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Waterborne paints containing nano-sized crystalline domains formed by comb-like polymers

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ABSTRACT

Semicrystalline, waterborne copolymer latexes of stearyl acrylate-co-short chain (meth)acrylate (a mixture of methyl metacrylate, *n*-butyl acrylate, acrylic acid and acrylamide) have been synthesized by using different 2-step polymerization strategies. The effect of monomer composition and polymerization strategies on the crystallinity and mechanical properties of polymer films were investigated. These semi-crystalline latexes were successfully used as binders in paint formulations and the effect of crystallinity and copolymer microstructure on the mechanical properties (e.g. hardness, scrub resistance, etc.) and hydrophobicity of the paint films was studied.

1. Introduction

Solvent-borne paints contain high levels of volatile organic compounds (VOCs) and have been traditionally used on wood and metal surfaces, providing a high gloss finish, but long drying times and strong odor [1]. In contrast, waterborne paints have faster drying times and lower level of VOCs. Because of government regulations the paint industry is dramatically reducing the environmental impact of paints by switching from solvent-borne to waterborne paints [2–4].

Waterborne paints are complex formulations that include polymer latexes as binders to hold the film together and supply coating integrity, pigments that provide the paint with color and hiding power, thickeners that modify rheology to achieve a good pseudoplastic behavior, wetting agents and dispersants. Wetting agents are amphiphilic compounds that reduce the surface tension of the coating facilitating substrate wetting and aiding pigment particles to be wetted by the binder. Dispersants prevent flocculation of the pigment particles [1]. The binder accounts for at least half of the formulation weight and the properties of the coating film are to a large extend, governed by the binder. Therefore, the choice of the binder is of paramount importance.

Conventional (meth)acrylic latexes are widely used for the formulation of protective coatings in automotive, appliance, and coil coating applications. The key properties of acrylic coatings are good exterior durability; film clarity; UV-, heat- and alkalinity stability; good dirt pickup/crack resistance balance [1,5–7]; and good adhesion and film forming properties [8,9]. Generally, these polymers are amorphous. However, there are indications that the presence of crystalline domains may be beneficial for coatings. Thus, it has been demonstrated that crystalline domains produced in situ within waterborne polymer particles by miniemulsion polymerization of a long chain acrylate [10] improved the mechanical properties of the films cast from these latexes [11]. In addition, these crystalline domains enhanced the barrier properties and water resistance of the films [11]. As these are critical characteristics in coatings, in particular for exterior use, it is interesting to know if the presence of crystalline domains in the latex may improve the performance of formulated coatings. Therefore, in this work, waterborne (meth)acrylic dispersions containing crystalline nano domains were synthesized and used for the first time in paint formulations. It was observed that the presence of crystalline domains reinforced the mechanical properties of both binder latexes and formulated paints and improved the water resistance of paint films. However, the presence of crystalline domains surprisingly decreased the scrub resistance of paint films.

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Table 1
Summary of the synthesized copolymer latexes with different monomer composition and polymerization strategies.

	Series A	Series B	Series C	Series D	Blend[a]	SA/SC(M)A[b] (wt/wt)
Miniemulsion polymerization	1A	–	–	–	–	100/0
	–	–	4C	4D	Blend 4	40/60
	–	–	–	3D	–	30/70
	–	–	2C	2D	Blend 2	20/80
	–	–	–	1D	–	10/90
Emulsion polymerization	Semibatch seeded	1B	–	–	–	0/100

[a] Blending Latex 1A and Latex 1B.
[b] SC(M)A: MMA/BA/AA/AM = 49/49/1/1 wt%.

2. Experimental

2.1. Materials

Technical grade monomers, methyl methacrylate (MMA, BASF), *n*-butyl acrylate (BA, BASF), acrylamide (AM, BASF), acrylic acid (AA, BASF), and stearyl acrylate (SA, Aldrich) were used without purification. Potassium persulfate (KPS, Fluka) as water soluble radical initiator, sodium bicarbonate ($NaHCO_3$, BASF) (to control the miniemulsion viscosity by reducing the electrostatic interactions among droplets) and Disponil® FES 32 (fatty alcohol ether sulfate + 4 ethylene oxide, sodium salt) (BASF) as anionic surfactant were used as received. Deionized water was used as polymerization media.

2.2. Synthesis of latexes

Table 1 summarizes the latexes synthesized. The comonomer composition was varied from SA/SC(M)A = 0/100 to SA/SC(M)A = 40/60 wt/wt, where SC(M)A was MMA/BA/AA/AM = 49/49/1/1 wt%. The SA amount in copolymers was limited in order to be able to form films at room temperature. Different strategies were used for the preparation of SA/SC(M)A copolymer latexes. SA is a water insoluble monomer, and therefore miniemulsion polymerization that does not require monomer transport through the aqueous phase [12,13] was used. Series A is a homopolymer synthesized by miniemulsion polymerization at 70 °C using KPS (0.5 wt% based on SA) as initiator. In Series C, the latexes were prepared by first homopolymerizing in miniemulsion a part of SA (60% conversion) at 70 °C, after which the pre-emulsion of SC(M)A monomers (SC(M)A monomers + water + surfactant) and initiator solution (KPS + water) were separately fed to the reactor during 3.5 h under starved conditions and temperature was increased to 85 °C. In this series, an amorphous copolymer of SA/SC(M)A was expected to be formed in the second stage of the process. In Series D, SA was completely polymerized in miniemulsion (100% conversion) using the same conditions as Series A, and then the reactor was heated to 85 °C and the pre-emulsion of SC(M)A monomers and initiator solution were fed to the reactor during 3.5 h in separated streams. The reference latex, Run 1B, that was devoid of SA, was synthesized by seeded semibatch emulsion polymerization. The reactor was charged with a polystyrene seeds (particle diameter = 31 nm, 0.1 wt% based on monomer) and 20 wt% of water in the formulation, purged with nitrogen and heated to the reaction temperature (85 °C). Then, the SC(M)A pre-emulsion (mixture of water, SC(M)A monomers and Disponil FES 32) and the initiator solution (0.5 wt% based on SC(M)A monomers) were fed to the reactor during 2.5 h in separated streams. Then copolymerization was continued for 1 h.

Blending was used to prepare semicrystalline latexes as well. For this the amorphous SC(M)A copolymer latex (Run 1B) was mixed with poly(SA) latex (Run 1A) to obtain semicrystalline latexes with different copolymer composition and crystallinity (Blends 2 and 4, Table 1).

For the preparation of SA miniemulsion, the SA pre-emulsions (the mixture of SA, $NaHCO_3$ (0.16 wt% based on SA), Disponil FES 32 (2 wt% based on SA) and water) were prepared as described elsewhere [10]. These coarse emulsions were sonicated by using a Sonopuls HD 2070/2200 Sonifier (amplitude 100% and 100% duty cycle) over 20 min under magnetic stirring and in an ice bath to avoid overheating. Then, the miniemulsion was fed into an APV 2000 laboratory homogenizer, whose first valve was set to 6×10^7 Pa and whose second valve was set to 6×10^6 Pa. Two cycles were used to obtain stable and homogeneous SA miniemulsion. The organic content of SA miniemulsions was 35%.

The miniemulsion and emulsion polymerizations were carried out in a 1 L glass reactor vessel immersed in an oil bath and equipped with an anchor impeller, platinum resistance thermometer, condenser, two dosing systems, nitrogen inlet and sampling tube.

The final concentration of Disponil FES 32 emulsifier in copolymer latexes was 1.5 wt% based on monomers and the final solids content in all copolymer latexes was 45 wt%.

2.3. Preparation of waterborne paints

The latexes of Series B, C and D and also two blends of latexes 1A and 1B (Runs in Table 1) were used to prepare paints. The waterborne exterior paints were prepared according to the BASF guiding formulation RV436 in a two step process using the formulation in Table 2. First, the mill base was prepared using the formulation in Table 3 by mixing the dispersant (Dispex® AA 4140 NS, BASF), thickener (Natrosol® 250 HR, Ashland), defoamer (Foamaster® MO 2134, BASF), freeze–thaw stabilizer (propylene glycol, butyl diglycol, both from BASF), coalescent agent (Texanol™, Eastman) and water while stirring at about 400 rpm using a high speed disperser (DISPERMAT® LC30). The pigment (Kronos® 2190 (TiO_2), Kronos, Inc) and fillers (Omyacarb® 5 GU ($CaCO_3$), Omya; and Finntalc M15, Mondo Mineral, Inc) were then added slowly at 2000 rpm. Then, the mixing continued for 15 min. Finally, the polymer latex, the defoamer (Foamaster MO 2134, BASF) and the rheology modifier (Rheovis® PE 1330, BASF) were incorporated to the mill base and mixed at 1000 rpm for 10 min. The pH of copolymer latex was

Table 2
Waterborne paint formulation.

Ingredient	Name	Amount (g)	vol (%)
Mill base		159.25	43.91
Defoamer	Foamaster MO 2134	0.75	0.54
Rheology modifier	Rheovis PE 1330	1.00	0.62
Polymer latex		89.00	54.93
Pigment volume content (PVC) (%)		66.16	
Paint weight solids (wt%)		58.01	
Paint volume solids (vt%)		68.54	