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**Journal of Coatings Technology and
Research**

ISSN 1547-0091

Volume 14

Number 3

J Coat Technol Res (2017) 14:543-553

DOI 10.1007/s11998-016-9877-2



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Enhancing the coating properties of acrylic/casein latexes with high protein content

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Abstract Casein-derived materials are highly attractive as a consequence of their environmental friendliness and excellent film-forming properties. Due to the casein hydrophilicity, films containing a large protein content are highly susceptible to water, thus limiting their use in coating applications. A novel approach for synthesizing waterborne acrylic–casein latexes with large content of protein and high degree of compatibilization between both components is presented. The employed synthesis strategy involves the use of a highly methacrylated casein in an emulsifier-free emulsion polymerization of acrylic monomers with the aim of controlling both the fraction of grafted biomaterial and the amount of acrylic chains linked onto the protein backbone. The performance of the resulting materials was evaluated in a water-based coating application. The used methacrylation approach allowed the maximum compatibilization of 33% of casein in the hybrid polymer. The as-obtained casein-derived films were proven to exhibit superior water resistance, which would open a new possibility for designing biobased coatings in several fields.

Keywords Acrylic/casein latexes, Methacrylated casein, High protein incorporation, Water-based binders

Introduction

Currently, there are great efforts to limit the use of fossil raw materials due to the emissions of carbon dioxide and the associated effects on the global climate. For these reasons, biobased feedstock have gained importance in the chemical industry.^{1,2} Among them, proteins have become highly attractive due to their good biocompatibility, high adsorption capacity, and excellent coating performance.³ In this regard, casein is one of the most abundant proteins in bovine milk that possesses various singular properties.^{4,5} Casein is a phosphoprotein consisting of α_{s1} -, α_{s2} -, β -, κ -, and γ -casein, where the 55% of their amino acids present polar groups, among carboxylic (25.8%), amine (15.1%), and hydroxyl (14.6%) groups. A detailed amino acid composition of bovine casein has been reported by Lauer and Baker (1977).⁶ Unfortunately, polar groups on casein chain can lead to materials with a weak water resistance and poor mechanical performance, thus limiting their application.⁷ Therefore, chemical modification of casein structure is required to improve its properties.

One of the most common approaches is to introduce new hydrophobic segments onto the casein molecule via graft polymerization of acrylic monomers.^{8–19} Indeed, polyacrylate modified casein latexes have been prepared via surfactant-free emulsion polymerization using thermal dissociative and redox initiators for their application in leather finish,^{14–17} self-cleaning,¹⁸ and opaque coatings.¹⁹ However, casein is easily oxidized in the presence of these kinds of initiators, producing undesirable yellowish materials. An efficient method to overcome the oxidative problems has been developed

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by Li et al.¹¹ which is based on the use of the redox pair tert-butyl hydroperoxide (TBHP)/casein amine groups. Moreover, in the above studies very few efforts have been made to investigate the correlations between acrylic/casein compatibility and coating performance.

In a previous work,²⁰ we investigated the grafting of methyl methacrylate (MMA) onto casein via emulsion polymerization performed in the presence of varied protein concentrations. We found that when using high casein contents (higher than 12% weight based on monomer, [wbm]) the fraction of grafted casein was limited. As a consequence, a large amount of ungrafted casein was present in the materials, which adversely affected their final properties (e.g., poor water resistance).²¹ The incorporation of large casein amounts in biobased materials is highly desirable for reducing the product's carbon footprint and a better exploitation of this renewable resource. Thus, the development of new strategies to improve acrylic–casein compatibility is of great importance in the field of materials science and technology. Under this scenario, the chemical modification of casein appears to be a promising route to increase the casein/acrylic compatibility and overcome the weak characteristics of high protein content materials.

An already explored alternative involves protein acrylation with acrylic acid (AA) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as activator.²² With this strategy, casein acrylation degree was restricted by protein coagulation due to the increasing presence of AA. Therefore, the synthesized acrylated casein exhibited a low degree of acrylation (maximum eight acrylic groups per casein molecule) and it was used for producing middle protein content latexes (maximum casein content = 25 wbm). Although this proposal showed an improvement in the fraction of grafted biomaterial, it was not enough to reach good water resistance, where hybrid films were disintegrated after 24 h of immersion in such medium and achieved a maximum swelling of 360%. Casein is a big hydrophilic protein, and a higher number of grafting points are needed to obtain a highly compatibilized material.

This work investigates the synthesis of acrylic–casein hybrid latexes with high protein concentration ([casein] = 50 wbm) and controlled casein/acrylic compatibility. The proposed strategy is based on the use of highly methacrylated casein in the emulsifier-free emulsion polymerization of acrylic monomers. The chemical modification of casein, through an aminoglycidyl ether reaction, allows synthesizing nanoparticles with an appropriate control of both the fraction of grafted protein and the amount of bounded chains onto the biomaterial backbone. The performance of the hybrid materials produced, with different degrees of compatibility, is evaluated in terms of their coating properties, with emphasis on water resistance and mechanical performance.

Experimental

Materials

Casein from bovine milk (Sigma, technical grade) consisting of α_{s1} -, α_{s2} -, β -, and κ -casein in the ratio of 4:1:4:1, 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: sodium carbonate (Na_2CO_3 , Cicarelli) as buffer to regulate the pH, tetrahydrofuran (THF, Cicarelli), absolute ethanol (Cicarelli), sodium borate (Anedra), 2-mercaptoethanol (Fluka), sodium dodecyl sulfate (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.

Synthesis of hybrid latexes with high protein content

The synthesis strategy for obtaining hybrid latexes with large protein content and highly compatibilized with the acrylic polymer involves the casein methacrylation together with the generation of free radicals onto the protein chain by the redox initiation with TBHP in an emulsifier-free emulsion polymerization. Figure 1 schematizes the synthesis of methacrylated casein, which is carried out before the emulsion polymerization.

Methacrylated casein was obtained by an aminoglycidyl ether reaction, where the amine groups of casein nucleophilic attack 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.²³ Thus, the modified casein presents new methacrylic functionalities able to radically propagate during the polymerization and incorporate an acrylic chain onto the protein backbone. Note that during the methacrylation, secondary hydroxyl groups are also formed, which might contribute to the hydrophilicity of the final hybrid materials. However, the incorporation of long hydrophobic polymer chains onto protein molecule more than compensates the influence of such hydrophilic groups on the properties of the produced latexes.

Casein methacrylation reaction was carried out in an aqueous solution of Na_2CO_3 (pH > 10) at 50°C for 4 h. Caseins with different degrees of methacrylation (DM) were synthesized by using varied GMA/casein molar ratios (2, 10, 20, and 30), assuming 30,000 g/mol as the average molar mass of the protein.

After the methacrylation step, polymerization was carried out following the procedure with neat casein detailed elsewhere.²¹ In a short time, the methacrylated protein solution temperature was raised to 80°C and the acrylic monomers were loaded. After that, the resulting dispersion was purged with N₂ for 30 min before injecting the TBHP to redox initiate the polymerization with the available casein amine groups.¹¹ Polymerizations were run for 180 min with continuous bubbling of N₂, and samples were withdrawn along the process at regular time intervals. Casein grafting is produced by propagation of both primary amine radical and pendant methacrylic groups onto the biocomponent chain. In the case of the reference latex synthesized with neat casein, the protein was previously dissolved at 50°C, before polymerization.

The whole process (casein methacrylation and hybrid latexes synthesis) was carried out in a 0.5-L jacketed reactor equipped with thermostatic bath, thermometer, condenser, stirrer, N₂ inlet, and sampling device. Table 1 presents the recipe of the emulsion polymerizations of acrylic monomers carried out in the presence of 50% wbm of casein (neat or methacrylated).

Characterization of the methacrylated casein and latexes

Casein methacrylation was characterized by (1) proton nuclear magnetic resonance (¹H NMR) and (2) a spectrophotometric assay using OPA for quantifying the effective percentage of GMA bounded to casein.²⁴ Samples withdrawn before and after the methacrylation reaction were analyzed by ¹H NMR in a Bruker Advance II 300 spectrometer and using the watergate sequence to suppress the water signal. Effectiveness of casein methacrylation was quantified by determining

the reduction in amine groups of casein, through a spectrophotometric assay using OPA. The reaction of OPA reagent with primary amine groups of proteins forms 1-alkylthio-2-alkyl-substituted isoindoles, which show an absorption band at 340 nm.²⁵ Then, amino groups consumption during methacrylation reaction (or in other words, the amount of GMA linked to casein) was determined with the measured absorbance at 340 nm of the methacrylated casein against neat casein, together with a calibration constant that relates absorbance with amino concentration (obtained with glycine as standard).

The monomer's conversion (x) was determined gravimetrically, while casein (neat or methacrylated) was not considered in the x calculation. Average particle diameters (d_p) were measured at 30°C by dynamic light scattering, using a Brookhaven BI-9000 AT photometer at a detection angle of 90°. The number of particles per liter of latex (N_p) was estimated from measurements of d_p , x , and the casein linked to the hybrid particles.

The casein degree of grafting (i.e., the fraction of casein grafted to the acrylic polymer, CDG) was determined following the procedure described elsewhere.²⁰ First, ungrafted casein was quantified by UV spectroscopy after it was separated from latexes

Table 1: Recipe of acrylic/casein latexes

Reagent	Amounts (% wbm)
BA	80
MMA	20
Neat/methacrylated casein	50
TBHP	0.2
Na ₂ CO ₃	2.5
H ₂ O	600

wbm weight based on monomers

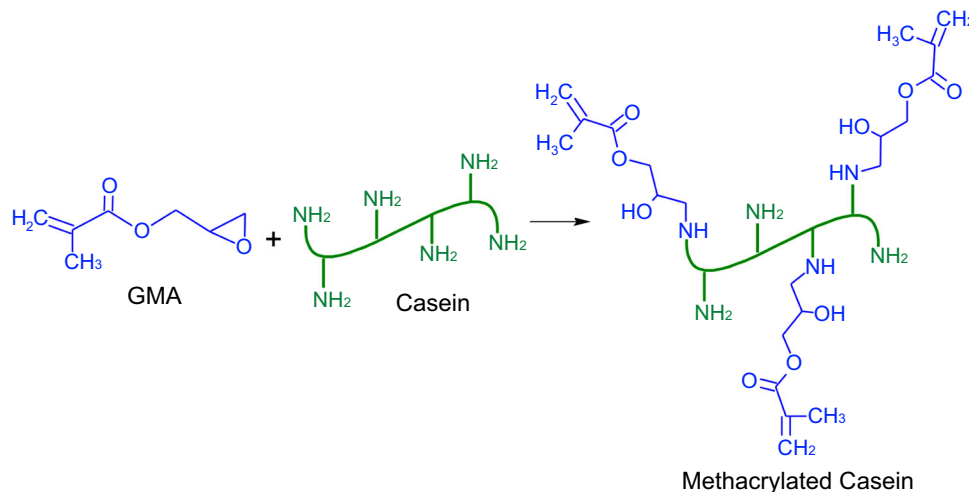


Fig. 1: Scheme of casein methacrylation

through multiple centrifugation and redispersion steps. Grafted casein was calculated as the difference between initially loaded and ungrafted protein.

Also, the insoluble polymer fraction (IF) of the hybrid materials was quantified as the ratio between the dried weights of the sample before and after the Soxhlet extraction with THF for 24 h. Note that the insoluble fraction contains the acrylic gel from BA/MMA copolymer, the ungrafted casein (which is also insoluble in THF), and the acrylic-graft-casein copolymer.²⁰

Latex particles were observed by transmission electron microscopy (TEM), with a TECNAI G2 20 TWIN (200 kV, LaB6). To this effect, a drop of diluted latex (solids content = 0.01 wt%) was placed on a formvar-coated copper grid. After drying, negative dark staining was obtained by adding a drop of 1 wt% UAc solution (at high pH, uranyl ions of UAc aggregate into colloidal particles).²⁶

Characterization of the hybrid films with high protein content

The polymer films were prepared by casting the latexes and then dried at 22°C and 55% RH over 7 days.

The effect of compatibility on the thermal degradation of the hybrid materials was studied by thermogravimetric analysis (TGA). To this effect, samples (around 10 mg) were heated from 40 to 600°C with a heating rate of 10°C/min under nitrogen atmosphere using a Mettler-Toledo Thermogravimetric Analyzer model TG-50. The maximal decomposition temperature ($T_{d,max}$) was determined as the temperature at main peak of the derivative weight loss curve.

Film opacity was evaluated through the method proposed by Irissin-Mangata et al.²⁷ which is based on the determination of the sample absorption spectrum in the UV-visible range (400–800 nm). Then, film opacity was defined as the area under the absorption spectrum divided by the sample thickness. Measurements were taken by triplicate for each sample.

Face-to-face blocking resistance of the films was evaluated following previous reports.²¹ The test for each sample was run three times, and the results were correlated with rates 0–10 (minimum and maximum blocking resistance, respectively) defined by ASTM D 4946-89.

The open time of the latexes was evaluated by Adaptive Speckle Imaging Interferometry (ASII) in a Horus equipment (Formulation). For the analysis, latexes were cast on a glass (90 μm wet) and drying was studied over 2.45 h.

The mechanical properties of the hybrid films were characterized through tensile and hardness tests by using a universal testing machine (INSTRON 3344), at 23°C and 50% RH. For the tensile test, films with dogbone shape of length 9.53 mm and cross section $3.18 \times 1 \text{ mm}^2$ were strained with an elongation rate of 25 mm/min. On the other hand, film hardness

was correlated with the maximum value of the force measured in compression when the sample is penetrated 1 mm with a 2 mm in diameter cylinder plane probe. For both analyses, at least five specimens of each sample were tested.

The dynamic viscoelastic behavior of samples was investigated using a strain-controlled rotational rheometer (MCR 301, Anton Paar Physica) with parallel-plate geometry (8 mm diameter). Specimens 8 mm in diameter and 1 mm in thickness were tested. Experiments were conducted at 1 Hz, with a linear temperature variation from 130 to 25°C and a cooling rate of 5°C/min, 0.1% of deformation, and 4 N normal force.

For water and organic solvent resistance analysis, film specimens of 20 mm in diameter and 1 mm of thickness were immersed in distilled water and MEK at room temperature. Specimens were removed from the medium (water or MEK) at a regular time, dried with a filter paper, and immediately weighed before being immersed. This procedure was repeated over 7 days or until the film showed damage, measuring in each case the relative mass absorbed (A_W and A_{MEK}) and weight loss (WL_W and WL_{MEK}), expressed as the percentage of the dissolved mass of the dried film.

The biodegradation ability of hybrid films was qualitatively determined as the materials weight loss (W_{loss}) under composting conditions. To this effect, burial experiments were carried out following a procedure described in previous reports.^{15,21} Shortly, film samples of 1 mm of thickness and 20 mm in diameter were buried in a moisturized commercial compost with the next characteristics: total dry solid = 45% of the wet solids; pH = 6.5; and nonvolatile solids content = 40% of the wet solids. The samples were removed every 7 days, carefully cleaned, and dried in an oven at 60°C. Finally, W_{loss} was calculated as the percentage of the lost mass of the dry film.

Results and discussion

Synthesis of the acrylic/casein latexes with high protein content

In a previous step of the emulsion polymerization, methacrylated caseins were synthesized following the scheme of Fig. 1. Figure 2 shows the ^1H NMR of the reaction mixture before and after casein methacrylation for a DM of 30. It can be seen that oxirane groups (protons at 2.6, 2.8, 3.2, and 3.4 ppm) from the GMA were barely present after the methacrylation reaction, indicating its consumption in the course of the aminoglycidyl ether reaction. Also, the methacrylate group (protons at 5.7 and 6.1 ppm) remained available in the methacrylated casein for the further propagation reaction. The percentage of GMA bound to casein, evaluated from the casein amino groups consumption during the methacrylation reaction with the OPA

spectrophotometric assay, showed results that were almost complete: 100, 100, and 95% for the GMA/casein molar ratios of 2, 20, and 30, respectively. Both results (^1H NMR and the OPA spectrophotometric assay) confirm that highly methacrylated caseins were successfully synthesized.

After obtaining methacrylated casein, the hybrid latexes were synthesized, which are codified with the letter “H” (which corresponds to hybrid) followed by the abbreviation DM and a subscript indicating the theoretical degree of methacrylation of casein. Thus, in the experiment “H-DM₃₀,” casein with DM of 30 was used in the latex synthesis, while “H-DM₀” was obtained from neat casein. Table 2 summarizes the final values of x , d_p , N_p , CDG, and IF of the

synthesized hybrid latexes, while the evolution of x along the polymerizations is shown in Fig. 3. Note that the increment of methacrylic functionalities from 2 up to 30 decreases both the polymerization rate and the final x , while increasing d_p . This behavior is due to the incorporation of methacrylic functionalities onto protein chains which reduces the availability of amino groups to later initiate the polymerization with TBHP (Fig. 1). Therefore, a lower radical concentration is obtained, which also produces a lower number of nucleated polymer particles (N_p was diminished from 5.03×10^{16} for neat casein to 2.68×10^{16} for H-DM₃₀).

From Table 2, it is seen that casein methacrylation combined with the redox initiation TBHP/ NH_2 -casein allowed the grafting of large amounts of protein in the

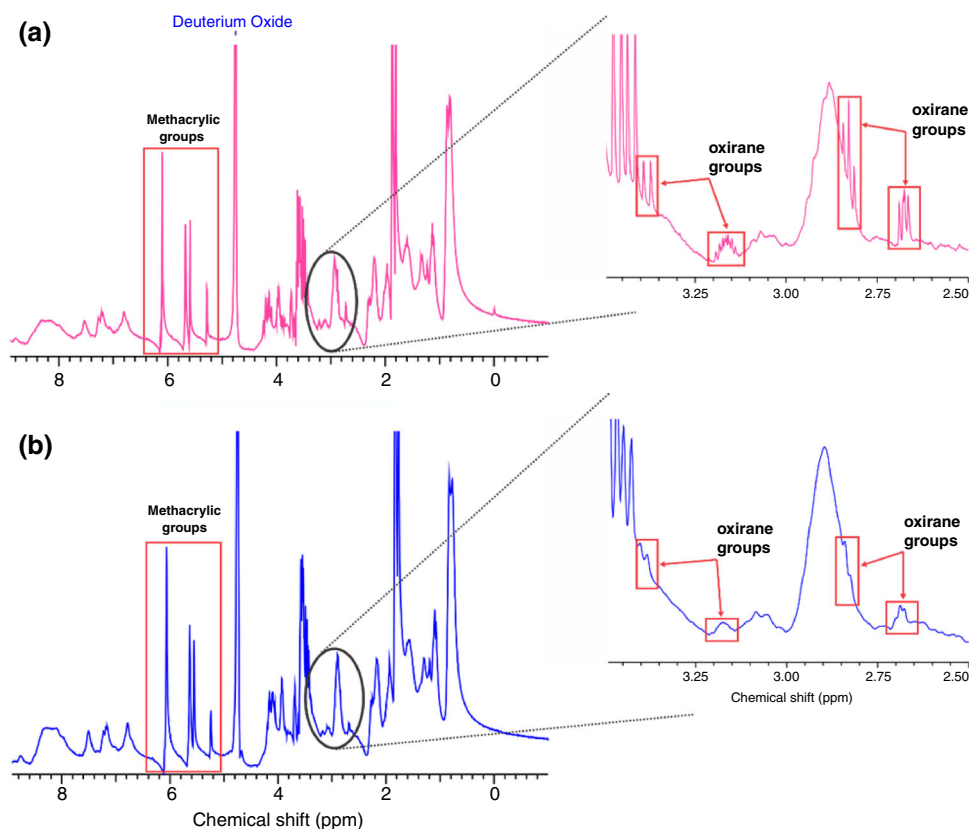


Fig. 2: ^1H NMR spectra of the (a) GMA–casein mixture before and (b) after the methacrylation reaction for a GMA/casein molar ratio of 30

Table 2: Main properties of the acrylic/casein hybrid latexes containing 50% wbm of protein

Experiment	x (%)	d_p (nm)	N_p (#/L)	CDG (%)	IF (%)
H-DM ₀	91	165	5.03×10^{16}	10	92
H-DM ₂	88	176	4.39×10^{16}	28	96
H-DM ₁₀	85	178	4.40×10^{16}	41	96
H-DM ₂₀	79	191	3.61×10^{16}	56	98
H-DM ₃₀	78	218	2.68×10^{16}	82	99

hybrid materials, thus improving the system compatibility. The variation of the casein functionality degree increased the fraction of grafted casein to polymer from 10% (for H-DM₀) to 82% (for H-DM₃₀), representing a significant augment in the mass of linked biomaterial of more than 720% with respect to the unmodified protein. Also, the variation of the casein methacrylation degree helped to control the number of grafting points onto the protein molecule. Note that IF was increased with the number of pendant methacrylic

units onto casein. Thus, taking into account the number of double bonds incorporated onto the protein and the high casein concentration used, it is expected that these higher levels of IF could be also correlated with the formation of some crosslinked structures inside the particles.

These results indicate that the use of methacrylated casein combined with the redox initiation with TBHP is an efficient approach to produce hybrid materials with high protein content and controllable compatibility. This is due to the fact that both the fraction of ungrafted biocomponent and the number of acrylic chains linked to the casein backbone can be reasonably regulated by varying the degree of methacrylation in the previous step of casein modification.

Figure 4 compares the TEM micrographs of latexes synthesized with neat casein (H-DM₀) and with a highly methacrylated protein (H-DM₂₀). Micrograph of latex with nonmodified casein (Fig. 4a) presents dark zones, which correspond to the ungrafted protein stained with UAc. On the other hand, H-DM₂₀ micrograph (Fig. 4b) shows higher compatibility and strong attachment between casein and acrylic polymer (free casein is practically not observed in this latex), supporting the CDG improvement obtained by casein methacrylation.

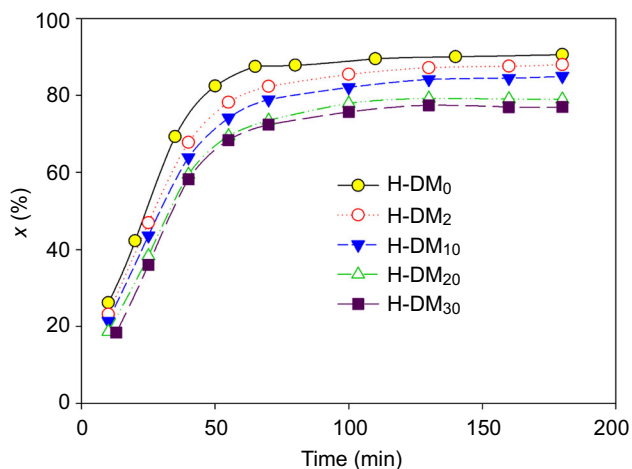


Fig. 3: Evolution of conversion during the BA/MMA emulsion copolymerization in the presence of 50% wbm of casein with different degrees of methacrylation

Coating performance of the hybrid materials with high protein content

Table 3 summarizes the results of $T_{d,max}$ and opacity for the hybrid films. Note that the increase in the

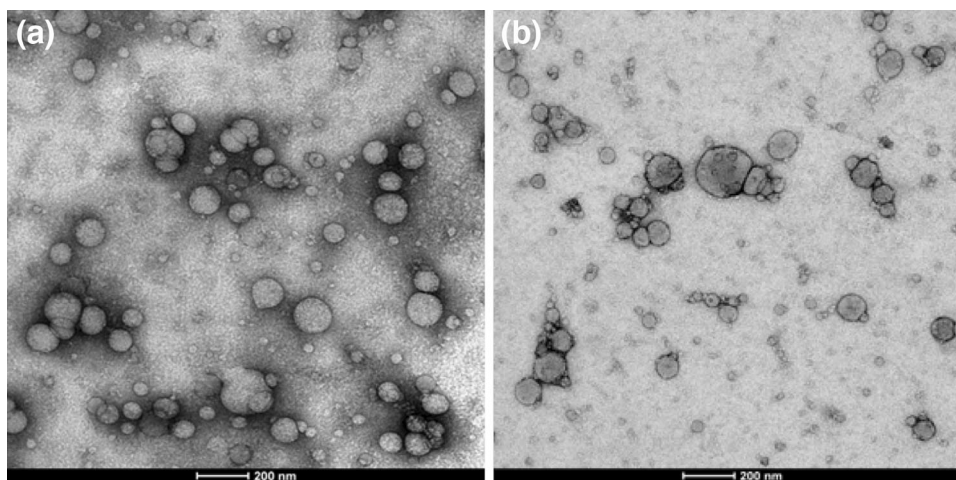


Fig. 4: TEM micrographs of the hybrid latexes (a) H-DM₀ (neat casein) and (b) H-DM₂₀

Table 3: Final values of $T_{d,max}$ and opacity for the hybrid films

	H-DM ₀	H-DM ₂	H-DM ₁₀	H-DM ₂₀	H-DM ₃₀
$T_{d,max}$ (°C)	381.3	385.3	372.3	386.3	383.3
Opacity (AUxnm/mm)	658.6	293.8	148.1	123.9	112.3

protein grafting extent of the hybrid materials by casein methacrylation did not markedly affect the degradation temperature of the nanocomposites, since all of the samples presented a $T_{d,max}$ close to that of the pure acrylic film (382°C). However, the increase in the amount of grafted casein by using methacrylated casein progressively reduced the peak of thermal degradation rate (dW/dT) at $T_{d,max}$, as can be observed from the derivative weight loss curves (Fig. 5). Thus, dW/dT decreased from 1.831%/°C for H-DM₀ down to 0.838%/°C for H-DM₃₀. This behavior could be due to the fact that the pure casein presents a lower decomposition rate than the pure acrylic, and therefore, the grafted protein would act as a heat transport barrier.¹⁵ Figure 5 also shows that the presence of casein in hybrid films improved its thermal resistance by appearing as a secondary degradation peak at a high temperature (between 450 and 600°C), which could correspond to highly crosslinked structures.

The film esthetics is a key parameter in many commercial applications, particularly in decorative coatings. Therefore, optical properties are relevant and have great impact on the materials functionality.²⁸ When using neat casein (H-DM₀), a large amount of ungrafted protein is present in the material, and the film showed a high opacity of 658.6 AUxnm/mm

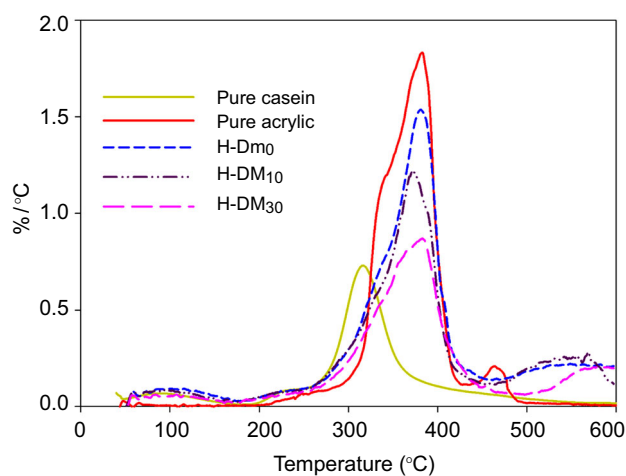


Fig. 5: Thermogravimetric analysis for films from pure components and hybrid materials prepared on the basis of methacrylated casein with different DM

(Table 3). This is because the presence of ungrafted casein promotes its segregation in large and nonmiscible domains, and as a consequence, the differences in refractive indexes of phases increase the film opacity.^{21,29} However, when the materials compatibility was significantly increased by casein methacrylation, film opacity progressively decreased to values close to that of the pure acrylic film (126.3 AU × nm/mm). In this way, the films esthetics was notably improved.

Despite the numerous advantages of the waterborne coatings, such as easy water cleaning, low odor, and low environmental impact, coating science and technology find a true challenge in designing binders that simultaneously attain smooth film formation at room temperature, high antiblocking resistance and hardness, and long open time.

Standard waterborne binders have poor block resistance and hardness. However in a recent work,²¹ we have demonstrated that the addition of casein to acrylic formulations can improve the blocking resistance, since the protein is a stiff component that confers hardness to the film bulk and reduces the tack adhesion energy,^{30,31} while minimum film-forming temperature (MFFT) is not affected because of the high plasticization effect of water during the film formation process. All of the hybrid films evaluated here have an MFFT lower than 2°C and are nonblocking, presenting the highest antiblocking rate. It is an indication that the improved compatibility attained by casein methacrylation does not degrade these properties.

One of the remaining problems related to the use of water-based systems is their shorter open time than the solvent-based systems. The open time of paints is the period during which a painter can make corrections to the freshly applied paint film without leaving marks.^{32,33} While open time of typical water-based paints is around 5–10 min, solvent-based ones are in the range of 30–40 min.³⁴ The measured open time of the hybrid latexes resulted in 90 min for H-DM₀, 55 min for H-DM₂₀, and 30 min for H-DM₃₀, which are comparable to solvent-based paints. The higher open time of the hybrid latexes in comparison with conventional water-based paints could be attributed to the large amount of casein, which is an amphiphilic compound that acts as a surface active agent keeping water inside the film for a longer period of time.³⁵ Moreover, open time decreases with the degree of

Table 4: Mechanical properties of hybrid films

Film	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (N)
Pure acrylic	0.33 ± 0.03	0.63 ± 0.1	4698 ± 12	5.0 ± 0.4
H-DM ₀	145 ± 15	10 ± 0.5	208 ± 7	162 ± 5
H-DM ₂	63 ± 6	8 ± 0.2	351 ± 13	115 ± 6
H-DM ₁₀	86 ± 8	11 ± 0.3	301 ± 19	138 ± 11
H-DM ₂₀	169 ± 10	14 ± 0.8	169 ± 26	149 ± 8
H-DM ₃₀	191 ± 11	15 ± 0.1	98 ± 7	163 ± 6

casein methacrylation as a consequence of the fraction of ungrafted casein for acting as water-soluble surface active agent is reduced. Also, there is a great advantage in the use of this polymer/protein system from the environmental point of view, because the presence of casein avoids the addition of organic compounds, such as glycol derivatives, to control the rheology and delay the evaporation of water.³³

The mechanical properties of pure acrylic and hybrid materials are summarized in Table 4. As it can be seen, pure acrylic with low glass transition (around -33°C) is easily elongated at low tensile strength, with an extension at break close to 4700% and presenting a reduced hardness. When incorporating casein, a hard component, films are strengthened, and therefore, hybrid materials showed superior mechanical properties than the pure acrylic film. Also, it can be observed that the behavior of hybrid films are strongly dependent on both the amount of ungrafted casein and the crosslinking degree of the materials. Thus, the increase in CDG from 10% (for unmodified casein) to 28% (for H-DM₂) decreased the Young's modulus, tensile strength, and hardness, but improved the elongation capability. This behavior is attributed to the reduction in ungrafted casein into the films, which acts as a reinforcing filler of the polymeric matrix.²¹ However, although CDG was increased by using methacrylated casein with higher DM, films showed the opposite trends in the previously described properties due to the increasing crosslinking density in the materials microstructure (see H-DM₁₀ to H-DM₃₀ mechanical properties). Moreover, the degree of crosslinking also affected the film's hardness, observing an improvement in this property for levels of functionalization higher than 10 methacrylic groups per casein molecule.

Note that IF measures the fraction of crosslinked polymer, which resulted close to 100% in all of the cases with methacrylated casein, but it does not quantitatively reflect the crosslinking density of materials. On the other hand, the improved degree of compatibilization reached by casein methacrylation (i.e., by increasing CDG) shows a trend in the mechanical properties which is consistent with an augmentation of crosslinking density. In order to confirm the increase in polymer crosslinking density with casein methacrylation, the dynamic viscoelastic behavior of polymer films was investigated. Figure 6 shows the storage (G') and loss (G'') moduli, as a function of temperature for film samples synthesized with methacrylated casein. It can be seen that both G' and G'' become higher as DM increased, confirming the augmenting of the materials crosslinking density.

From previous results, the incorporation of methacrylated casein to the acrylic formulation largely fulfilled two key requirements for coating applications such as the high film hardness and blocking resistance, without affecting the film-forming capability of the acrylic polymer. In other words, some of the produced hybrid latexes with high protein content could be

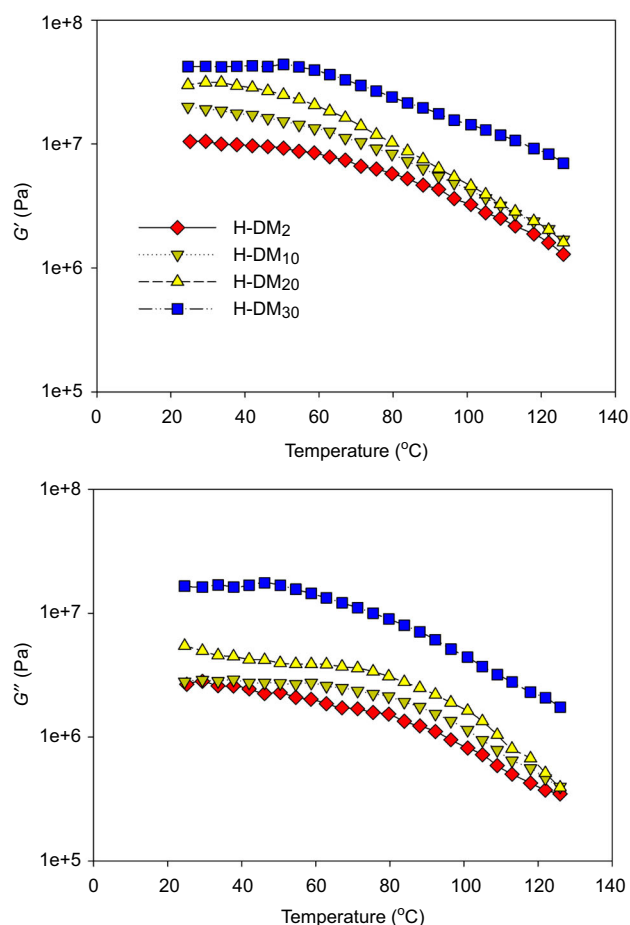


Fig. 6: Effect of casein methacrylation degree on the dynamic moduli, G' and G'' , of the hybrid films

excellent alternatives as binders for waterborne coatings.

Because casein is a highly hydrophilic macromolecule, hybrid films present a greater water sensitivity than the pure acrylic film (Fig. 7a). Thus, the main drawback for a potential industrial application as coatings for the casein-based materials containing high protein content is their deficient water resistance. This poor performance is related to the low compatibility achieved with nonmodified casein, where a high amount of ungrafted protein is present in the film. The ungrafted casein is easily transferred to the water phase, and this migration process disintegrates the films. A picture of film specimen H-DM₀, which disintegrated immediately after water immersion, is also included in Fig. 7a. From Fig. 7a, it can be observed that the incorporation of methacrylated casein considerably improved the water resistance by notably reducing both the percentage of absorbed water (A_w) and dissolved mass (WL_w) and increasing the immersion time before the films presented damage. Maximum immersion time before the film was damaged or the experiment was stopped (7 days) is presented on A_w bars of Fig. 7a. Films H-DM₁₀ and

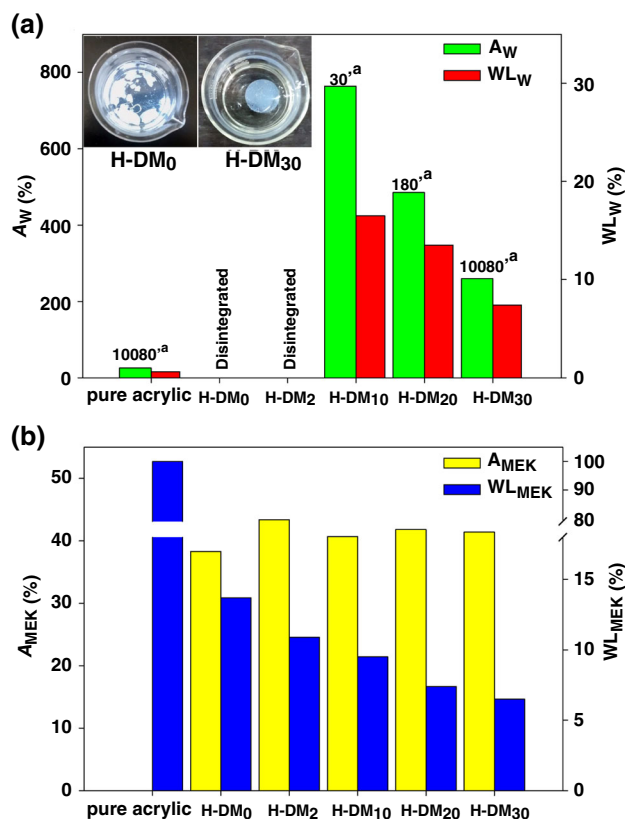


Fig. 7: Water (a) and solvent (b) resistance values for pure acrylic and the hybrid films synthesized from methacrylated casein with different DM. ^aImmersion time in minutes before the films presented damage. Pictures on the upper part of plot (a) show the water resistance experiments for film H-DM₀ immediately after immersion and for film H-DM₃₀ after 7 day of immersion

H-DM₂₀ resisted immersion times of 30 and 180 min, respectively. When using modified casein with 30 methacrylic functionalities, an outstanding performance was reached, with immersion times greater than 10,080 min (7 days) and final WL_w of around 7%. The picture of film specimen H-DM₃₀ included in Fig. 7a shows that it preserved its integrity at the end of the test. The observed enhancement in the water resistance by using methacrylated casein with higher DM (Fig. 7a) is attributed to the increase in compatibility and the crosslinking density of films. These results show that casein methacrylation successfully overcame the poor water resistance of the hybrid films with high protein content.

On the other hand, Fig. 7b shows the results of MEK resistance for the hybrid materials. Note that the absorbed solvent mass (A_{MEK}) was not significantly affected by the amount of casein incorporated into the nanocomposites, obtaining values around 40% for all of samples. However, the degree of compatibility reduced the weight loss of the films (WL_{MEK}), probably due to the increase in both acrylic (hydrophobic component)/casein (hydrophilic component) synergy

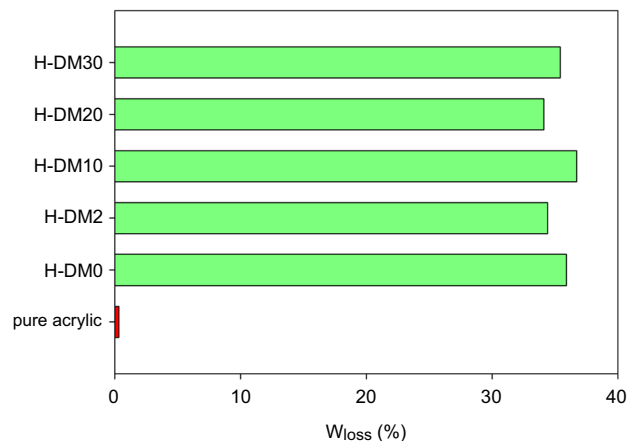


Fig. 8: Soil degradation of the acrylic film in comparison with hybrid films with different DM

and crosslinking density in the materials. Compared to the performance of pure acrylic, which is completely swollen in MEK (WL_{MEK} = 100%), the presence of casein provides an adequate barrier to organic solvents, which is improved when increasing compatibility between both components.

Weight loss under composting condition

The degradation results of the materials after 14 days of burial in composting conditions are shown in Fig. 8. One of the biggest drawbacks of the pure acrylic film is its very low degradability, which only exhibits a weight loss of around 0.34% (Fig. 8). However, the incorporation of a highly degradable natural protein into the acrylic formulations notably improved the biodegradation capability of the hybrid films. In all cases, weight losses of around 35% were obtained, which is in agreement with the content of biomaterial in the films (33%). Also, the weight loss of the hybrid materials was not appreciably affected by the DM of the casein, indicating that the increase in the number of non-degradable acrylic chains grafted to the protein did not reduce the degradation ability of the films.

Conclusions

Production of acrylic/casein latexes with large protein content is highly desirable for reducing the product's carbon footprint and for efficient exploitation of this sustainable resource. Unfortunately, the incorporation of high casein concentrations in acrylic formulations limits the compatibility between both components, resulting in a film with poor water resistance that restricts the industrial application of these materials as coatings. A novelty synthesis strategy was successfully developed to overcome this drawback. The employed methodology was based on the chemical modification

of casein to produce a functionalized protein which contained pendant methacrylic groups able to radically polymerize in a conventional emulsion process. The use of chemically modified casein allowed for obtaining hybrid materials with high protein content and increased degree of compatibilization between both components, reaching CDG values as high as 82%. In this way, it was possible to significantly overcome the limited performance obtained through the traditional grafting method by redox initiation, wherein the chemically incorporated casein was only 10%.²¹ The compatibilization improvement enhanced the film properties, such as thermal decomposition, mechanical behavior, organic solvent permeability, and particularly water resistance, showing a higher synergetic effect between the biopolymer and the synthetic polymer. Finally, the enhanced performance of the obtained hybrid films converts these materials in a promising alternative for their industrial application as coatings.

Acknowledgments The financial support received from CONICET, ANPCyT, the Secretary of Science, Technology and Research of Santa Fe State, and the Secretary of University Policies from the Educational Ministry (all of Argentina) is gratefully acknowledged. We also acknowledge Prof. María Jesus Barandiaran (University of the Basque Country) for her help with the open time and TEM characterizations.

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