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New strategy to improve acrylic/casein compatibilization in waterborne hybrid nanoparticles

Matías L. Picchio,[1] Roque J. Minari,[1] Veronica D. G. Gonzalez,[1] María J. Barandiaran,[2] Luis M. Gugliotta[1]

[1]Polymer Reaction Engineering Group, INTEC (Universidad Nacional del Litoral-CONICET), Güemes 3450, Santa Fe 3000, Argentina

[2]Institute for Polymer Materials, POLYMAT, Departamento de Química Aplicada, University of the Basque Country, Centro Joxe Mari Korta, Avenida Tolosa 72 20018, Donostia-San Sebastián, Spain

Correspondence to: L.M. Gugliotta (E-mail: lgug@intec.unl.edu.ar)

ABSTRACT: The grafting of casein to acrylic polymers is needed to fully exploit the possibilities of hybrid nanoparticles containing such materials. The explored alternative up to now, based on the primary radical formation onto the protein chains through the redox initiation between the casein amino groups and a hydroperoxide, produces a limited degree of compatibilization to guarantee the synergic effect between both components. A novel strategy that overcomes these limitations is presented. The strategy is based on the use of a crosslinkable casein, which in addition to the characteristic grafting capacity by redox initiation with hydroperoxides, contains acrylic groups able to radically polymerize. The degree of grafting of both acrylic and casein is significantly increased by functionalizing casein with varied amounts of pendant propagating points per protein. Moreover, it is observed that the improved degree of compatibility obtained when using the crosslinkable casein considerably enhanced the properties of the acrylic/casein films, such as their mechanical behavior and resistance to both water and organic solvent. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42421.

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INTRODUCTION

Substitution of petroleum based monomers by renewable resource derived materials is one of the most important challenges that is facing the polymer industry, because of the dwindling of crude oil reserves and the increasing concern to lower the environmental footprint. Among the different bio-based resources, natural proteins as casein constitute a promising candidate as they bear amino and carboxyl functionalities that present unlimited opportunities to introduce modification in their structure. Indeed, casein derived from milk has been used for a long time in paper coatings, adhesives, and paint binders because of the reduced environmental impact, high degradability, good stained acceptance, finishing glazed aspect, and good substrate penetrability that they produce.[1,2] However, the casein films present low resistance to wet rub and to water immersion, susceptibility to microbial attack, and poor mechanical properties.[1] For these reasons, the attempts to modify and improve the properties of casein by incorporating synthetic polymers, such as acrylates has gained technological interest.[3]

Li *et al.* reported the grafting of casein with methyl methacrylate (MMA) conducted via emulsion polymerization, by initiating the polymerization according to a redox reaction between an alkyl hydroperoxide and the amino groups of the casein,[4,5] where the formed amino radicals initiate the graft polymerization. They achieved around 40–50% of grafting efficiency, defined as the weight percentage of branched poly(methyl methacrylate) (PMMA) with respect to the total polymerized MMA. However, they did not report on the percentage of casein incorporated in the system.

In a recent work,[6] 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 pphm (parts per hundred monomer) to 25 pphm, the amount of incorporated casein increased, and the situation was reversed up to 50 pphm – the maximum range studied. Furthermore, although almost all the casein was grafted at low concentrations (3 pphm), the percentage of grafting decreased as the casein concentration in the formulation increased. As a result, two kinds of particles were

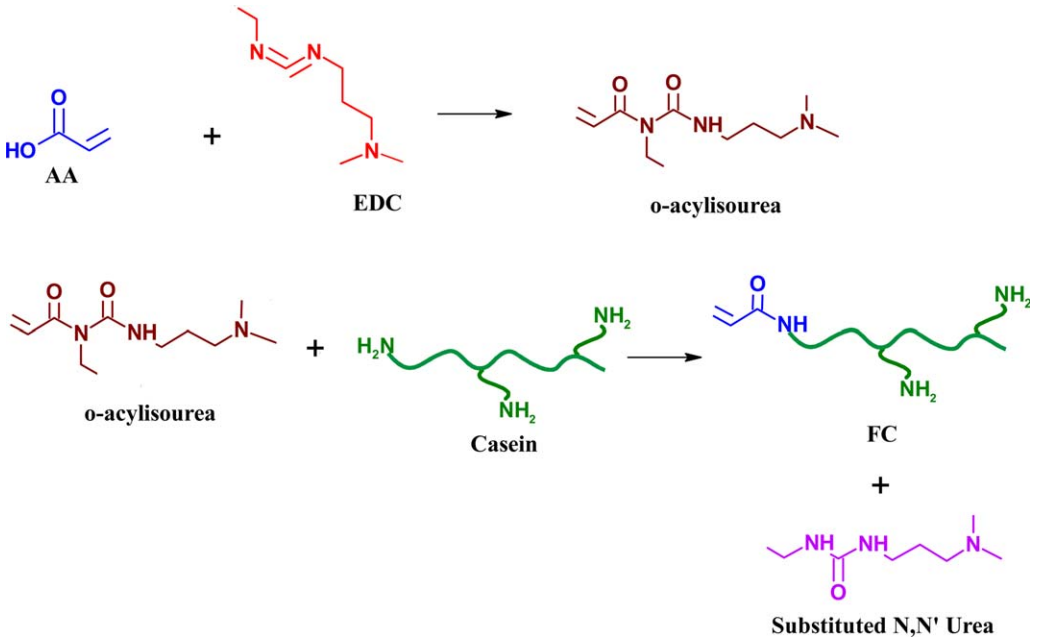

Figure 1. Casein functionalization with acrylic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtained: the hybrid ones mainly formed by PMMA-graft-casein and the other particles containing only PMMA homopolymer. Non-uniform latexes usually lead to heterogeneous films, which are undesirable because they adversely affect final properties.[7]

In this work, a novel strategy to improve compatibility between the casein and the acrylic copolymer is explored. The strategy is based on the use of functionalized-crosslinkable casein (FC) that, in addition to the characteristic grafting capacity by redox initiation with a hydroperoxide, contains acrylic groups able to be radically polymerized. This article involves: (i) the synthesis and characterization of two FC with different amount of acrylic groups; (ii) the inclusion of FC in the emulsion polymerization of MMA in order to evaluate the possible improvement in the degree of compatibility between casein and PMMA; (iii) the validation of the improved compatibility obtained by using FC with an acrylic formulation based on butyl acrylate (BA)/MMA, commonly used in coating formulations; and (iv) the evaluation of the film properties in comparison to those obtained from neat casein.

EXPERIMENTAL

Materials

Technical grade casein from bovine milk (Sigma), MMA, BA, and acrylic acid (AA) containing traces of MEHQ as inhibitor (99.0% purity, Aldrich) were used. The employed initiator was *tert*-butyl hydroperoxide, 70 wt % in H_2O (TBHP, Aldrich). Other used reagents were: pro-analysis grade sodium carbonate (Na_2CO_3, Cicarelli) as buffer to regulate the pH, HPLC grade tetrahydrofuran (THF, J.T. Baker), technical grade methyl ethyl ketone (MEK, Anedra), pro-analysis grade absolute ethanol (Cicarelli), analytical grade sodium borate (Anedra), 2-mercaptoethanol (≥99.0%, Fluka), pro-analysis grade sodium dodecyl sulfate (SDS, Anedra), and glycine amino-acid (≥99.0%, Sigma). Activation of carboxylic groups of AA during casein functionalization reaction was carried out with *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimine hydrochloride (EDC, ≥99.0% purity, Fluka). HPLC grade O-phthalaldehyde (OPA, Sigma) was used as fluorescent amino marker. Deuterium oxide (D_2O, ≥99.9% purity, ENSI) was employed as deuterated solvent in the ^1H NMR measurements. Microscopy grade uranyl acetate 1 wt % solution (UAc, EMS) and formvar® (polyvinyl formal, Fluka) were used for preparing TEM samples. All the reagents were used as received without any kind of purification. Distilled and deionized water was used throughout the work.

Synthesis of the Acrylic Functionalized Casein (FC)

FC was prepared by the formation, in the presence of EDC, of an amide bond between the casein and the AA in a two-step reaction following the procedure described elsewhere.[8] The functionalization route is presented in Figure 1. EDC binds to the carboxyl group of AA to form a highly reactive o-acylisourea intermediate. This intermediate component attacks some amino groups of the protein producing amides with vinyl bonds. The synthesized FC presents a new acrylic functionality that together with the amine groups has the capacity to propagate via radical polymerization.

The functionalization reaction was carried out at room temperature, in aqueous medium, during 24 h. Two FC were synthesized, with 2 AA (FC2) and 8 AA molecules (FC8) per casein molecule (assuming 30,000 g/mol as the number average molecular weight of casein). Small amounts of AA are required to synthesize the FC, resulting AA/casein mass ratios equal to 0.0048 and 0.0192 for FC2 and FC8, respectively. The used EDC molar concentration was 2-fold higher than that of AA. Functionalization was carried out in aqueous media, which

Table I. General Recipe for the Synthesis of Acrylic/Casein Latex

Reagent	Amounts (pphm)
Acrylic monomers	100
Neat/Functionalized Casein	6–50
TBHP	0.2
Na_2CO_3	5.332

represents an important advantage, because the resulting FC solution can be directly used in the polymerization reaction.

Synthesis of the Casein/Acrylic Latexes

Polymerizations of acrylic monomers, which involved MMA and BA/MMA formulations with TBHP as initiator, and in the presence of variable amount of casein (neat and FC) were carried out in a 0.2 L jacketed reactor equipped with thermostatic bath, digital thermometer, condenser, stirrer, N_2 inlet and sampling device. In the case of employing FC, the resulting solution of the FC synthesis (without any purification) was directly used after adding Na_2CO_3 to regulate the pH. In the case of using neat casein, it was dissolved in a water solution of Na_2CO_3. In both cases, the required pH is higher than 10, where the association of casein macromolecules by hydrophobic interaction is reduced.[9] Then, the solution temperature was raised up to 80°C and the acrylic monomers were loaded. Finally, the resulting dispersion was purged with N_2 for 30 min before injecting the TBHP. Table I presents a general recipe of the performed polymerizations. Samples were withdrawn during polymerization at regular time intervals.

Characterization

Casein functionalization was evaluated by: (i) measuring the Zeta potential of the protein solutions; (ii) ^{1}H NMR spectroscopy; and (iii) quantifying the effective % of AA bounded to casein with the OPA method.[10,11] Zeta potential was measured with a Malvern Nano ZS equipment. The ^{1}H NMR spectra were obtained with a 300 MHz Bruker spectrometer. Before ^{1}H NMR measurements, samples dialysis was carried out by several centrifugation and redispersion steps using a centrifugal filter tube with a molecular weight cut off of 3000 g/mol (Merk-Millipore, Amicon Ultra 4 mL Centrifugal Filter Units), which retains the protein and allows the washing of free AA and EDC. To this effect, 0.4 mL of the dialyzed samples containing D_2O (0.05–0.1 mL) in a 5 mm NMR tube were measured using the WATERGATE sequence to suppress the signal of water. The OPA method consists in the reaction of this reagent with primary amino groups of proteins to form highly fluorescent 1-alkylthio-2-alkyl substituted isoindoles, which show an absorption band at 340 nm.[12] This reaction was carried out in the presence of 2-mercaptoethanol, at pH = 9.5 and at room temperature. For the analysis, 100 μL of sample (1% wt/wt of the FC) were mixed with 2 mL of freshly prepared OPA reagent (80 mg of OPA in 2 mL absolute ethanol, 50 mL of 0.1 M sodium borate solution, pH 10, 5 mL of 20% SDS solution, and 0.2 mL of 2-mercaptoethanol bring to 100 mL with water). Absorbance of the FC (A_{FC}) at 340 nm was measured against neat casein (A_{NC}) by UV spectroscopy. The amino groups concentration was determined on the basis of the measured absorbance and a calibration constant (k) that relates the absorbance with the amino concentration, obtained with glycine as standard. Then, the % of AA bounded per casein molecule was calculated as follows:

$$\text{AA bounded per casein molecule } \% = \frac{(A_{NC} - A_{FC})}{k \times [AA]} \times 100 \quad (1)$$

where [AA] is the acrylic acid concentration employed in the casein functionalization reaction.

Conversion of acrylic monomers (x) was measured by gravimetry and particle diameter (d_p) by dynamic light scattering (DLS), using a Brookhaven BI-2030. The molecular architecture of the casein/acrylic hybrid latexes was mainly characterized by determining the fraction of casein grafted to the acrylic polymer (casein grafting efficiency, CGE), and the fraction of the polymerized acrylic monomers that contain grafted casein (acrylic grafting efficiency, AGE).[6]

The CGE was determined by correlating the mass of the grafted casein present in the hybrid latex with the mass loaded of casein. To separate the ungrafted casein from the latex a procedure of multiple centrifugation and redispersion was applied as follows: (i) the diluted latex at 1% of solids content was centrifuged, in a HealForce model Neofuge 15R, at a relative centrifugal force (RCF) of 25,000 g during 4 h; and (ii) the supernatant was separated and the pellet was redispersed with a 1 wt % SLS solution and shook overnight, to promote the desorption of the ungrafted casein from the polymer particle. The procedure of centrifugation/separation/redispersion was repeated until not detecting casein in the supernatant.

All supernatants from each repeated centrifugation were analyzed by UV spectroscopy in a Perkin-Elmer Lambda 25 UV-Visible spectrophotometer and the ungrafted casein concentration was obtained by combining the peak area at 280 nm with a calibration of casein concentration. Then, the mass of grafted casein was obtained as the difference between the loaded and the ungrafted casein.

AGE is defined as the weight of grafted acrylic polymer divided by the weight of total polymerized monomers. Therefore, the ungrafted acrylic polymer was soxhlet extracted with THF during 24 h //from the latex sample, dried in the oven at 60°C, and weighted before and after the extraction. THF dissolved the pure acrylic polymer, but not the casein and the grafted polymer. Then, grafted acrylic polymer required to calculate AGE was determined by taking into account the mass before and after the extraction and the sample casein content.

The morphology of latex particles was studied by means of transmission electron microscopy (TEM), using a TECNAI G2 20 TWIN (200kV, LaB6). To this effect, a drop of diluted latex (around 0.01 wt % of solids content) was placed on a formvar-coated copper grid and after drying it a drop of 1 wt % UAc solution was added. At high pH, uranyl ions of UAc aggregate into colloidal particles, resulting in the dark staining around solid objects that is used for negative staining.[13] Micrographs were taken at different magnifications depending on particle size.

Film Formation and Characterization

The polymer films were prepared by casting the latexes into silicone molds and then they were dried at 22°C and 55% relative humidity over 7 days to achieve a constant weight of the film.

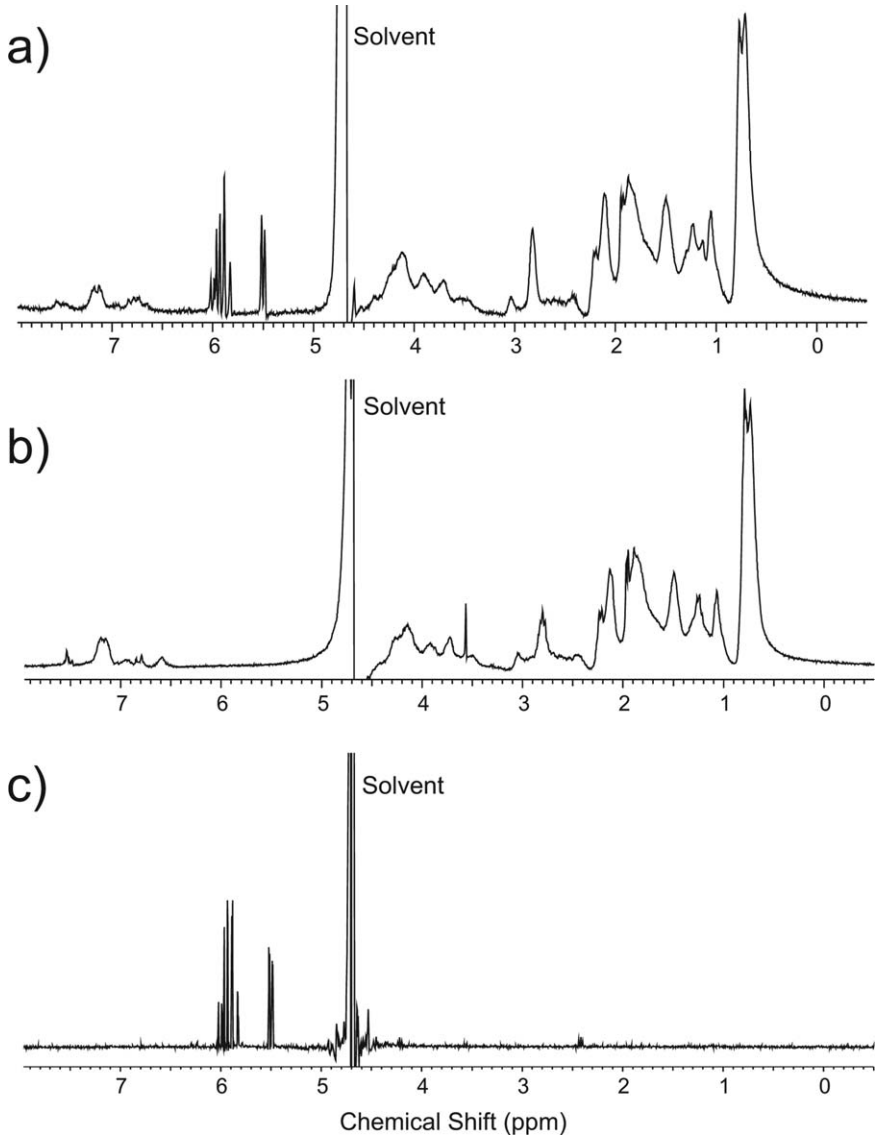

Figure 2. ^{1}H-NMR spectra of the aqueous solution containing D_2O of the dialyzed functionalized casein FC8 (a), neat casein (b), and acrylic acid (c).

The polymer films were carefully peeled from the silicone substrate, obtaining films with a final thickness of about 1 mm.

For the tensile tests, film specimens with dumbbell shape of length 9.53 mm and cross section 3.18×1 mm^2 were cut. Tests were carried out in a universal testing machine (INSTRON 3344), at 23°C, 50% relative humidity, and elongation rate of 25 mm/min. At least five specimens of each sample were tested.

One of the most important disadvantages of casein films is the low resistance to water immersion. On the other hand, acrylic films are strongly affected by organic solvents. For these reasons the improvement of compatibility of acrylic/casein nanocomposites was evaluated by measuring the water and organic solvent resistances. For such analysis, two film specimens of 20 mm in diameter were immersed in distilled water (W) and in MEK at room temperature. Specimens were removed from the medium (W or MEK) at a regular time (every hour the first 12 h and then once per day), dried with filter paper, and immediately weighed before immersing again. This procedure was repeated for 7 days or until the film presented damage. In each case, the relative mass absorbed (A_W and A_{MEK}) and the weight loss (WL_W and WL_{MEK}), expressed as the percentage of the dissolved mass of the dried film, were calculated.

RESULTS AND DISCUSSION

Synthesis of Functionalized Casein

The occurrence of functionalization was observed by a reduction of the potential between the dispersion medium and the stationary layer of the fluid attached to the functionalized casein with respect to the neat casein, as a consequence of substitution of some amino groups of the protein by amide bonds. Thus, the Zeta potential at a pH = 7 was reduced from −35.8 mV for the neat casein to −17.5 mV for FC8.

Moreover, a strong evidence of the casein functionalization reaction was obtained by ^{1}H NMR spectroscopy. Figure 2(a) shows

Table II. MMA Polymerization in the Presence of Varied Amount of Neat and Functionalized Casein. Main Characteristics of the Final Latexes

Entry	Casein (pphm)	x (%)	d_p (nm)	CGE (%)	AGE (%)
L1	Neat (25)	91	120	26	68
L2	FC2 (25)	98	132	57	87
L3	FC8 (25)	85	115	62	95
L4	Neat (50)	89	113	5	53
L5	FC2 (50)	83	96	23	97
L6	FC8 (50)	83	135	52	94

the ^{1}H NMR spectrum of the crosslinkable casein FC8 after dialyzing, where the unbounded AA, which is highly water soluble, should be completely eliminated after several dialysis steps. Therefore, the peaks between 5.4 and 6 ppm, which do not appear in the spectrum of the neat casein [Figure 2(b)] correspond to the vinyl protons of acrylic groups bounded to the casein. ^{1}H NMR of AA is also shown in Figure 2(c). The percentage of AA bounded to casein was evaluated by the OPA method, resulting 66% and 85% for FC8 and FC2, respectively.

Synthesis of Hybrid Casein/PMMA Nanoparticles

Table II and Figure 3 show the results of the 10% solids content MMA polymerization in the presence of two different concentrations of both neat casein and FC. It is worth mentioning that, at the reaction conditions, the hybrid PMMA/casein latexes stability was not affected by the reduction of the Zeta potential of FC with respect to neat casein, in the sense that coagulum formation was not observed.

The vinyl bonds incorporation in the casein does not significantly affect the evolution of monomer conversion and particles diameter. The reduction of monomer conversion observed in L3 (with FC8) with respect to L1 (with neat casein) and L2 (with FC2) could be a consequence of the decreasing amount of the available amino groups of FC8 to redox initiates the polymerization with TBHP. However, the increment of FC8 content up to 50 pphm (L6) did not produce an additional reduction in the monomer conversion, due to the available amine groups are also increased, despite that several amine groups were replaced by vinyl ones.

The most important improvement obtained by casein modification was an increase in the degree of compatibility of casein-acrylic nanoparticles, which is observed by the considerable increasing of both CGE and AGE with respect to the neat casein. Notice that AGE values obtained with neat casein were similar to the 50% PMMA grafting reported by Zhu and Li.[5] When using 25 pphm of casein, the variation of the vinyl bonds content of FC (from 2 to 8) did not significantly modify the improvement of CGE and AGE. In both cases a CGE value of approximately 60% was obtained, with an increase in the mass of grafted casein of more than 120% with respect to the neat protein, while almost all of the PMMA (87–95%) contain FC grafted. However, the number of propagating points per casein molecule does affect CGE when 50 pphm of casein was used. In this case, the fraction of grafted casein was increased from 5% (with neat casein), to 23% (with FC2), and 52% (with FC8). Also, almost all the PMMA contained grafted FC, with AGE values around 95%, which significantly overcome the 53% of AGE achieved with neat casein. It indicated that with FC almost all of the particles were compatibilized, due to the fact that the fraction of PMMA homopolymer was significantly reduced when FC2 or FC8 were employed. In other words, more homogenous latexes were obtained with FC than neat casein.

Figure 4 presents the evolution of CGE measured during the polymerizations. Notice that casein grafting with FC did not remain constant as in the cases with neat casein (L1 and L4).

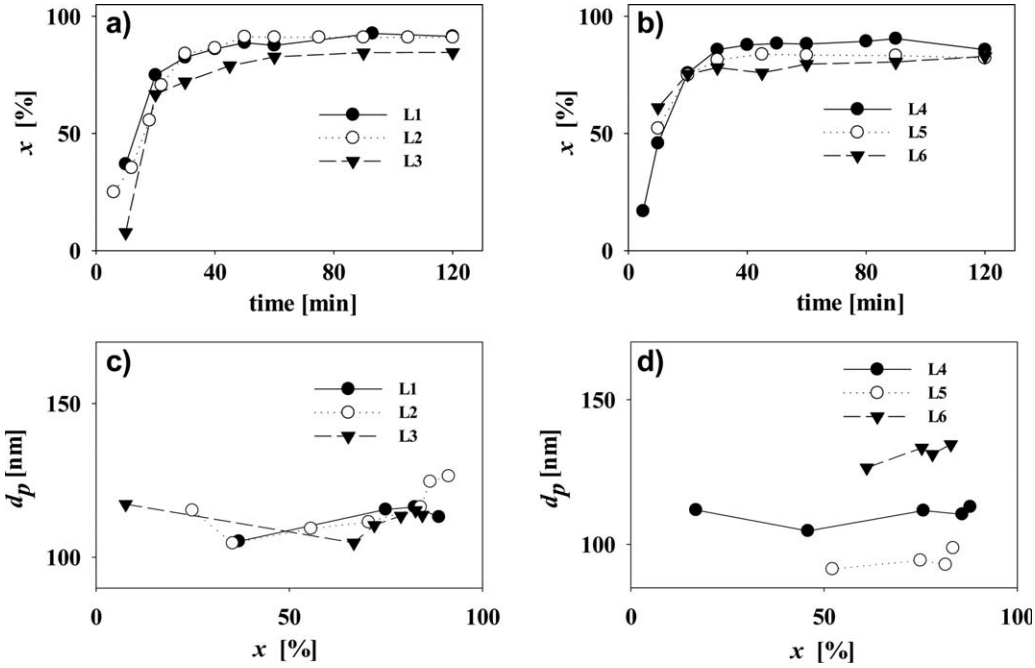

Figure 3. MMA polymerization in the presence of varied casein concentration (neat and FC). Evolutions of: conversion (a,b) and particle diameter (c,d).

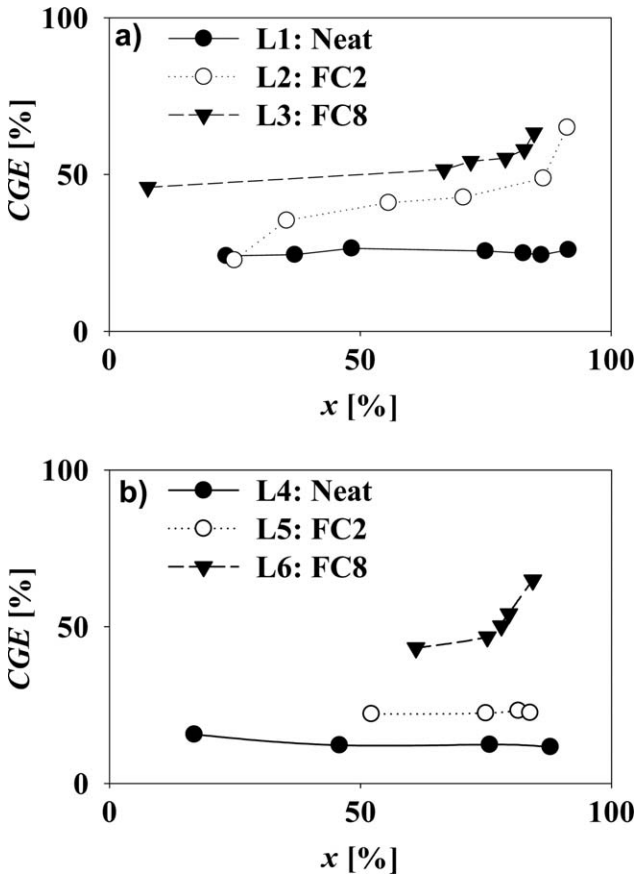

Figure 4. Evolution of CGE along the MMA polymerization in the presence of neat casein and FC at different concentrations. (a) 25 pphm of casein; (b) 50 pphm of casein.

With 25 pphm of FC2 the fraction of casein grafted at the beginning of polymerization was almost equal to that of the neat casein, but the further propagation of the FC vinyl bonds increased CGE. The increment in the number of propagating points per casein chain of FC8 gave higher levels of CGE from the beginning of polymerization, due to the early propagation of pendant acrylic groups of the FC. Notice that with FC, CGE evolution sharply increased at the end of the polymerization, indicating that propagation of pendant vinyl bonds of FC became more important when the MMA concentration was reduced.

Figure 5 shows the TEM micrographs of nanoparticles obtained with 25 pphm of neat casein (L1), and with functionalized casein FC8 (L3). Nanoparticles synthesized with neat casein present a looser stained structure in their border, which corresponds to the casein with a low degree of grafting [Figure 5(a)]. However, when using FC8 [Figure 5(b)], more compact nanoparticles are clearly observed, indicating a higher compatibility and a strong attachment between casein and acrylic polymer. This observation is supported by the higher CGE and AGE values obtained with FC.

Synthesis of Casein/Poly(BA-MMA) Based Nanoparticles

The functionalized caseins were also used in the copolymerization of different BA/MMA monomer formulations with 20% of solids content employing the general recipe of Table I. Table III summaries the results obtained with 6, 12, and 25 pphm of both casein types (neat and FC) and a varied monomer ratio BA/MMA to maintain a constant theoretical glass transition temperature ($Tg = -10^{\circ}C$) for the resulting nanocomposite. Notice that, independently of the employed casein (neat or FC), the final x was appreciably lower with 6 pphm of protein than with 12 and 25 pphm. This behavior was expected because the reaction is started by the presence of amino and *tert*-butoxy radicals, produced by interaction of the hydroperoxide molecules with the amino groups present in the casein backbone. Therefore, the lower the amount of casein, the smaller the quantity of amino groups available for interacting with the TBHP. As a consequence, the radical concentration was decreased.

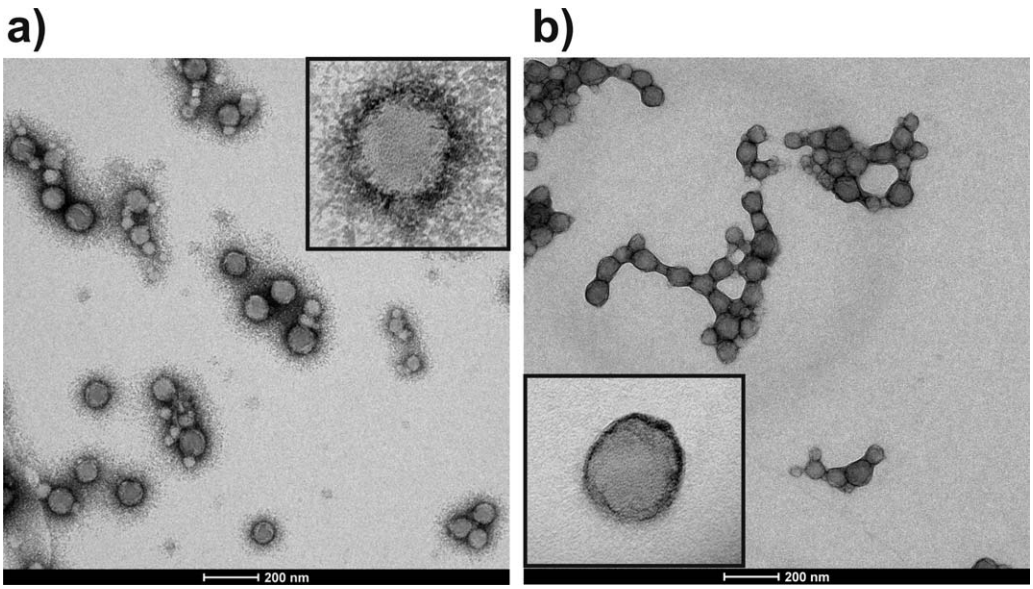

Figure 5. TEM micrographs of the hybrid latexes (a) L1 (neat casein) and (b) L3 (FC8).

Table III. Copolymerizations of BA/MMA in the Presence of Varied Neat Casein and FC Concentration. Main Characteristics of the Final Latexes

Entry	Casein (pphm)	BA/MMA	x (%)	d_p (nm)	CGE (%)	AGE (%)
L7	Neat (6)	65/35	58	166	63	38
L8	FC2 (6)	65/35	70	162	65	52
L9	FC8 (6)	65/35	39	247	98	56
L10	Neat (12)	70/30	83	154	42	54
L11	FC2 (12)	70/30	86	159	40	74
L12	FC8 (12)	70/30	86	270	89	83
L13	Neat (25)	80/20	91	122	37	81
L14	FC2 (25)	80/20	84	151	35	81
L15	FC8 (25)	80/20	86	262	84	86

Unstable latex with appreciable coagulum content.

Although the final *x* was not importantly affected by the use of FC instead of neat casein, particle diameters were significantly bigger with FC8 than those obtained with either neat protein or FC2. The higher d_p obtained with FC8 was probably due to the poorer stabilization provided by FC8, as the Z-potential of FC8 was drastically dropped with respect to neat casein. In the case of L9, the reduced stabilization power of FC8 together with its low content (6 pphm) became this latex unstable, forming coagulum and affecting the measuring of *x*.

While no appreciable improvement in CGE was observed by including the crosslinkable protein FC2, the fraction of acrylic grafted was increased with respect to that of neat casein, as a consequence of the available pendant vinyl bonds onto FC2 (Table III). The incorporation of FC8 importantly enhanced both CGE and AGE, independently of the FC8 content of the latexes, where almost all of the loaded protein contained grafted acrylic polymer (CGE resulted higher than 80%).

Evaluation of Casein/Poly(BA-MMA) Based Films Compatibility

Table IV shows the tensile test results of hybrid casein/acrylic films together with those of pure casein and pure acrylics, indicated with the BA/MMA ratio: 65/35, 70/30, 80/20. On the one hand, it can be observed that the incorporation of a hard brittle component, as casein, became hybrid films less resistant to deformation, i.e., breaking at lower elongation, than pure acrylic films. On the other hand, it was found that hybrid films were able to support higher deformations (with lower tensile strength), than that observed for pure casein film. It could be also noted that incorporation of FC2, for instance L8 and L11 reactions, where only increased the fraction of acrylic grafted without modifying the casein grafting, enhanced elongation of hybrid films. When both grafted acrylic and casein were importantly increased by incorporating FC8 (L9, L12, and L15), the elongation of hybrid films was significantly improved, resulting hybrid materials with the highest elongation at break. This is an indication that when the amount of free hard brittle component is substantially reduced (or in other words, by increasing the casein compatibility with the acrylic polymer), the hybrid films achieved higher elongations closer to that of the pure acrylics. For example, the case of film L9, with the lowest content of FC8 (6 pphm) and an almost lacking of ungrafted casein (CGE = 98%), reached an elongation as good as that of the pure acrylic.

Since casein has a hydrophilic character, it was observed that pure casein films presented a very poor resistance to water immersion, disintegrating immediately after immersion (WL_W = 100%, Table IV). In contrast, acrylic films presented a very good resistance to water immersion with a moderated A_W. Therefore, the incorporation of acrylic polymer into casein should improve the water resistance, but contrary to what expected, films obtained with neat casein also disintegrated after water immersion (WL_W = 100%). This poor water resistance is

Table IV. Film Properties of Casein/Poly(BA-MMA) Nanocomposites

Film	Tensile test		Water resistance			MEK resistance	
	Tensile strength (MPa)	Elongation at break (%)	A_W (%)	Immersion time (min)	WL_W (%)	A_{MEK} (%)	WL_{MEK} (%)
Casein	45.9[14]	8[14]	-	-	100	4	11
BA/MMA (65/35)	2.9	1418	18.0	<10080	0.6	-	100
L7	3.2	720	-	-	100.0	183.9	61.3
L8	2.9	835	48.8	10	30.0	170.3	25.6
L9	1.4	1564	98.5	40	27.3	166.7	24.4
BA/MMA (70/30)	2.5	1886	25	<10080	0.7	-	100
L10	2.4	652	-	-	100.0	166.7	36.7
L11	1.6	964	117.7	20	16.9	99.4	26.6
L12	2	1324	240.4	360	19.1	96.8	26.7
BA/MMA (80/20)	0.63	4698	28	<10080	0.6	-	100
L13	5.4	370	-	-	100.0	70.6	23.8
L14	2.9	313	132.2	30	27.5	59.5	20.8
L15	3.0	730	361.1	1440	22.2	84.2	18.0

Immersion time before presenting film damages.

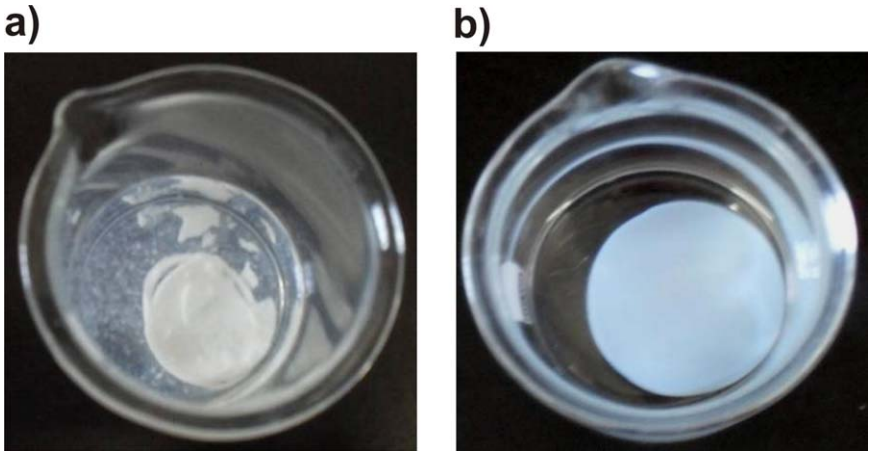

Figure 6. Picture of water resistance experiments of: (a) film L13 immediately after water immersion and (b) film L15 before presenting damages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

related with the low compatibility achieved when neat casein is used, where a high amount of ungrafted casein is present in the film. The ungrafted protein is transferred to the water phase and this migration process disintegrates the films. Figure 6(a) shows the film specimen of L13 immediately after water immersion. The incorporation of FC considerably improved the resistance to water immersion (Table IV), increasing the immersion time before presenting damages (Figure 6(b) shows the film specimen of L15 swollen by immersion in water). It could be noticed that film specimens presented damages earlier as lower were both FC film content and degree of compatibilization (i.e., films with higher water resistance were obtained with FC8 than with FC2). It is observed that despite A_W increased with the degree of compatibilization, likely because of the higher swelling of the films due to the greater immersion time, the percentage of dissolved mass (WL_W) decreased.

Acrylic films were completely swollen when they were immersed in MEK ($WL_{MEK} = 100\%$, Table IV). The incorporation of a hydrophilic component, as casein, improved the organic solvent barrier, where all hybrid films resisted the 7 days of immersion in MEK. For the same casein content, it was observed in most of the cases that both A_{MEK} and WL_{MEK} were reduced by increasing the grafted fraction of both casein and acrylic.

The superior compatibility achieved by increasing the grafting between both components clearly enhanced the synergy between hydrophobic and hydrophilic materials. The results of tensile test and resistance to both water and MEK showed that by enhancing the compatibility between both components the film properties were considerable improved.

CONCLUSIONS

Waterborne acrylic-casein nanoparticles are technologically important because they attempt to achieve outstanding properties with respect to the neat materials by chemically linking both components. The evaluation of casein/acrylic films showed that the synthesis strategy based on primary radical formation onto the protein chains through the redox initiation between the casein amino groups and a hydroperoxide, did not achieve the required degree of compatibilization to guarantee the synergic effect between both components. A crosslinkable casein has been synthesized which, in addition to the characteristic grafting capacity by redox initiation with hydroperoxide, contained pendant acrylic groups able to be radically polymerized. Compared with the neat casein, the use of FC significantly enhanced the compatibilization of hybrid nanoparticles obtained by emulsion polymerization of acrylic monomers. In the MMA polymerization, the use of FC proved to significantly overcome the limit degree of grafting achieved by only using the radical formation onto the amino groups of casein (around of 50% of grafted PMMA). The improved compatilization reached with FC considerably enhanced the film properties, measured by the mechanical behavior and the resistance to water and organic solvent, showing higher synergy between casein (a hydrophilic material) and acrylic polymer (a hydrophobic material).

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