



## Waterborne acrylic–casein latexes as eco-friendly binders for coatings



Matías L. Picchio<sup>a,b</sup>, Mario C.G. Passeggi Jr.<sup>c</sup>, María J. Barandiaran<sup>d</sup>, Luis M. Gugliotta<sup>a</sup>,  
Roque J. Minari<sup>a,\*</sup>

<sup>a</sup> Group of Polymers and Polymerization Reactors, INTEC (Universidad Nacional del Litoral-CONICET), Güemes 3450, Santa Fe 3000, Argentina

<sup>b</sup> Facultad Regional Villa María (Universidad Tecnológica Nacional), Av. Universidad 450, Villa María 5900, Argentina

<sup>c</sup> Physics of Surfaces and Interfaces Laboratory, IFIS Litoral (Universidad Nacional del Litoral-CONICET), Güemes 3450, Santa Fe 3000, Argentina

<sup>d</sup> POLYMAT and Departamento de Química Aplicada, University of the Basque Country UPV/EHU, Centro Joxe Mari Korta, Avenida Tolosa 72, 20018, Donostia-San Sebastián, Spain

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### ABSTRACT

The use of casein as renewable resource to produce eco-friendly hybrid latexes has an increasing importance in industrial applications especially for high performance waterborne coatings. This work describes the synthesis of hybrid acrylic–casein latexes by emulsion polymerization of acrylic monomers in presence of varied casein concentration, and in absence of emulsifier which is usually a challenge for preparing stable nanocomposite latexes. The production and microstructure characterization of the casein–acrylic nanoparticles, as well as the properties of the films obtained from the hybrid latexes are here reported. The synthesized acrylic–casein latexes are able to form films with promising properties for a potential application as waterborne bio-based coatings.

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### 1. Introduction

In recent years, considerable efforts have been made by the polymer industry to develop environmentally benign processes that avoid the emission of volatile organic compounds (VOC) and to substitute petroleum based monomers by renewable raw materials. In the coatings field, waterborne dispersed polymers used as binders, appear as an environmentally friendly alternative to solvent-based coatings [1]. Also, proteins have a large potential for the substitution of currently used petrochemicals, since monomers and polymers can be derived from these resources [2]. Indeed, casein derived from bovine milk, is a very practicable biomaterial with good biocompatibility and biodegradability, easily available at high purity and low cost [3]. Casein had long been used in film formation applications, as principal binder in leather finishing, paper coating and adhesive, due to its good stained acceptance, finishing glazed aspect, good substrate penetrability and strong adhesive force [4,5]. However, the casein films are highly susceptible to microbial attack, to wet rub and present low flexibility and extensibility [6].

One of the biggest challenges for binders employed in waterborne coatings is to simultaneously attain two contradictory

requirements: (a) a low minimum film formation temperature (MFFT < 15 °C), to ensure a smooth film formation under applications at room temperature; and (b) acceptable blocking resistance and film hardness, which is usually accomplished by polymers with a  $T_g$  above the room temperature. Traditionally, coalescing agents are used to plasticize the binder during film formation, decreasing its  $T_g$  and allowing the formation of a smooth film at room temperature. Once the film is formed, the coalescent evaporates and the film may recover its hardness and blocking characteristics. However, in addition to the environmental problem of releasing VOCs to atmosphere, the marketplace is also demanding coatings with less odor, and the coalescing solvents in a latex paint are clearly one source of odor. Other alternative to solve this issue is to introduce a harder phase to a soft binder that will bloom to the top of a film as it dries. Typically, solutions involve the use of blends of hard/soft latex particles [7–16] or surface-active agents as silicon-based materials, waxes and/or fluorinated additives. In this scenery, the use of a natural compound with a high  $T_g$  (~180 °C), as casein, in combination with a soft acrylic polymer appears as a promising system to produce waterborne nanostructured binders that simultaneously attain these antagonistic requirements.

Emulsion polymerization of acrylic monomers in the presence of casein has been previously studied in aqueous media using persulfate initiators and in absence of emulsifier [17–21], due to the marked amphiphilic character of casein that makes it an important surface-active agent [22]. In such works [17–21], the

\* Corresponding author. Tel.: +54 3424559174; fax: +54 3424511079.

E-mail address: [rjminari@santafe-conicet.gov.ar](mailto:rjminari@santafe-conicet.gov.ar) (R.J. Minari).

effect of concentrations of initiator, monomer and casein on the grafting extent, was studied. Also, casein-based latexes as film-forming materials were previously synthesized by utilizing persulfate initiators together with sodium hydrogensulfite as a redox pair [23,24]. However, casein is easily oxidized in the presence of these initiators, producing yellowish coatings which are undesirable from the esthetic point of view [3]. Recently, a crosslinkable acrylic resin/protein composite emulsion was obtained by mixing a latex containing ketone carbonyl groups with a certain amount of gelatin or casein, which act as a crosslinking agent [25]. Composite films with improved hardness, tensile strength, and water and solvent resistance were obtained.

Li et al. also reported the synthesis of casein–poly(methyl methacrylate) (PMMA) nanoparticles via emulsifier-free emulsion polymerization [26,27]. Grafting of casein with PMMA was conducted by initiating the polymerization according to a redox reaction between an alkyl hydroperoxide and the amino groups of the casein. Then, the propagation of amino casein radicals produces the protein graft polymerization and the formation of compatibilized nanoparticles. In a recent work [28], we quantified the grafting degree of casein along the MMA emulsion polymerization performed in the presence of varied casein concentration. We observed that as the concentration of casein increased from 3 parts per hundred monomer (pphm) to 25 pphm, the amount of incorporated casein increased, and the situation was opposite up to 50 pphm, the maximum range studied. As a result, two kinds of particles were obtained: the compatibilized ones mainly formed by PMMA-graft-casein and the other ones containing only PMMA homopolymer. However, due to the high  $T_g$  of both the bio- and synthetic components, this hybrid system is not valuable for coating formulations.

In this work, the performance of hybrid acrylic–casein latexes as potential binders for coatings was investigated. Firstly, the synthesis of waterborne nanoparticles with different monomer ratios, butyl acrylate (BA)/methyl methacrylate (MMA), and casein concentrations is presented. The redox initiation system proposed by Li et al. [26], which involves tert-butyl hydroperoxide (TBHP) and the casein amines, was here adopted. Next, film properties were analyzed, including film morphology, opacity, MFFT, hardness, blocking, and elongation. Finally, the film biodegradability in composting conditions was evaluated.

## 2. Materials and methods

### 2.1. Materials

Technical grade casein from bovine milk (Sigma), MMA and BA monomers containing traces of mono methyl ether hydroquinone as inhibitor (Aldrich) were used. The employed initiator was TBHP (Aldrich). Other used reagents were: sodium carbonate ( $\text{Na}_2\text{CO}_3$ , Cicarelli) as buffer to regulate the pH, methyl ethyl ketone (MEK, Anedra), benzene (Bz, AnalytiCals) and sodium dodecyl sulfate (SDS, Anedra). All the reagents were used as received without purification. Distilled and deionized water was used throughout the work.

### 2.2. Polymerization process

Polymerizations of BA/MMA in the presence of variable amount of casein were carried out in a 0.5 L glass jacketed reactor equipped with thermostatic bath, digital thermometer, condenser, stirrer,  $\text{N}_2$  inlet and sampling device. The BA/MMA ratio was varied from pure BA to 63/37 wt/wt as follows: 100/0, 80/20, 70/30, 65/35 and 63/37. The casein//BA/MMA ratio was adopted as to get a constant theoretical  $T_g$  in the range of ( $-10^\circ\text{C}$ ) for the resulting nanoparticles. In addition, a BA/MMA copolymer (60/40) without casein,

**Table 1**

General recipe for the synthesis of poly(BA-co-MMA)–casein hybrid latexes.

Reagent	Amounts (pphm) <sup>a</sup>
BA + MMA	100
Casein	3–50
TBHP	0.20
$\text{Na}_2\text{CO}_3$	2.5
$\text{H}_2\text{O}$	600

<sup>a</sup> pphm: parts per hundred monomer.

which has an estimated  $T_g$  of ( $-10^\circ\text{C}$ ) was also synthesized for comparison purposes. Polymerizations were carried out as follows. Casein was first dissolved in the reactor, in a water solution containing 2.5 pphm of  $\text{Na}_2\text{CO}_3$  (pH 11) and at  $50^\circ\text{C}$ . At pH higher than 10, maximum casein solubility is reached and a looser micelle structure is obtained due to a reduction in the association of molecules by hydrophobic interaction [29]. Then, the solution temperature was raised up to  $80^\circ\text{C}$  and monomers were loaded. The resulting dispersion was purged with  $\text{N}_2$  for 30 min before injecting the TBHP. Polymerizations were run for 300 min with continuous bubbling of  $\text{N}_2$  and samples were withdrawn along the process at regular time intervals. Table 1 presents a general recipe of the performed polymerizations.

### 2.3. Latex characterization

The overall monomer conversion ( $x$ ) was determined gravimetrically and it was defined as the weight ratio between the acrylic polymer and the total amount of acrylic monomers in the formulation (casein was not considered in the  $x$  calculation).

Average particle diameters ( $d_p$ ) were measured at  $30^\circ\text{C}$  by dynamic light scattering, using a Brookhaven BI-9000 AT photometer at a detection angle of  $90^\circ$ . Samples were prepared by diluting a fraction of the latex in deionized water, in order to obtain count rates between 100 and 300 kcounts per second. Particle size distribution (PSD) was determined by capillary hydrodynamic fractionation employing a CHDF2000 (Matec Applied Sciences) equipment. Samples were diluted in deionized water to 1.5% of solids content.

The fraction of casein grafted to the acrylic polymer (casein grafting efficiency, CGE) was determined by correlating the mass of grafted casein to the loaded protein. A procedure of multiple centrifugation and redispersion was applied to separate the ungrafted casein from the latex, obtaining the mass of grafted casein from the difference between the loaded and the non-linked casein [28].

### 2.4. Film characterization

The polymer films were prepared by casting the latexes onto silicone molds and then they were dried at  $22^\circ\text{C}$  and 55% relative humidity during 7 days to assure a constant weight of the film. The polymer films were carefully peeled from the silicone substrate, obtaining a film with a final thickness of about 1 mm.

The morphology and nanomechanical properties of the films were determined by using a commercial Nanotec Electronic Atomic Force Microscope (AFM) operating in tapping and jumping modes, respectively. All the AFM experiments were performed in air at room temperature. Acquisition and image processing were performed using the WSxM free software [30]. Rotated monolithic Budget Sensors All-In-One-Al cantilevers (Budget Sensors, Sofia, Bulgaria) made of silicon with a 30 nm thick aluminum reflex coating and a tip radius  $<10$  nm were used. While the nominal resonance frequency and spring constant of the cantilever used in tapping mode were 350 kHz and 40 N/m, in jumping mode were 80 kHz and 2.7 N/m. Cross-sectionals were obtained by (cryo)microtomy (Leica EM UC6). The root mean squared (RMS) of the roughness of each

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