



Performance of latexes containing nano-sized crystalline domains formed by comb-like polymers



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ABSTRACT

The effect of incorporating nano-sized crystalline domains formed by comb-like polymers in waterborne latexes on the mechanical and barrier properties as well as on the water sensitivity of the films cast from these latexes was investigated. Crystalline domains were formed by homopolymerization of stearyl acrylate, which also led to the formation of a very soft amorphous phase. (Co)polymerization of short chain (meth)acrylates formed the main film-forming phase. It was found that the application properties improved with respect to regular latexes devoid of crystalline domains. In addition, the properties of poly (stearyl acrylate) containing latexes were affected by the interplay between its very soft and crystalline domains. The behavior of this system is further complicated by the fact that the T_g of short chain (meth) acrylates that depended on the polymerization strategy, strongly affected the film properties.

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1. Introduction

Waterborne (meth)acrylic based latexes commonly obtained by (mini)emulsion polymerization are used in applications such as coatings, adhesives, and cement additives [1–6]. Most of these applications involve the formation of a film from the polymeric dispersion. Generally, these polymers are amorphous and they have inferior mechanical properties (toughness), water resistance, barrier properties and durability as compared with polyolefins.

Crystalline domains are known to impart improved mechanical and barrier properties of polymers [7–16], but the studies on the properties of the films cast from waterborne latex particles containing crystalline domains have been scarce [17–20]. Parker et al. [17] synthesized semicrystalline acrylic polymers by using synthetic wax monomers in aqueous suspension polymerization and aqueous dispersion polymerization. They showed that polymers with crystalline domains had potential applications as adhesives, wood coatings and textile coatings; however, no detailed study on the performance of these polymers was reported. Pepe et al. [18] synthesized semicrystalline waterborne wood coatings by copolymerization of ethylene and vinyl acetate monomers. They observed that the incorporation of polyethylene segment crystalline domains

improved the barrier properties of waterborne wood coatings. Agirre et al. [19] observed temperature-responsive behavior by incorporation of crystalline domains in waterborne pressure sensitive adhesives. Moreover, the authors reported that with the right distribution and concentration of crystalline polymers a simultaneous increase in both shear resistance and peel strength was achieved. Jasinski et al. [20] synthesized poly(thioether ester) nanolatex containing crystalline domains. The authors reported that the crystalline domains were efficient barrier to water penetration and improved the poly-(thioether ester) latex hydrolytic stability.

The presence of crystalline domains in the amorphous (meth) acrylic copolymer latexes may be beneficial as they may improve the mechanical properties of these soft polymers. Moreover, these crystalline domains may enhance the barrier properties and water resistance of the films, which are critical characteristics in some applications such as paints, in particular for exterior uses, and other protective coatings. We have recently reported the synthesis of waterborne (meth)acrylic dispersions containing crystalline domains for coating applications [21]. The crystalline domains were produced in situ within waterborne particles by miniemulsion polymerization [22] of a long chain acrylate. In this work, for the first time, the effect of crystalline and hydrophobic domains on the properties of polymer latexes for coating applications has been investigated. It is shown that as compared with the latexes devoid of crystalline domains that currently dominate the market, these

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latexes showed better mechanical and barrier properties as well as higher hydrophobicity and improved water resistance. These properties are controlled by the interplay between the amorphous and crystalline parts of the material, which in turn depend on the polymerization strategy.

2. Experimental section

2.1. Latex synthesis

Table 1 summarized the latexes prepared for this study. The materials used in the synthesis of the latexes as well as the characterization techniques employed are given in the supporting information. The latexes were synthesized following the 2-stage miniemulsion polymerization strategies described in reference 21.

Series A is the batch miniemulsion homopolymerization of stearyl acrylate (SA). In Series B and C, a miniemulsion of SA was polymerized as batch in a calorimeter reactor (RTCal™, Mettler-Toledo) and when the conversion of SA reached 60%, a mixture of short chain (meth)acrylate (SC(M)A) (methyl methacrylate, MMA; butyl acrylate, BA; and acrylic acid, AA; MMA/BA/AA = 49/49/2 wt %) was fed either as a shot (Series B) or continuously for 3h (Series C). In Series D, the initial miniemulsion of SA was polymerized in batch until reaching full conversion and then, the mixture of SC(M)A monomers was fed continuously during 3h. All polymerizations were carried out at 70 °C using 0.5 wt% of potassium persulfate and 1 wt% of sodium dodecyl sulfate, both based on monomers. In addition, batch and semibatch emulsion copolymerizations of the SC(M)A monomers were carried out in order to have latexes devoid of crystalline domains that served as reference. The latex obtained in batch emulsion polymerization can be compared with Series B and those obtained in Series C with the latex produced by semibatch emulsion polymerization.

2.2. Characterization

The morphology of polymer films and the particle coalescence were studied by means of scanning electron microscopes (SEM, Hitachi S 4800) at air-film and substrate-film interfaces as well as at

the surfaces of fractured films cast at 23 and 60 °C. The fractured surfaces were prepared by cryogenic fracturing at –40 °C. Images were obtained at 15 kV from gold coated samples.

Mechanical properties of the films were determined by tensile tests according to the ASTM D882 standard test. The films with the thickness of 700 μm were dried in Teflon molds at 60 °C for one week to obtain films without defects (some latexes did not form good films at 23 °C) and the measurements were carried out in a Stable Micro System TA HD Plus Texture Analyzer by using a 5 kN load cell under controlled conditions (23 °C and 55% of humidity). The test speed was 0.42 mm s⁻¹. The results reported were the average of 5–10 repeated measurements and the reproducibility was good.

To study the water sensitivity of the films, the liquid water uptake and static contact angle to water were measured. 700–800 μm thick films were cast from the latexes in Teflon molds under both controlled environment (23 °C and 55% humidity) and at 60 °C for one week.

For water uptake, the films were weighed (m_0) and immersed in distilled water at room temperature (23–25 °C). Then, they were removed at given times, dried with paper, weighed (m_t) and placed again in distilled water. The water uptake was calculated as:

$$\text{Water uptake(\%)} = \frac{m_t - m_0}{m_0} \times 100 \quad (1)$$

The reported data for each film is the average of 3 samples and the reproducibility of the measurements was good.

Static contact angle (CA) measurements of films were performed by the sessile drop method with distilled water, using a goniometer OCA 20 with a high-performance image processing system (Data Physics Instruments GmbH), in air under controlled environment (23 °C and 55% humidity). The data presented are the average of 20–30 readings. In order to remove the surfactant, the films were immersed in distilled water for one night and then dried for one week at ambient temperature.

Water vapor transmission experiments were carried out using a gravimetric cell. The films were cast from the latexes in Teflon molds and dried under both controlled environment (23 °C and 55% humidity) and at 60 °C for one week. The thickness of the films was

Table 1
Crystallinity, glass transition temperature and particle sizes of the latexes.

Run ^a	SA/SC(M)A ^b (wt/wt)	Xc ^c (%)	T _g ^d (°C)	d _p (nm)	Secondary nucleation
1A	100/0	41.5	17	197	–
Batch miniemulsion of SA (60% conversion) + Shot of SC(M)A monomers					
4B	40/60	11.80	20.5	169	No
5B	30/70	5.74	19.6	141	Yes
6B	20/80	4.17	27.5	133	Yes
7B	10/90	1.70	31.0	126	Yes
Batch miniemulsion of SA (60% conversion) + 3 h addition of SC(M)A monomers					
4C	40/60	12.95	12.7	167	No
5C	30/70	7.66	13.7	155	Yes
6C	20/80	4.61	13.0	145	Yes
7C	10/90	2.34	13.0	120	Yes
Batch miniemulsion of SA (100% conversion) + 3 h addition of SC(M)A monomers					
4D	40/60	16.40	14.0	161	Yes
5D	30/70	12.30	14.0	150	Yes
6D	20/80	8.22	15.3	142	Yes
Emulsion copolymerization					
Batch (1E)	0/100	–	36.0	81	–
Semibatch (2E)	0/100	–	17.8	67	–

^a In all cases full monomer conversion was achieved at the end of the process [21].

^b SC(M)A monomers: MMA/BA/AA = 49/49/2 wt%.

^c Referred to the whole polymer.

^d For Run 1A, the onset temperature was taken as T_g, whereas for the rest, the inflection point temperature was considered.

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