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High biobased content waterborne latexes stabilized with casein

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ABSTRACT

Growing environmental regulations are enforcing the synthesis of sustainable and ecofriendly materials. While waterborne processes, as emulsion polymerization, allow producing polymeric materials with low solvents emission, the reduction of their carbon footprint can be achieved by replacing petroleum-derived raw materials by biobased reagents. In this scenario, this work aims to synthesize high biobased content waterborne latexes by emulsion polymerization of two partially biobased commercial monomers (2-

octyl acrylate, OA, and isobornyl methacrylate, IBOMA) in presence of previously methacrylated casein (bovine milk protein), which acts as a surfmer (i.e., an emulsifier capable of being radically polymerized). The kinetic study of the emulsion polymerization of OA and IBOMA allows optimizing the formulation, thus resulting that the incorporation of a low fraction of a more soluble monomer is required to reach acceptable polymerization rates and high monomer conversion. The as-obtained films show promising performance in terms of their mechanical properties, resistance to solvents and biodegradability in organic compost, which could pave the way for the synthesis of high biobased (>75 %) content binders for waterborne coatings.

1. Introduction

Over the last decade, health and environmental concerns within the polymers industry have forced researchers and manufacturers to shift to sustainable, eco-friendly and energy efficient systems. Based on current capabilities, the coatings and adhesives industry has pursued various approaches for improving these points. In this sense, waterborne polymers produced by emulsion or miniemulsion polymerization appear as an ecological alternative to solvent-borne resins, reducing the emission of volatile organic compounds (VOCs).[1] On the other hand, to achieve more sustainable systems and decrease significantly the carbon footprint (which comes mainly from the raw materials) of polymeric products, there is a trend and industrial interest to replace oil-derived monomers by biobased or renewable sources.[2–4] In this context, the synthesis of hybrid materials based on proteins, such as casein, zein, collagen, among others, has been reported, because natural proteins provide several advantages, like excellent biodegradability, biocompatibility, low toxicity, and sometimes they can be obtained as a byproduct of other industries which favors circular economy.[1,5–7] Furthermore, due

to the presence of different amino acids in the proteins structure, many functional groups such as ammonia (-NH₃), amine (-NH₂), thiol (-SH) and carboxylic acids (-COOH) allow the protein chemical modification, to improve their properties or to obtain a polymerizable building block.[1,8–10]

More specifically, casein, a milk protein, has been widely studied for obtaining waterborne coatings, through the synthesis of acrylic/casein nanocomposites. The amphiphilic character of casein allowed the emulsifier-free synthesis of latexes by emulsion polymerization,[11] and it gave great advantages to the final material, such as a good film forming ability, balanced mechanical properties (hardness, flexibility and blocking resistance), and partial biodegradability.[12] However, the found optimal protein content was low because a high casein content significantly degraded the water resistance of the resulting hybrid films. Therefore, the chemical modification of casein to obtain a polymerizable protein (i.e., containing vinyl bonds in its molecule) was pursued to promote the grafting between the acrylic phase and the protein phase; thus, reducing the hydrophilic character of casein.[13,14] Despite this approach represented an important advance toward the production of nanocomposites with higher casein content, the total biobased content of the final coating material remained relatively low (close to 20-33%).[15] Therefore, a promising alternative to increase the final biobased content of the material would be the use of biobased monomers.

Although in the last decade most of the biobased monomers have been used to produce thermosetting polymers (phenolic compounds, polyepoxides, polyurethanes) and thermoplastic polymers (polyesters, polyamides) by step growth polymerization in bulk or solution,[4,16,17] there are many novel biobased monomers designed to react by free radical polymerization in dispersed media (e.g., suspension, emulsion and miniemulsion).[3,4,18] In this sense, monomers derived from vegetable oils (2-octyl

acrylate, isobornyl acrylate, piperonyl methacrylate, soybean acrylated macromonomer), fatty acids (methyl erucate derivated, acrylated ricinoleic acid, acrylated methyl oleate, oleic methacrylate, linoleic methacrylate), pine resin (isobornyl methacrylate) or glucose (isosorbide monomethacrylate),[4,19–25] have been used to replace petroleum-based monomers such as styrene, (meth)acrylic acid esters (e.g. 2-ethylhexyl acrylate, butyl acrylate, methyl methacrylate) among others, in the synthesis of coatings, industrial interior wood finishes, and pressure sensitive adhesives.[2,4,22]

In this work, the synthesis of casein-based hybrid nanocomposites with increasing final biomaterial content was studied through batch emulsion polymerization using casein as polymeric stabilizer. For this purpose, two biobased monomers were used, isobornyl methacrylate (IBOMA) and 2-octyl acrylate (OA), derived from pine resin and castor oil, respectively.[22] To investigate the effect of incorporating these biobased monomers, similar latexes were synthesized using oil-based methyl methacrylate, MMA, and butyl acrylate, BA, as the reference, while keeping the theoretical glass transition temperature (T_g) of the acrylic copolymer equal to $-10\text{ }^\circ\text{C}$. To this effect, the soft monomer component (BA), with a homopolymer T_g of $-54\text{ }^\circ\text{C}$, was replaced by OA of 73% bio-renewable content and a homopolymer T_g close to $-44\text{ }^\circ\text{C}$; and the hard monomer (MMA), which has a homopolymer T_g near $105\text{ }^\circ\text{C}$, was replaced by the IBOMA of 71% bio-renewable content and a homopolymer T_g of $150\text{ }^\circ\text{C}$. Different monomers' formulations were tested with the goal of maximizing the biomaterial content in the final material. The effect of monomer formulation on polymerization kinetics and particle nucleation mechanism, and on relevant films properties, such as water resistance, biodegradability and mechanical behavior, were evaluated.

2. Experimental

Materials

Technical grade casein from bovine milk (Sigma) was used as natural protein, glycidyl methacrylate (GMA, Aldrich) as functionalization reagent, methyl methacrylate (MMA, Aldrich) and butyl acrylate (BA, Aldrich) as petroleum-based monomers and isobornyl methacrylate (IBOMA, Visiomer Terra) and 2-octyl acrylate (OA, Arkema) as biobased monomers. Tert-butyl hydroperoxide (TBHP, water solution containing 70% of active initiator, Aldrich) was employed as initiator and sodium carbonate (Na_2CO_3 , Aldrich) as buffer. Other reagents used were: Bruggolite 7 (FF7, Brügemann Chemical), tetrahydrofuran (THF, Cicarelli), sodium dodecyl sulphate (SDS, Anedra), Alkyldiphenyloxide disulfonate (Dowfax 2A1, solution containing 45% of active surfactant, from Dow Chemical), methyl ethyl ketone (MEK, Anedra) and organic compost (45% total solid content on a wet basis; 40% non-volatile solids content on a wet basis; pH 6.5, from Terrafertil). All the reagents were used without further purification and distilled-deionized water was used throughout the work.

Polymerization process

The casein based latexes were synthesized through a two-step procedure which involves first a casein methacrylation with GMA, and its later use in the emulsion polymerization of vinyl monomers, initiated by redox couple formed by TBHP and the amino groups of casein.[26] Functionalized casein with 8 methacrylic groups per molecule of protein was used. This modification was carried out following the procedure described in Picchio *et al.*[13], which involves an amine-glycidyl ether reaction. For this, the casein was dissolved in a water solution of Na_2CO_3 (0.4%, pH = 11) at 50 °C, then GMA was added, and kept under stirring for 4 hours at the same temperature. After obtaining the methacrylated casein, the solution temperature was raised up to 80 °C and the monomers

mixture was loaded. The resulting emulsion was purged with N₂ for 30 min before injecting the TBHP. Table 1 presents a general recipe, for the synthesis of a hybrid latex, while detailed recipes of all experiments are listed in Table S1 of the supporting information (SI). Formulation was adjusted to produce an acrylic polymer with a theoretical T_g equal to -10 °C. For synthesizing the protein-free latex, 1% wbm of Dowfax 2A1 was used as surfactant to replace casein, and TBHP-FF7 as redox initiator couple. Casein functionalization and polymerizations were carried out in a 500 ml jacketed reactor equipped with thermostatic bath, mechanical stirrer, a reflux condenser, digital thermometer, N₂ inlet, and a sampling device.

Table 1. General recipe for the synthesized hybrid latexes

Reagent	Amount (% wbm ^a)
Monomer mixture	100
Casein	25
TBHP	0.17
Na ₂ CO ₃	0.9
H ₂ O	225

^(a)wbm: weight based on monomer mixture.

Latex characterization

The monomer conversion (x) was determined gravimetrically and calculated as the weight ratio between the acrylic polymer and the initial amount of monomers in the recipe (casein was not considered in the calculation). Average particles' diameter (D_p) was measured by dynamic light scattering (DLS), Nanosizer (Malvern) at 25 °C. The casein grafting efficiency (CGE), defined as the fraction of casein grafted to the acrylic polymer, was determined by measuring the concentration of soluble free casein in the latex.[26] For this, multiple washing stages with deionized water and SLS solution were applied onto the diluted latex (1 % of solids), to separate the free casein (ungrafted protein). The

concentration of free protein was measured by UV spectroscopy in a Perkin-Elmer Lambda 25 UV-Visible spectrophotometer, by combining the peak area at 280 nm with a calibration curve of different casein concentration.

Film characterization

The polymeric films were prepared by casting the latexes in silicone molds, for 7 days at 25 °C and 55% of relative humidity (RH).

For tensile tests, four specimens of each sample were cut with dumbbell shape according to ASTM D882 (9.53 mm of length and 3.18mm×1mm of cross section). The tests were carried out in a universal testing machine TA HD plus Texture Analyzer equipment (Texture Technologies), at 23 °C and 50 % relative humidity, by applying an elongation rate of 25 mm/min, according to ASTM D638.

For water and organic solvent resistance analysis, two specimens of each sample (discs of 10 mm of diameter and 1 mm of thickness) were immersed during 6 hours in distilled water or MEK at room temperature. At a regular time, disc samples were removed from the respective solvent, dried with an absorbent paper, weighted and immersed again. The water and MEK absorption (A_W and A_{MEK} , respectively) were determined by the difference between the mass of the swelling film with respect to the initial dried one.

The surface hydrophobicity of the material was determined by measuring the static contact angle (CA) of water on film surfaces. To this effect, six distilled water droplets of 20 μ L each were deposited onto dried films surface (120 μ m wet thickness). CA were processed by the LBADSA method which was implemented as a java plug-in for the ImageJ software.[27]

The biodegradation ability of the hybrid films in composting conditions, were determined after burying two sample discs (10 mm of diameter) into a vessel containing moisturized commercial compost. Soil burial degradation tests were run under controlled conditions

(55 % RH of compost moisture at 30 °C). Samples were removed at 30 and 60 days, carefully cleaned and then dried in an oven at 70 °C up to a constant weight. The biodegraded fraction of the film was determined as the mass fraction lost from the initial film, and expressed with respect to the total casein loaded.

3. Results and discussion

In the present work, the synthesis of high biobased waterborne latexes stabilized with casein has been explored. For this, hybrid latexes with 25% of protein were synthesized by emulsion polymerization using biobased monomers to increase the total biobased content of the final material. First, the emulsion polymerization of OA and IBOMA stabilized by native and functionalized casein was attempted, and compared with the copolymerization employing a conventional surfactant.

Emulsion copolymerization of IBOMA and OA in the presence of casein (native or functionalized)

The theoretical biobased content and results of \bar{x} , D_p and CGE of the investigated emulsion copolymerizations of OA and IBOMA are summarized in Table 2.

Table 2. *Emulsion polymerization of biobased monomers (OA/IBOMA=72/28 w/w) in the presence of native or functionalized casein.*

Experiment	Casein	Biobased fraction ^(b) (%)	\bar{x} (%)	D_p (nm)	CGE (%)
OA/IBOMA ^(a)	-	72.4	90	142	-
CN-OA/IBOMA	Native	78.0	96	126	25.7 ±0.8
CF-OA/IBOMA	Functionalized	78.0	3	-	-

^(a) Free casein experiment with Dowfax 2A1 as emulsifier and TBHP-FF7 as redox initiator. ^(b) Calculated from the theoretical recipe.

As can be seen in Figure 1 and Table 2, there is a big difference when employing native or functionalized casein. While batch emulsion copolymerization of OA and IBOMA did not proceed with functionalized casein (CF) (experiment CF-OA/IBOMA),

copolymerizations with Dowfax 2A1 and native casein (CN) yielded a high conversion close to 90 and 96 % for OA/IBOMA and CN-OA/IBOMA experiments, respectively. Although a micellar particle nucleation is expected when Dowfax 2A1 is used as emulsifier and the couple TBHP-FF7 as initiator, the formation and growth of hybrid casein-based particles follows a different polymerization mechanism (summarized in Figure S1 of the SI), as it was presented by Li *et al.*[11] and Picchio *et al.*[26]. According to this mechanism, before starting the polymerization, the reaction system is composed by casein (dissolved in aqueous phase and forming micelles) and monomers (partially solubilized in the aqueous phase, forming droplets, and swelling the hydrophobic interior of the casein micelles). When TBHP is incorporated, the redox initiation between this initiator and the amino groups of the casein produces 2 propagating species in the aqueous phase, amino and tert-butoxy radicals.[11] These radicals could promote different particle formation mechanisms, which depend on the radical nature[26] and the monomer availability in the water phase. While paths I and II involve the propagation of both radical species with the soluble monomer in water phase until self-assembling in particle precursor nanodomains, in path III the rather hydrophobic tert-butoxy radicals produced in the aqueous phase could enter into the casein micelles swollen with monomer and form a polymer particle with an equivalent mechanism to the classical micellar nucleation. In the CN-OA/IBOMA and CF-OA/IBOMA experiments, the very low solubility of monomers OA and IBOMA (Table S2 of the SI) significantly reduces their availability in the aqueous phase, hindering the particle formation paths I and II (Figure S1).

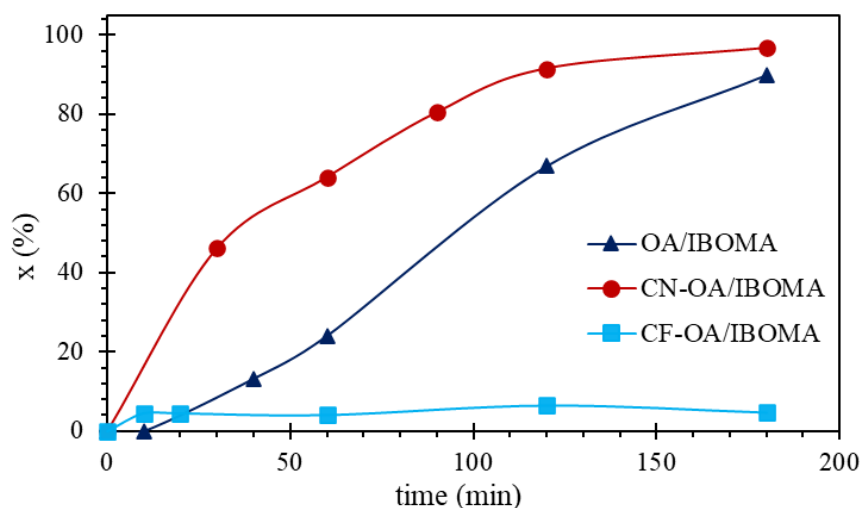


Figure 1. Monomer conversion obtained in the emulsion polymerization of biobased monomers (OA/IBOMA=72/28) in the presence of native or functionalized casein, compared with the free casein experiment.

Figure S2 and Table S3 of the SI compare the emulsification capability of both proteins used (CF and CN), where the critical micellar concentration (CMC) of casein was only slightly affected by the methacrylation process. As particle formation is expected to occur by micellar nucleation due to the very low solubility of the biobased monomers (path III of Figure S1 of SI), the low polymer yield obtained when CF is used cannot be attributed to its slight difference in the emulsifier capability. In this scenario, the partially water soluble CF which contains vinyl bonds in its backbone could act as radicals sink, consuming the tert-butoxy radicals produced by redox initiation reaction in the aqueous phase. This reaction which involves the incorporation of tert-butoxy units onto the casein backbone is not enough to change the protein water solubility and promote the particle formation via the nucleation path II (Figure S1 of SI). It is worth remarking that the concentration of vinyl bonds provided from methacrylated casein (2.87×10^{-2} mol/L) is much higher than that of TBHP (8.13×10^{-3} mol/L).

Although a hybrid casein-based latex using biobased monomers and containing native casein was synthesized, the resulting material presented very low water resistance (see, Figure S3, of the SI) as a result of the low CGE that it presents (25.7 %, Table 2). In other words, the use of native casein results in a nanocomposite with low degree of compatibilization between the protein and the acrylic phase.[13] Therefore, in the following section we explore polymerization strategies that use methacrylated casein to improve the compatibility between both phases and for producing highly water resistant films.[13,14]

Synthesis of hybrid latexes based on functionalized casein, employing biobased and petroleum-based monomers

First, emulsion copolymerization stabilized with functionalized casein and monomers with higher water solubility were attempted to favor nucleation of particles by paths I and II mechanism in Figure S1. Oil-based BA and MMA were copolymerized first and the combination of BA and IBOMA and OA and MMA were also considered; in all cases targeting the same theoretical T_g of the copolymer. Table 3 and Figure 2 presents the characterization of the latexes and the evolution of the conversion, respectively.

However, unlike the case where both biobased monomers were used with CF, polymerization yields conversions higher than 90% in the presence of at least one of the oil-based monomers, either BA or MMA (Figure 2). This should be due to the higher water solubility of the oil-monomers (MMA and BA), compared with the biobased monomers (OA and IBOMA). Thus, the particle nucleation mechanism route depends on the availability of vinyl bonds in the water phase (see Table S4 of the SI). When MMA is present in the monomer mixture (CF-BA/MMA and CF-OA/MMA) the vinyl bonds available in the aqueous phase (0.164 and 0.158 mol/L, respectively) exceed those provided by CF (0.0287 mol/L). In the case of CF-BA/IBOMA, although the vinyl bonds

available in water (0.016 mol/L) are lower, it is comparable with CF vinyl contribution. Also, due to BA and MMA concentration in the formulation exceeds their water solubility, the estimated monomer availability in aqueous phase of Table S4 of the SI could be maintained while monomer droplets are present in the polymerization media. Once monomer droplets disappear, the monomer concentration in the water phase would continuously decrease as the polymerization proceeds. This hypothesis is true if both monomers present similar reactivity ratio, but when they are highly different the distribution of monomers through the phases is affected. Despite that, these results indicated that the presence of a minimum amount of a monomer soluble in water is required for the polymerization to proceed to high conversions.

Table 3. Emulsion polymerization of biobased monomers in the presence of functionalized casein. Effect of replacing biobased monomer by its analogous petroleum-based monomer.

Experiment ^(a)	Monomer mixture ^(b)				Biobase fraction (%) ^(c)	x (%)	Dp (nm)	CGE (%)
	BA	MMA	OA	IBOMA				
CF-BA/MMA	60	40	-	-	20	90	154	59.7 ± 8.8
CF-OA/MMA	-	37	67	-	59.1	92	144	65.7 ± 5.1
CF-BA/IBOMA	65	-	-	35	39.9	93	130	54.2 ± 0.6

^(a) All polymerizations were made with functionalized casein. ^(b) The comonomer ratio was selected to obtain a Tg of the acrylic phase close to -10°C, according to the Fox expression.[28]

^(c) Calculated from the theoretical recipe.

On the other hand, as it can be seen in Table 3, the partial replacement of the petroleum-based monomer had a small effect on the final diameter of the particles, and on the degree of protein grafting, which were similar to the values obtained when only oil-based monomers were used. As expected, the incorporation of functionalized casein allowed to obtain a higher degree of protein grafting (CGE higher than 50%, for the three cases), compared to the use of non-functionalized casein (CGE = 25.7%), demonstrating the importance of using modified protein. Due to this high degree of CGE, the obtained three

materials resisted water immersion for 6 h without disintegrating (these results will be discussed in “*Application properties obtained from hybrid films*” section).

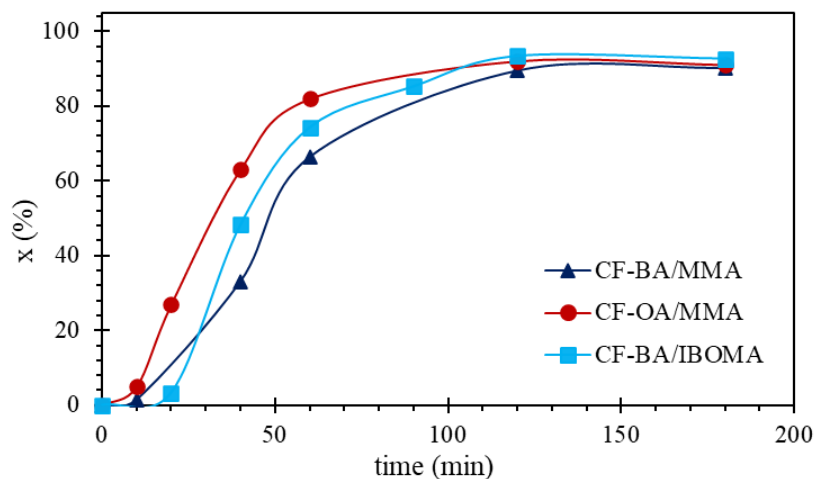


Figure 2. Monomer conversion obtained along the emulsion copolymerizations described in Table 3 with CF, employing BA, MMA and biobased monomers (OA and IBOMA) in the formulation.

Synthesis of waterborne nanocomposites based on functionalized casein and biobased monomers. Optimization of biobased content.

According to the previous results, the synthesis of waterborne latex containing functionalized casein and OA/IBOMA required the presence of a monomer with some water solubility to promote particle nucleation and the progress of the polymerization. Therefore, it follows that it should be possible to synthesize OA/IBOMA copolymers stabilized by modified casein if sufficient amount of a monomer available in the aqueous phase. For the sake of simplicity, this was assessed by incorporating a small amount of MMA (a monomer with substantially higher water solubility than OA and IBOMA, see Table S2) to the formulation as displayed in Table 4. As it can be seen, the OA fraction in the monomer mixture was kept constant, while a small amount of IBOMA was replaced

by MMA. In this way, the biobased fraction of the final material was minimally reduced from 78% when OA/IBOMA was used in the monomer mixture, to 75% when the maximum explored amount of MMA (5%) was incorporated.

Table 4. Emulsion polymerization of biobased monomers with functionalized casein as stabilizer, incorporating a small amount of MMA.

Experiment ^(a) CF-OA/IBOMA/	Monomer mixture			Biobase fraction (%) ^(b)	x (%)	Dp (nm)	CGE (%)
	OA	IBOMA	MMA				
MMA_0	72	28	0	78.0	3	-	-
MMA_1	72	27	1	77.4	7	-	-
MMA_3	72	25	3	76.2	79	125	56.3 ±4.9
MMA_4	72	24	4	75.7	90	126	67.9 ±3.6
MMA_5	72	23	5	75.1	95	127	63.5 ±1.5

(a) All polymerizations were made with functionalized casein. (b) Calculated from the theoretical recipe.

As it can be seen in Figure 3, the addition of 1% of MMA (MMA_1) was not enough for the polymerization to proceed and conversion was just some points higher than that obtained in the experiment without MMA. This could be due to the fact that the availability of double bonds provided by the monomers in the aqueous phase (0.032 mol/L, Table S4 of the SI) was similar to that provided by functionalized casein (0.0287 mol/L), and after the consumption of this amount of MMA, polymerization did not proceed.

When MMA content was increased to 3% in the formulation, the polymerization progressed slowly reaching 79% conversion after 3 hours of reaction. Furthermore, by increasing the content of MMA to 4 and 5% (experiments MMA_4 and MMA_5), conversions higher than 90% were reached, indicating that these amounts of MMA allowed particle nucleation and polymerization to progress until acceptable values of polymer yield. It is noteworthy to note that in the four considered cases, the MMA concentration in the aqueous medium is below the saturation conditions (Table S2 in the SI) and it increases as the amount of MMA in the monomer mixture is augmented, thus

contributing to increase the water phase polymerization. The strategy of incorporating only a small amount of MMA allowed to optimize the biobased fraction content of nanocomposites without degrading final monomer conversion.

Figure S4 of the SI shows the cryo-TEM of latex MMA_5 where free casein was removed, with its respective particle size distribution. Spherical particles with a broad particle size distribution were synthesized in agreement with the data reported by Picchio *et al.* when functionalized casein was employed with oil-based monomers.[13]

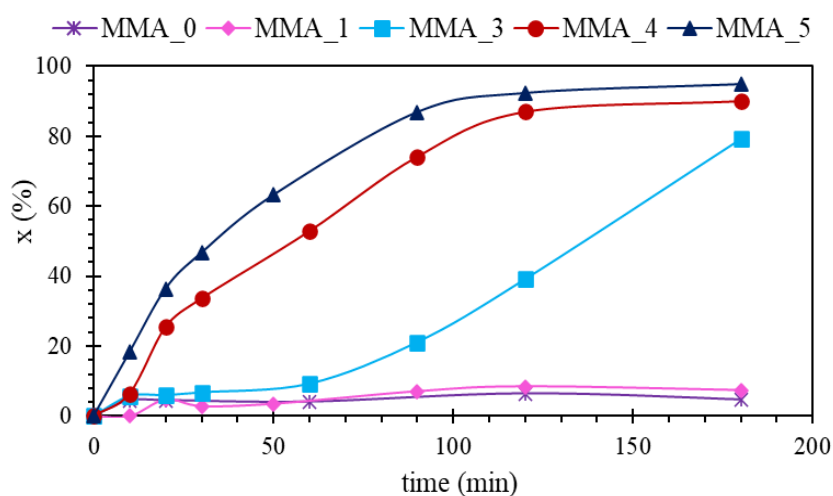


Figure 3. Monomer conversion obtained in the emulsion copolymerization with CF of OA/IBOMA by incorporating a small amount of MMA in the bio-monomer formulation.

Application properties obtained from hybrid films with high biobased content

In this section the results of the characterizations of the materials synthesized in the previous section (CF-BA/MMA; CF-OA/MMA, CF-BA/IBOMA, MMA_4 and MMA_5) are shown. The results for MMA_0 and MMA_1 were not included because of the obtained monomer conversion was almost nil. In the case of MMA_3, the obtained monomer conversion after 4 h of reaction was relatively low (79%), so the obtained film exhibited a higher protein/polymer ratio, resulting the comparison with those achieved

from MMA_4 and MMA_5 latexes not adequate. It should be mentioned that only the most relevant properties are presented in the main text, and the rest can be found in the SI (section S.4 of SI, which includes DSC, anti-blocking, and minimum film formation temperature results for the hybrid films).

, The incorporation of biobased monomers reduced the elongations at break of the films (Figure 4 and Table S6 of SI) as it was observed by Badia et al., when the MMA was substitute by IBOMA in PSAs formulations. Furthermore, the film obtained from CF-BA/MMA latex reached the maximum elongations at break at $184.7 \pm 13.9\%$, followed by the hybrid materials synthesized with a single biobased monomer ($123.3 \pm 8.3\%$ and $136.6 \pm 4.0\%$ for CF-OA/MMA and CF-BA/IBOMA, respectively), and finally the films containing both biobased monomers reaching the lowest elongations at break ($83.6 \pm 6.3\%$ and $82.5 \pm 5.3\%$ for MMA_4 and MMA_5, respectively). However, all samples showed similar tensile strength between 10.1 ± 0.4 to 15.3 ± 0.1 MPa. These results are in agreement with those reported by Picchio *et al.*, who showed that when the degree of compatibilization between casein and acrylic polymer was increased, the tensile strength of these materials was reduced and the elongation at break increased.[13]

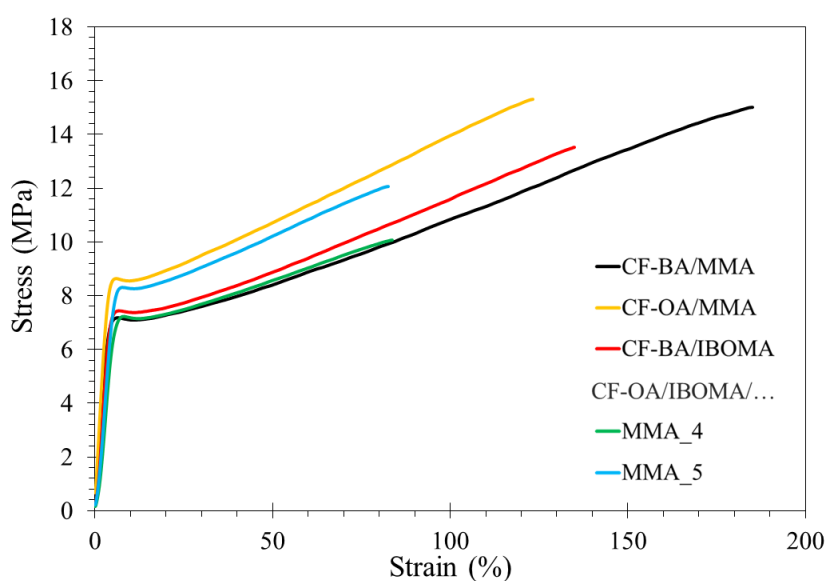
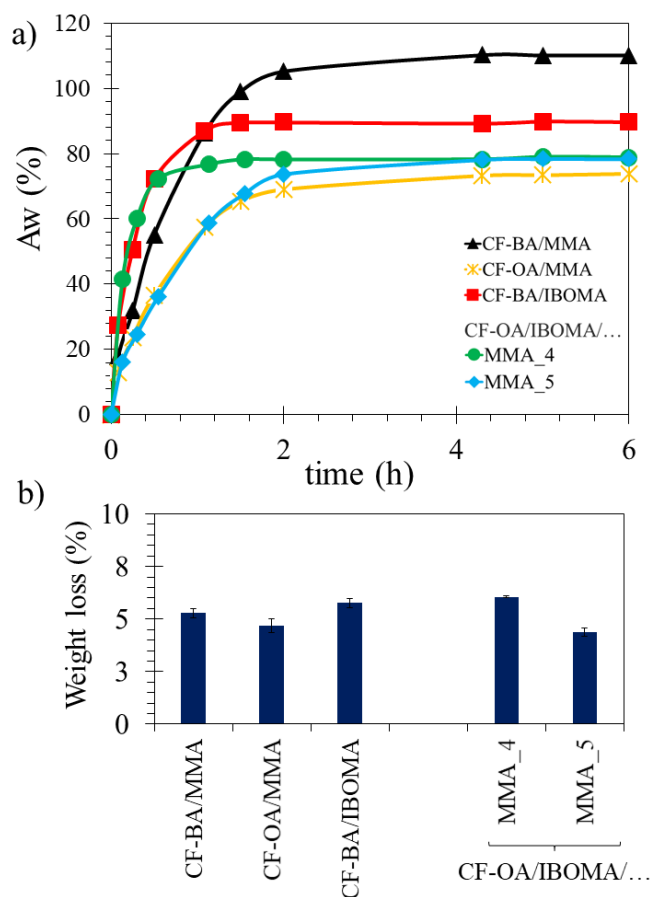


Figure 4. Stress-strain curves for hybrid films.

One may observe the advantage of incorporating the biobased monomers in the improvement of the water resistance of the final films, when it is compared to the material synthesized with only petroleum-based monomers ($A_w = 110\%$ for CF-BA/MMA). As it is known, a greater compatibilization between the protein and acrylic phases, that is, greater grafting of the protein, increases the water resistance of casein-based hybrid materials.[13] In this sense, the high degree of CGE reached by the CF-OA/MMA, MMA_4 and MMA_5 samples (66, 68 and 65%, respectively) contributed to the reduction of swelling, reaching an equilibrium value of A_w close to 80% (Figure 5.a). While, as expected in the case of CF-BA/IBOMA, the final A_w value was slightly higher ($\approx 90\%$), because this hybrid latex has a lower fraction of biobased materials and CGE (54%). Furthermore, after the absorption test, the weight loss suffered by the samples was determined (Figure 5.b), showing that for all hybrid films based on functionalized casein, the weight loss did not exceed the 6% of the initial value; contrary to CN-OA/IBOMA

film (in which casein native was used), where the film was completely disintegrated in



the same immersion time (Figure S3).

Figure 5. Water absorption (A_w) (a) and weight loss of films after 6 h of immersion (b).

The surface hydrophobicity, which is the ability of the material to repel water, can be an interesting application parameter for coatings. This can be measured by the contact angle (CA) formed by a drop of water deposited on the surface of the film, resulting in a more hydrophobic material when the CA formed is greater. In this sense, pure acrylic OA/IBOMA films have a high CA ($85.5 \pm 4.6^\circ$), after their surface was washed to remove the excess of emulsifier, in accordance with those reported for other equivalent systems.[29] However, hybrid materials present lower CA values (Figure 6), due to the hydrophilic character of the casein, which increased the water absorption and reduced their surface hydrophobicity. As shown in Figure 6, the CA increases slightly when increasing the biobased fraction of the films.

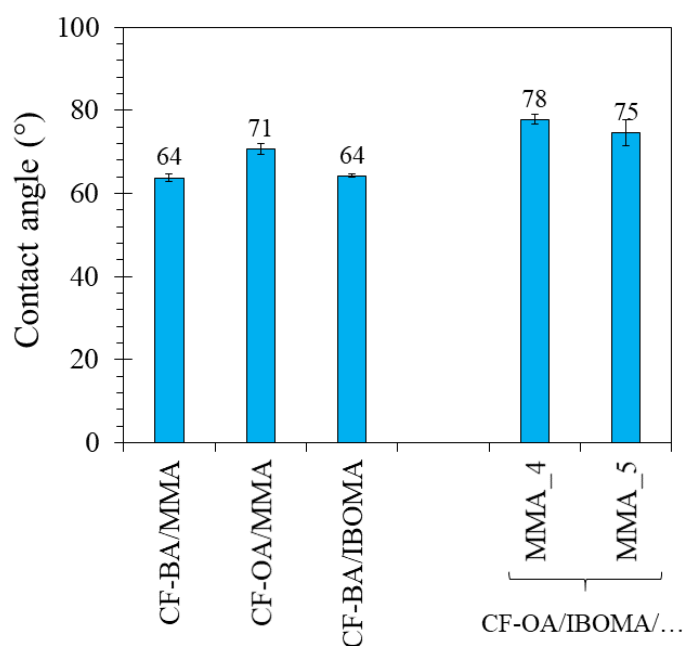


Figure 6. Surface hydrophobicity of hybrid films, determined by contact angle.

On other hand, as it can be seen in Figure 7, all materials showed good resistance to organic solvents (such as MEK), with a very low weight loss close to 4% (Figure 7.b), compared with pure acrylic film (without casein) which is dissolved in organic solvents.[30] The addition of casein gives hybrid materials resistance to organic solvents, due to the high insoluble fraction (> 90%) that these materials usually possess.[13] As can be seen in Figure 7.a, the MEK absorption values (A_s) were reduced by increasing the use of biobased monomers. In this way, films without biobased monomers reach an A_s value of 83.8%, while when incorporating one biobased monomer (CF-OA/MMA and CF-BA/IBOMA) it is reduced at 60 and 57%, respectively. The minimum values ($A_s = 41$ and 31%) were reached for the samples that contained the highest biobased fraction in their composition (MMA_4 and MMA_5, respectively).

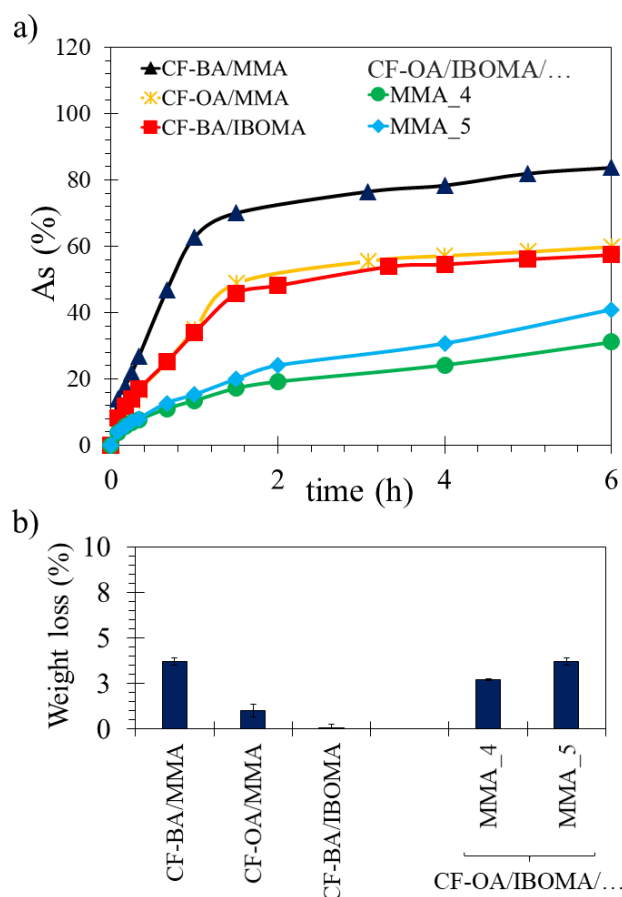


Figure 7. Organic solvent absorption (A_s) (a) and weight loss of films after 6 h of immersion (b). MEK was used as organic solvent.

The great advantage of casein-based hybrid materials is their ability to be partially biodegraded when they are buried in organic compost. As it can be seen in Figure 8, in a relatively short period of time (two months) all hybrid materials lost almost 70% of weight with respect to the loaded protein (i.e., the biodegradable fraction), equivalent to 15% of the total weight of the material; except for the hybrid material CF-BA/MMA, which reached a lower degradation (60%). These results show that the presence of biobased monomer in the hybrid films produced a slight improvement in the biodegradability of the casein phase.

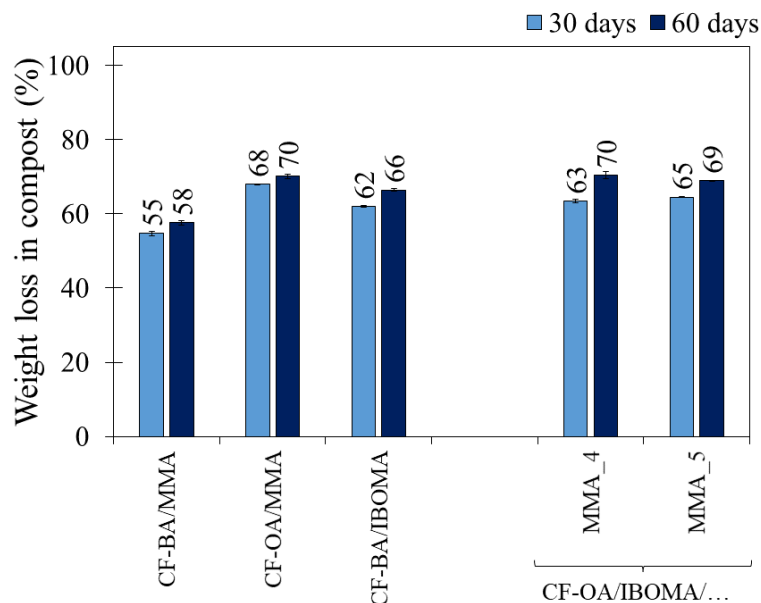


Figure 8. Biodegradability in organic compost of hybrid materials.

4. Conclusions

Casein-based hybrid materials with high final biomaterial content (up to 75%) were synthesized by batch emulsion polymerization. To this effect, two biobased monomers were used, isobornyl methacrylate (IBOMA) and 2-octyl acrylate (OA) to replace petroleum-based monomers, as MMA and BA. The very low solubility of biobased monomers played a determining role in the particle nucleation mechanism during polymerization. Thus, when methacrylated casein was used instead of native casein, polymerization of IBOMA and OA did not occur, because under these conditions (where monomers are scarcely available in water) the nucleation of particles did not occur and hence, polymerization stopped. This drawback was overcome by introducing a small amount of a more water-soluble monomer in the formulation. To proof the concept, MMA was used and it was found that between 3-4 wt% of MMA in the formulation was enough to produce waterborne latexes stabilized by casein with biobased contents above 75%. Note that the use of biobased monomers with higher water solubility is straightforward. Finally, it was demonstrated that the hybrid materials, especially the latexes containing 4

and 5 wt% of MMA, showed good mechanical properties and good water resistance ($A_w = 80\%$) compared to the equivalent material obtained from petroleum-based monomers ($A_w = 110\%$). In addition, the high biobased waterborne dispersions stabilized by casein were partially biodegradable in compost, losing approximately 70% of their degradable fraction after 2 months of burial. Even though the fraction of biodegradable material (with respect to the final material) is lower than that required by environmental regulations for biodegradable materials (e.g. microplastics EU regulation), it is remarkable the significant improvement in terms of sustainability provided by this biobased coatings.

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