (60 wt%) poly(methyl methacrylate-co-butyl acrylate-co-methacrylic acid) latexes with particle sizes below 350 nm are successfully synthesized by seeded semi-batch emulsion polymerization using polymerizable surfactant Latemul®PD-104, polymerizable stabilizer Sipomer®Cops-1, and conventional emulsifier Dowfax 2A1. The water uptake of the films containing polymerizable surfactant/stabilizer is compared to that of the films containing the conventional surfactant. For films containing the same weight percent of surfactant, the ones containing Dowfax®2A1 absorb more water due to surfactant aggregation within particle interstices. When polymerizable surfactant Latemul®PD-104 and polymerizable stabilizer Sipomer®Cops-1 are used hydrophilic pockets are not formed and the water absorption is reduced.

1. Introduction

High solids content latexes are of growing interest since increasing the polymer content of a latex maximizes the reactor production, minimizes transportation and storage cost, gives more flexibility in product formulation, improves surface coverage when applied and reduces drying time, which can increase the marginal value of the product [1,2]. Therefore, most industrial processes involve high solids content (> 50 wt% solids) emulsion polymerizations.

From the application point of view (film formation and film properties), high solids content latexes with small particle sizes are preferred because they provide skin-free latexes whose particles deformed easier leading to a more homogeneous film [3–5]. However, the production of high solids content latexes with small particle size typically requires the use of large quantities of surfactant which is not desired for the final product application. The presence of free surfactant molecules within the final film can have a detrimental effect on the final product properties, such as in adhesion strength [6], shear strength [7], peel strength [8–10], water resistance [9,11–17] and, gloss and film appearance [18,19].

The water sensitivity is affected by the distribution of hydrophilic species, such as surfactants, in the final film. During film formation, surfactants that are physically adsorbed to the polymer particles can migrate toward the film-air or the film-substrate interface [3,16,17,20–25]. Surfactants that are strongly adsorbed during film formation process can also be trapped at particle/particle boundaries creating hydrophilic pathways in the film [5,26] and in some cases, the surfactant is pushed away from the particle/particle boundaries creating small pockets or aggregates throughout the film [17,25,27,28]. If the surfactant (or low molecular weight hydrophilic species such as salts) migrates to the air-film interface, the film becomes more hydrophilic resulting in lower contact angles measured at the film surface. Whereas the contact angle value is only affected by the hydrophilicity of the air-film interface, the water uptake of the films results from the interplay between the existence of hydrophilic pockets or aggregates inside the film, the capacity of those pockets for water absorption and their accessibility [16,29]. Note that as reported in [29] all polymer systems (including solvent borne films) water whiten, given the right conditions of time and temperature.When the film is in contact with water, hydrophilic pockets inside the film provide a strong osmotic driving force for the diffusion of water through the film leading to a prolonged water absorption [14].

The use of polymerizable surfactants in emulsion polymerization has been considered to be a promising way to reduce the negative effects caused by conventional surfactants. During the last years many works have been published dealing with the synthesis of high solids content latexes using polymerizable surfactants [10,17,30–40]. However, to the best of our knowledge, the synthesis of latexes with solids content of 60 wt% using polymerizable surfactants was only reported by Tang et el. [32] and Guo et al. [33]. In both works, 3-allyloxy-2-hydroxyl-propanesulfonic salt (AHPS) was used as a polymerizable stabilizer.

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Tang et al. [32] presented the synthesis of methyl methacrylate/butyl acrylate copolymers by semicontinuous emulsion polymerization varying the monomer ratio but keeping constant the amount of stabilizer used (1.2% weight based on monomer, wbm%). The particle sizes of the latexes synthesized using AHPS were 450–500 nm, which were larger than the latexes synthesized using the conventional surfactant sodium dodecyl sulfate (SDS). This was attributed to the different particle nucleation mechanism; whereas micellar nucleation occurred using SDS, homogeneous nucleation was predominant when AHPS was used. When the reactions were carried out varying the amount of AHPS from 1.2 to 4 wbm% (keeping the monomer ratio constant) they observed that increasing the amount of the polymerizable stabilizer the final particle size of the latex decreased from 460 to 340 nm. Latexes synthesized using AHPS presented improved tensile strength and water resistance in comparison to the latexes synthesized using the conventional surfactant SDS.

In the work carried out by Guo et al. [33], different poly(methyl methacrylate-co-butyl acrylate) and poly(butyl acrylate-co-methyl methacrylate-co-styrene) 60 wt% solids content latexes were synthesized by semicontinuous emulsion polymerization using 1.2 wbm% of AHPS. Although latexes with small particle sizes (220–260 nm) were obtained using 1.2 wbm% of AHPS, they did not present any improvement on product properties.

In the present work, the feasibility of using polymerizable surfactant/stabilizer to produce stable 60 wt% solids content acrylic latexes with small particle sizes (< 350 nm) is studied and compared with the use of a conventional anionic surfactant. The water sensitivity of the films formed from high solids content acrylic latexes stabilized either by polymerizable surfactant/stabilizer or by conventional surfactant is also discussed. The effect of the surfactant type (polymerizable or not) on the water uptake of the final films is also shown.

Table 1
Formulation used to synthesize the seed latex.

Compound	Initial charge (g)	Stream (g)
MMA	—	44.55
BA	—	44.55
MAA	—	0.9
Water[a]	507.61	—
KPS	0.45	—
$NaHCO_3$	0.14	—
Ammonia[b]	0.9	—
Dowfax®2A1[c]	0.9	—

[a] Added water + water coming from surfactant solution.
[b] 25% aqueous solution.
[c] Active matter.

Table 2
Formulation used to synthesize 60 wt% solids content acrylic latexes.

Compound	Initial charge (g)	Stream (g *or* mmol)
Seed latex	19.83	—
MMA	1	175.74g
BA	1	175.74g
MAA	—	3.57g
Water	135.50	78.68–85.64 g[a]
KPS	1.79	—
Surfactant[b]	—	4.95–12.39 mmol

[a] The amount of water used was slightly varied in order to adjust the formulation to 60 wt% of solids content. The amount of water corresponds to the total amount of water added (added water + water coming from surfactant solutions).
[b] Active matter.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, Quimidroga) and *n*-butyl acrylate (BA, Quimidroga) were used as supplied. Methacrylic acid (MAA, Quimidroga) was used as functional monomer. Potassium persulfate (KPS, Fluka) was used as thermal initiator. Dowfax®2A1 (45% aqueous solution of alkyldipheniloxide disulfonate, Trademark of The Dow Chemical Company) was used as conventional surfactant. Latemul®PD-104 (20% aqueous solution of ammonium polyoxyalkylene alkenyl ether sulfate, Trademark of Kao Corporation) was used as an anionic polymerizable surfactant and Sipomer®Cops-1 (40% aqueous solution of sodium 1-allyloxy-2-hydroylpropyl sulfonate, Trademark of Solvay) was used as anionic polymerizable stabilizer. The main characteristics (structure and molecular weight) of the surfactants/stabilizer used throughout this work can be found elsewhere [10,17]. Deionized water was used in all reactions. To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used.

2.2. Emulsion polymerization

60 wt% solids content acrylic (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes with a target particle size of 320 nm were synthesized by seeded semi-batch emulsion polymerization using different surfactants/stabilizer. Polymerizations were carried out in a 1L jacketed reactor fitted with a reflux condenser, a sampling device, a nitrogen inlet, feeding inlet, a Pt-100 probe and a stainless steel anchor type stirrer. Reaction temperature and inlet flow rate of the feed were controlled by an automatic control system, Camile TG (CRW Automation Solutions). The formulation used to prepare the seed is given in Table 1 and that of the seeded semi-batch reactions in Table 2.

The seed was prepared by semi-continuous emulsion polymerization at 75 °C and 220 rpm. An initial charge of water, surfactant, buffer ($NaHCO_3$) and ammonia were added to the reactor. The initial charge was purged with nitrogen during 30 min. After reaching 75 °C a shot of thermal initiator (KPS) was added and then, the monomers were fed during 3 h. After that, the latex was let to react batchwise during 1 h. A seed latex with 14.8 wt% solids content and 75 nm of particle diameter (measured by Dynamic Light Scattering) was obtained. It is worth noting that in the seeded semi-batch reactions the particle size of the seed decreased to 64 nm upon addition of the KPS to the reactor due to the increase of the ionic strength of the aqueous and the shrinking of the electrical double layer.

Seeded semi-batch emulsion polymerizations were carried out at 75 °C and 220 rpm. An initial charge containing the seed latex, water and a small amount of monomers were added to the reactor. The initial charge was purged with nitrogen during 30 min. After reaching the desired temperature (75 °C) a shot of thermal initiator (KPS) was added. Then the preemulsion containing the monomers, the surfactant and water was fed during 4 h and after that, the latex was polymerized batchwise during 1 h. The process variables studied were the surfactant type and amount.

Throughout this work, latexes made with conventional surfactant Dowfax®2A1 are designated as D60. Those made with polymerizable surfactant Latemul®PD-104 as L60 and latexes synthesized using the polymerizable stabilizer Sipomer®Cops-1 as C60. For each surfactant type different reactions were carried out varying the surfactant amount, which are designated with a different number (1–4). Reactions with the same number were synthesized using the same number of moles of surfactant (Table 3).

2.3. Characterization

The final solids content (SC) (surfactants/stabilizer were considered as solids) and monomer conversion were measured gravimetrically. The amount of coagulum was measured by filtering the final latex through an 85 μm nylon mesh followed by gravimetry.