



# Acrylic/casein latexes with controlled degree of grafting and improved coating performance



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## ABSTRACT

The production of acrylic/casein nanocomposites constitutes a promising alternative for developing new materials from renewable resources and with an important substitution of petroleum based monomers. Unfortunately, a low degree of grafting between both components limits their successful application in many fields. This proposal opens the opportunity for synthesizing polymer/casein nanocomposites with controlled degree of grafting by using, in the emulsifier-free emulsion polymerization of acrylic monomers, highly-methacrylated casein with varied degree of functionalization. The benefits of this strategy are assessed by analyzing the performance of the obtained hybrid nanocomposites for their application as bio-based waterborne coatings.

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## 1. Introduction

There is an urgent need to develop polymeric materials from renewable resources due to the fast depletion and dramatic price fluctuations of fossil oils, and the increasingly consumers preference toward bio-based products [1–3]. Among the different bio-based resources, natural proteins constitute a promising candidate as they contain amine and carboxyl functionalities that present unlimited opportunities to introduce modification in their structure [4]. Indeed, casein from bovine milk has been used for a long time as a film-forming material in many industrial applications [5,6]. However, the casein films present low resistance to water immersion, susceptibility to microbial attack, and poor mechanical properties [7]. For these reasons, the incorporation of synthetic polymers, such as acrylates, has gained technological interest because it attempts to modify and improve the properties of pure casein [8].

Emulsion polymerization of acrylic monomers in the presence of casein has been previously studied using thermal and redox initiators in absence of emulsifier [9–16]. However, in such works very few efforts have been made to characterize the molecular microstructure of the hybrid polymer. Li et al. [17,18] also reported the synthesis of poly(methyl methacrylate) (PMMA)/casein latexes via emulsifier-free emulsion polymerization. Grafting of casein with PMMA was conducted, by initiating the polymerization according to a redox reaction between an alkyl hydroperoxide and the amine groups of the casein. Then, the propagation of amine casein radicals initiated the graft polymerization and the formation of compatibilized nanoparticles. Following the Li et al. proposal, the grafting degree of casein along the MMA emulsion polymerization performed in the presence of varied protein concentration was quantified, observing that as the concentration of casein increased, the fraction of grafted protein decreased [19]. In other words, the use of high casein concentrations, which is highly desirable for a better exploitation of this renewable resource, limited the fraction of grafted acrylic/casein copolymer.

Recently, the film performance of acrylic/casein latexes in waterborne coatings was evaluated [20], finding that hybrid materials present promising properties. Unfortunately, films showed a poor resistance to water, as a consequence of the high amount

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of ungrafted casein in the hybrid latexes. The low degree of acrylic/casein grafting reached during the synthesis of these hybrid materials is the main drawback for their successful application.

A previously explored alternative to promote acrylic grafting onto casein chains is the protein chemical modification with acrylic acid (AA) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as activator [21]. The main disadvantages of this approach are: (i) the low casein acrylation, restricted by the AA concentration used during the protein modification, because the presence of AA could lead to protein coagulation (pH of casein isoelectric point = 4.0); and (ii) the high cost of EDC that limits the large-scale implementation. This approach improved the fraction of protein grafted, but the increment of compatibility degree, restricted by casein acrylation, was not enough to fulfill the requirements of an industrial film-forming application. Due to casein is a large protein, with an average molecular weight of 30000 g/mol, a superior number of grafting points are needed to obtain a material highly compatibilized.

This work proposes, as a strategy to overcome the previously found limitations in lowly compatibilized hybrid systems, the use of highly-methacrylated caseins (MC) together with the formation of free radicals onto protein chains by redox initiation in an emulsifier-free emulsion polymerization. The chemical modification of casein, based on an amine-glycidyl ether reaction, allows appropriately controlling the protein grafting of the hybrid nanoparticles by varying the protein methacrylation degree. The improved compatibility obtained by the proposed strategy was evaluated in a coating application by measuring sensitive properties of the hybrid films.

## 2. Experimental

### 2.1. Materials

Technical grade casein from bovine milk (Sigma), methyl methacrylate (MMA), butyl acrylate (BA) and glycidyl methacrylate (GMA) (Aldrich) were used as supplied. The employed initiator was *tert*-butyl hydroperoxide (TBHP, Aldrich). Other used reagents were: tetrahydrofuran (THF, Cicarelli), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, Cicarelli) as buffer to regulate the pH, absolute ethanol (Cicarelli), sodium borate (Anedra), 2-mercaptoethanol (Fluka), sodium dodecyl sulphate (SDS, Anedra), glycine amino-acid (Sigma) and methyl ethyl ketone (MEK, Anedra). O-phthalaldehyde (OPA, Sigma) was used as fluorescent amino marker. Uranyl acetate 1 wt% solution (UAc, EMS) and formvar® (polyvinyl formal, Fluka) were used for TEM sample preparation. All the reagents were used as received without any kind of purification. Distilled and deionized water was used throughout the work.

### 2.2. Synthesis of acrylic/casein hybrid latexes with high degree of compatibility

Hybrid latexes with high compatibility were produced by surfactant-free emulsion polymerization, using highly methacrylated casein together with BA/MMA as main monomers, and TBHP as initiator.

The methacrylated casein was synthesized by the amine-glycidyl ether reaction [22]. For this purpose, casein was first dissolved at 50 °C in a water solution containing 0.4% wt/wt of Na<sub>2</sub>CO<sub>3</sub> to regulate the pH. The reaction solution pH was higher than 10, where the association of casein macromolecules by hydrophobic interaction is reduced [23]. Then, GMA was loaded and the reaction was run for 4 h. Samples were taken at the beginning and at the end of reaction, and then analyzed by <sup>1</sup>H NMR.

**Table 1**  
Formulation for the synthesis of acrylic/casein latexes.

Reagent	Amounts [pphm*]
BA	80
MMA	20
Neat/Methacrylated Casein <sup>#</sup>	25
TBHP	0.2
Na <sub>2</sub> CO <sub>3</sub>	2.5
H <sub>2</sub> O	500

\*pphm: part per hundred monomer. <sup>#</sup> in all cases the neat amount of casein is 25 pphm, therefore for Methacrylated Casein additional amounts are considered as result of the GMA incorporation during the functionalization reaction.

The methacrylation reaction of casein proceeds by nucleophilic attack of their amine groups on the least substituted carbon of the oxirane group of GMA, producing the ring opening and the subsequent formation of an amine with a methacrylic group [24]. Thus, the synthesized MC presents a new methacrylic functionality, which together with the remainder amine groups, has the capacity to radically propagate during the polymerization.

Different molar ratios GMA/casein (2, 10, 20 and 40) were employed, assuming 30000 g/mol as the average molecular weight of casein, and taking into consideration that the amine groups per casein molecule available to react with oxiranes are 40 primary amines (on average) and a higher amount of secondary ones. Notice that methacrylation was carried out in aqueous media, which represents an important advantage due to the resulting MC solution can be directly used in the polymerization reaction.

After obtaining MC, the solution temperature was raised up to 80 °C and the (meth)acrylic monomers were loaded. The resulting dispersion was purged with N<sub>2</sub> for 30 min and then the TBHP was injected in order to redox initiate the polymerization with the available casein amine groups, producing amine and *tert*butoxy radicals. By propagation through the primary amine radical, casein grafted onto the polymer backbone is formed. On the other hand, *tert*butoxy radicals can propagate with the (meth)acrylic monomers producing (meth)acrylate polymer, as well as with the pendant methacrylic groups onto casein chain, forming grafted casein. Fig. 1 schematizes the employed strategy. The involved mechanisms in the production and growth of acrylic/casein hybrid nanoparticles are described in detail elsewhere [16].

Table 1 summarizes the formulation of the performed emulsion polymerizations of acrylic monomers in the presence of 25 pphm of casein (native and MC). This formulation was used aiming at obtaining a copolymer with a glass transition temperature (T<sub>g</sub>) suitable to be used as coating. In fact, BA/MMA (50/50) is usually used in conventional coating formulations. In this work, the hard MMA was partially substituted by the high T<sub>g</sub> bio-based modified casein. The whole process (MC synthesis and emulsion polymerization) was performed in a 0.5 L jacketed reactor equipped with thermostatic bath, thermometer, condenser, stirrer, N<sub>2</sub> inlet and sampling device. In the case of the latex synthesized with native casein, it was previously dissolved at 50 °C, before polymerization.

### 2.3. Characterization of the methacrylated casein and latexes

Casein methacrylation was evaluated by (i) <sup>1</sup>H NMR spectroscopy; and (ii) quantifying the effective percentage of GMA bounded to casein with the OPA method [25,26]. The <sup>1</sup>H NMR spectra were obtained with a Bruker Advance II 300 spectrometer, using the WATERGATE sequence to suppress the signal of water. The OPA method consists in the reaction of this reagent with primary amine groups of proteins to form highly fluorescent 1-alkylthio-2-alkyl substituted isoindoles, which show an absorption band at 340 nm [27]. The percentage of GMA bounded per casein molecule was determined on the basis of the consumption of casein amine

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