ACRYLIC-CASEIN LATEXES WITH POTENTIAL APPLICATION AS ADHESIVES

A. AGUZIN[§], J.I. JERKOVICH[§], J. TRUCONE[§], L.I. RONCO,
R.J. MINARI and L.M. GUGLIOTTA

Facultad de Ingeniería Química (Universidad Nacional del Litoral), Santiago del Estero 2829 (3000) Santa Fe, Argentina
INTEC (Universidad Nacional del Litoral – CONICET), Güemes 3450 (3000.), Santa Fe, Argentina
lgug@intec.unl.edu.ar
[§] *These authors made the same contribution to the work*

Abstract ⎯ **The replacement of monomers derived from petrochemical sources by biopolymers like proteins, together with the development of new materials with improved properties, have an increasing importance in industrial applications. In this context, the synthesis of acrylic-casein hybrid latexes was investigated through a low environmental impact strategy, such as the surfactant-free emulsion polymerization, with the aim of producing new industrial adhesives. Different aspects of the synthesis of hybrid latexes were addressed, such us i) the use of variable content of protein; ii) the control of grafting degree between polymers, using native casein (without chemical modification) or functionalized casein, and iii) the employment of a chain transfer agent to reduce molecular weights of the acrylic polymer. The effect of the analyzed variables on the polymerization kinetics, the degree of compatibility between polymers, and the application properties of the produced latexes as adhesives were investigated.**

Keywords ⎯ **Hybrid latex, Acrylic-casein, Adhesive.**

I. INTRODUCTION

Adhesives must meet many requirements, including to keep the substrates attached during the product useful life, even when it is exposed to important variable conditions (e.g., changes in temperature and humidity, or water exposure); but also to favor the adhesive removal during the recycling process (Houtman *et al*., 2004), as in the cases of bottle labeling and the cardboard industry. Currently, these demands are covered by different families of adhesives formulated on the basis of: i) synthetic acrylic latexes, ii) polysaccharides such us corn and potato starch, and proteins like casein, or ii) mix of these synthetic polymers and biopolymers (Petrie, 1999; Duesseldorf *et al*., 1995; Winter *et al*., 2015).

Adhesives formulated from proteins provide good adhesion, high removal capacity during recycling, and are highly biodegradable. However, they present low moisture resistance and water immersion, which is in many cases a serious problem for the perceived product quality. On the other hand, synthetic adhesives have excellent adhesion and resistance to changes in the storage conditions, but they are not biodegradable and can exhibit low removal capacity during the recycling process, which affects the productivity. In this context, the development of new adhesives based on a synergistic balance between both synthetic polymers and proteins is of high technological interest.

It is well known, that the application properties of hybrid latexes are superior to those obtained by simple physical mixing of two components, due to the synergy reached by the intimate contact of both materials in the hybrid nanoparticles, and the generation of graft copolymer (Kirsch *et al*., 2004).

Based on the improved behavior of hybrid latexes, the objective of this work is to develop them from an acrylic copolymer and casein, through a process of low environmental impact such as the surfactant-free emulsion polymerization, for their potential application as adhesives. The partial replace of monomers derived from petrochemical sources increases the adhesive biodegradability, making the whole ensemble (process and product) more sustainable, eco-friendly and suitable for food packaging. In addition, the degree of compatibility and synergy between the involved materials (protein and synthetic polymer) was controlled by using either a native casein (without chemical modification) or a methacrylated casein, together with the use of a chain transfer agent (CTA).

II. METHODS

A. Materials

The reagents used in the latex synthesis were: technical grade methyl methacrylate (MMA) and ethyl acrylate (EA) as monomers, technical grade casein from bovine milk, sodium carbonate (Na_2CO_3, Cicarelli) as buffer to regulate the pH, glycidyl methacrylate (GMA, Aldrich) as functionalizing agent of casein, tert-butyl hydroperoxide (TBHP, Aldrich) as initiator, N-Isopropylhydroxylamine (IPHA) at 1.5% wt/wt as radicals inhibitor, and *iso*-octyl-3-mercaptopropionate (*i*OMP, Aldrich) as CTA. Other employed reagents were tetrahydrofuran (THF, Cicarelli) and sodium dodecyl sulphate (SDS, Anedra). Distilled and deionized water were used throughout the work.

B. Functionalization of casein

The methacrylated casein was synthesized by the amine-glycidyl ether reaction. For this purpose, 11% wt/wt of

protein was first dissolved at 50 ℃ in a water solution containing 0.4% wt/wt of Na_2CO_3. Then, GMA was loaded and the reaction was carried out for 4 h. A molar ratio GMA/casein equal to 8 was used (assuming 30000 g/mol as the average molecular weight of casein), thereby many amine groups are available to react with oxirane groups of GMA, considering that casein has 40 primary amines (on average) per casein molecule, and a higher amount of secondary ones. Samples taken at the end of reaction were dialyzed (with a membrane of 10 kDa) to remove the unreacted GMA, and then analyzed by ^{1}H NMR.

C. Polymerization process

Acrylic-casein latexes were produced by surfactant-free emulsion polymerization using variable content of native casein or functionalized casein (5 – 30 parts per hundred monomer: pphm), according to the method reported by Picchio *et al.* (2014, 2016). Polymerizations were carried out in a 0.5 L jacketed glass reactor equipped with thermostatic bath, digital thermometer, condenser, stirrer, N_2 inlet and sampling device.

When native casein was used, it was first dissolved at 50 ℃ in a water solution of Na_2CO_3 (0.4 % wt/wt). For polymerizations employing the functionalized protein, the casein solution obtained during the functionalization reaction was diluted according to the protein content in the polymerization recipe. Then, the mix of monomers and CTA (1 pphm, when it was used) was added and the temperature was raised up to 80 ℃. Then, the resulting dispersion was purged with N_2 for 30 min, and the initiator TBHP (0.2 pphm) was injected in order to redox initiate polymerization with the available casein amine groups. Polymerizations were followed during 180 min, and N_2 was bubbled during the whole process. Samples were withdrawn at regular times for kinetic characterization. Solid content was 35 % for all reactions.

D. Characterizations

Casein methacrylation was evaluated by ^{1}H NMR spectroscopy with a Bruker Advance II 300 spectrometer. To this effect, samples were dissolved in D_2O.

Monomer conversion (x) was measured by gravimetry. Particle diameter (d_p) was determined by Dynamic Light Scattering (DLS) at 30 ℃ using a Brookhaven BI-9000 AT photometer, at a detection angle of 90º. At least 3 measurements were taken per sample and the average value was reported.

The degree of compatibility of the hybrid latexes was investigated by determining the fraction of casein grafted to the acrylic copolymer (casein grafting efficiency, CGE), and the fraction of the acrylic copolymer that contains grafted casein (acrylic grafting efficiency, AGE). CGE is defined as the weight fraction of grafted casein with respect to the loaded one, according to Eq. (1):

$$CGE = \frac{weight\ of\ grafted\ casein}{weight\ of\ loaded\ casein} 100 \qquad (1)$$

To determined CGE, a procedure previously reported by Picchio *et al.* (2014) was used. AGE was determined by Soxhlet selective extraction, using THF as a solvent, during 24 h. THF dissolves the pure acrylic copolymers,

while grafted acrylic-casein copolymer and free casein result insoluble. AGE was calculated as the ratio between the weight fraction of acrylic grafted copolymer with respect to the total polymerized acrylic monomers, as shown in Eq. (2):

$$AGE = \frac{weight\ of\ grafted\ acrylic\ polymer}{weight\ of\ loaded\ acrylic\ monomers\ .} 100 \qquad (2)$$

Average molecular weights (M_n and M_w) of the free acrylic copolymer, extracted from AGE characterization, were determined by size exclusion chromatographic (SEC). Measurements were carried out with a Waters 1515 chromatograph fitted with a differential refractometer (DR, Waters 2414); 4 poly(St/DVB) columns (nominal fractionation range 10^3–10^7 g/mol) and tetrahydrofuran as eluent. A direct calibration with a set of 10 (Shodex) narrow PS standards in the range 10^3–10^6 g/mol was used.

Rheological properties of hybrid latexes were measured using a viscometer Brookfield DV3T model DVRTRVCP (cone/plate) employing cones CP-40 (angle: 0.8°, radius: 2.4 cm) and CP-51 (angle: 1.56°, radius: 1.2 cm). A volume of 0.5 ml of latex was placed on the viscometer plate and viscosity was measured at 25℃ in a shear rate range of 3.84–960 1/s.

The removal capability of adhesives from a glass substrate with an alkaline solution was evaluated. For this purpose, a latex film of 120 μm was prepared on a glass plate. Then, it was dried at 50 ℃ for 90 minutes and submerged in a NaOH solution (1.5 % wt/wt) during 1.5 minutes, with constant agitation. Finally, the removal capacity of the latex film was classified by visual inspection as low, medium, or high.

III. RESULTS

A. Synthesis of functionalized casein

The methacrylation reaction of casein proceeds by nucleophilic attack of its amine groups on the least substituted carbon of the oxirane group of GMA, producing the ring opening and the subsequent formation of an amine with a methacrylic group (Wiberg, 1986). Thus, the synthesized modified casein presents a new methacrylic functionality able to radically propagate during the polymerization.

Figure 1 presents the ^{1}H NMR spectra of native casein and functionalized casein. Comparing both spectra, it could be observed between 5 and 6.5 ppm (Fig. 1 c,d) for the functionalized casein, the characteristic signals of methacrylic protons of GMA at 5.6 and 6.03 ppm, which are not present in ^{1}H NMR of native casein, indicating that methacrylated protein was successfully synthesized.

B. Synthesis of the acrylic-casein hybrid latexes

Herein, the results of the surfactant-free emulsion polymerization to produce acrylic-casein latexes are presented. As it was previously said, different aspects of the hybrid latex synthesis were addressed: i) variable casein concentration; ii) control of acrylic-casein com-
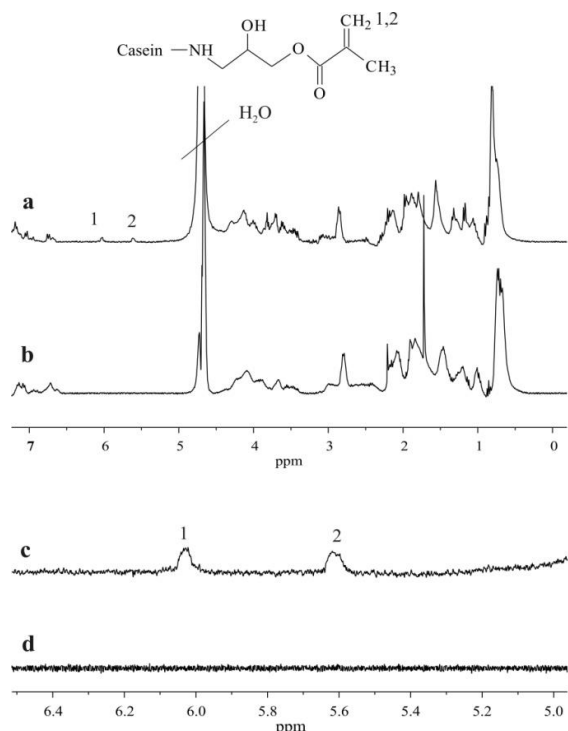
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Figure 1: ^{1}H NMR spectra of functionalized casein (a,c) and native casein (b,d).

Table 1: Final x and d_p for the synthesized hybrid latexes.

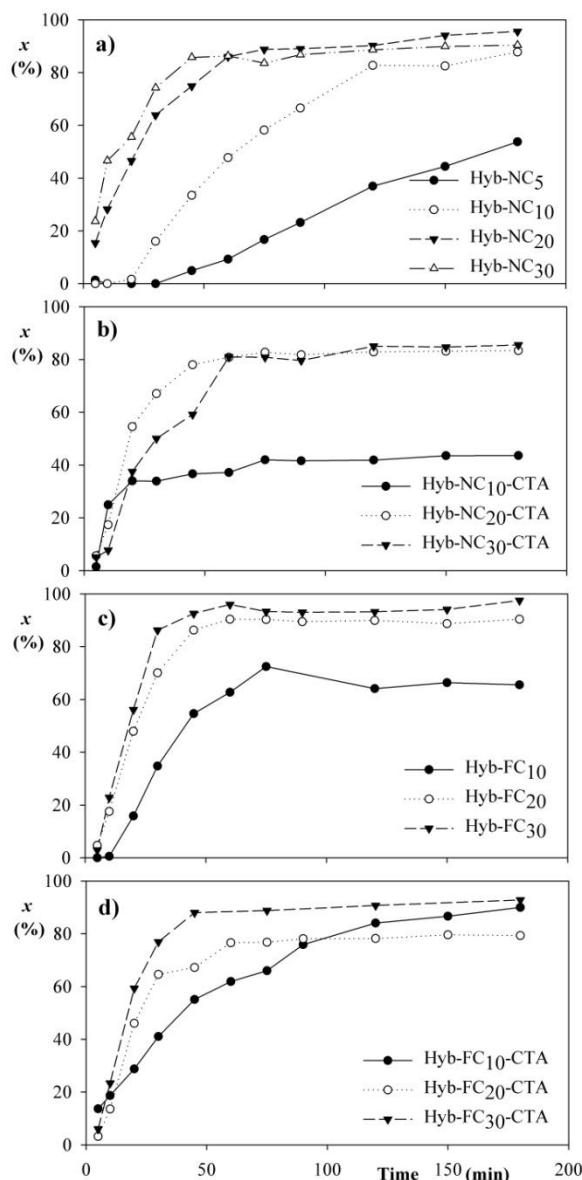| Experiment	x (%)	d_p (nm)
Hyb-NC$_5$	54	184
Hyb-NC$_{10}$	88	174
Hyb-NC$_{20}$	95	156
Hyb-NC$_{30}$	90	161
Hyb-NC$_{10}$-CTA	45	100
Hyb-NC$_{20}$-CTA	83	100
Hyb-NC$_{30}$-CTA	85	140
Hyb-FC$_{10}$	65	168
Hyb-FC$_{20}$	90	166
Hyb-FC$_{30}$	97	186
Hyb-FC$_{10}$-CTA	90	180
Hyb-FC$_{20}$-CTA	79	168
Hyb-FC$_{30}$-CTA	93	176

Figure 2: Evolution of x for polymerizations carried out with variable content of protein when using: native casein (a), native casein and CTA (b), funtionalized casein (c), and funtionalized casein and CTA (d).

patibility by using native casein (without chemical modification) or functionalized casein (methacrylated protein); and iii) control of the acrylic copolymer molecular weight by addition of a CTA.

The experiment codes contain the abbreviation NC or FC for native casein or functionalized casein, respectively, followed by a subscript that indicates the amount of casein employed (in pphm). For latexes synthesized with CTA, this abbreviation was also included at the end of the experiment code. Thus, Hyb-FC$_{10}$-CTA indicates an experiment carried out with 10 pphm of functionalized casein and CTA.

Table 1 shows the final results of x and d_p for the synthesized latexes, while Fig. 2 presents the evolution of x along the polymerizations for different groups of reactions. Depending on the selected initial formulation, latexes with final x between 45 and 95% and d_p in the range 100–185 nm were produced.

In general, the increase of casein concentration favored the polymerization rate and allowed achieving higher final x. According to Li *et al*. (2002), this behavior was expected due to the role of casein in the initiation reaction. Polymerization is initiated by redox reaction between the hydroperoxide molecules and the amino groups present in the casein backbone, producing amino and tert-butoxy radicals. Therefore, the increase of protein in the reaction medium produces a higher availability of amine groups, which are able to interact with TBHP, thus increasing radical concentration and polymerization rate.

The polymerization rate and final x of experiments carried out with functionalized casein were not affected. Although casein functionalization consumes some

amine groups reducing their availability for the initiation reaction, the degree of casein methacrylation used in this work (8 theoretical GMA molecules per casein chain) was low with respect to the total amount of amine groups present in the casein molecule (40 primary amines, on average, and a higher amount of secondary ones).

Figure 3 shows the results of AGE and CGE for the different groups of hybrid latexes. When using native casein, graft copolymer is produced by propagation of the acrylic monomers from the primary amine radical in the casein molecule, which in turn was generated by the redox initiation reaction. According to this mechanism, more grafted casein would be expected as the amount of casein increases in the formulation. However, for latexes synthesized with native casein (and without CTA) CGE was constantly reduced with casein content, while the amount of grafted casein increased with protein concentrations of up to 20 pphm, and then decreased when 30 pphm of casein was employed (Fig. 3a). The same effect was previously observed and analyzed by Picchio *et al.* (2014), during the surfactant free emulsion polymerization of MMA in the presence of casein. According to the mechanism of hybrid particle generation proposed by Picchio *et al.* (2014), when the protein concentration is low, particles are produced by self assembly of amphiphilic-grafted radicals containing the protein, just as Li *et al.* (2002) had previously reported. On the other hand, when the protein concentration is high, the availability of casein micelles (aggregates of casein molecules) is greater and particle formation mainly occurs through a second form of nucleation: by radical absorption into the casein micelles or by hydrophobic radicals coagulation, generating uncompatibilized particles (i.e., composed by ungrafted acrylic and casein).

When functionalized protein was employed in absence of CTA, both higher CGE and AGE were achieved (Fig. 3c), indicating that protein methacrylation improved the compatibility between both materials (acrylic copolymer and casein) in the hybrid nanoparticles. In addition, a greater mass of grafted casein was produced when increasing the protein content, even at high concentrations. This effect is due to the fact that the grafted copolymer is produced by both the redox initiation reaction and the propagation reaction with the pendant methacrylic groups onto casein chains. Therefore, the probability of generating grafted copolymer, by reaction of the double bonds incorporated into the casein chain, becomes greater at higher protein concentration.

On the other hand, the addition of CTA in the formulations reduced molecular weights of the acrylic copolymer, and affected both CGE and AGE. While sample Hyb-NC$_{10}$ exhibited high average molecular weights (M_n = 467,100 g/mol, M_w = 1,634,900 g/mol), they are significantly lower in the analogue experiments with CTA (M_n = 23,400 g/mol, M_w = 47,100 g/mol for Hyb-NC$_{10}$-CTA; and M_n = 42,600 g/mol, M_w = 118,100
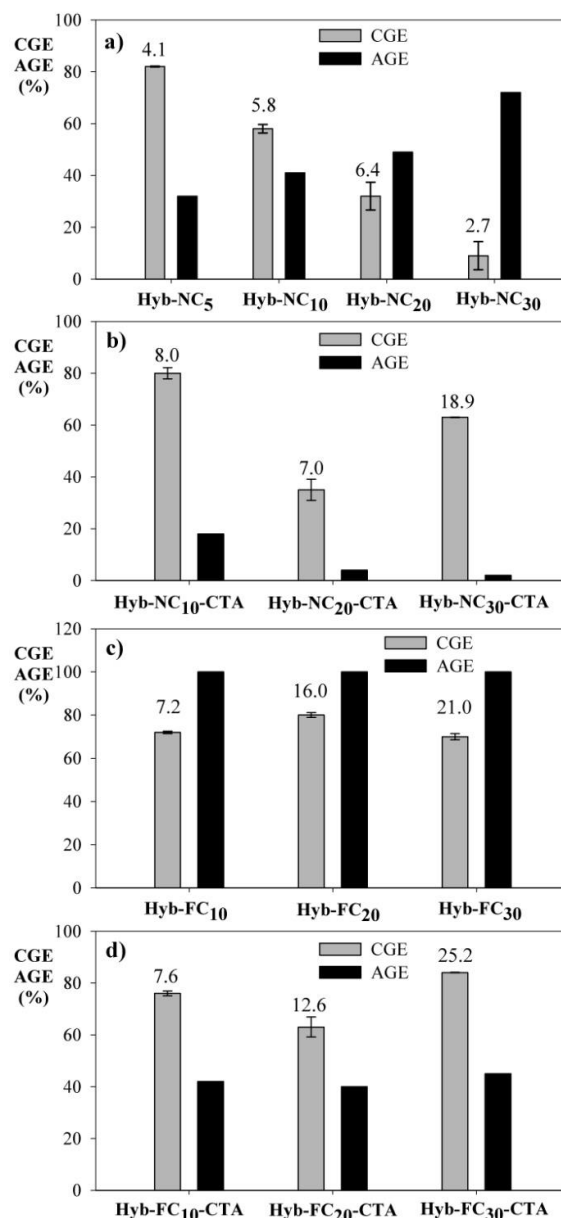

Figure 3: Results of AGE and CGE for hybrid latexes synthesized with variable content of proteins and using native casein (a), native casein and CTA (b), functionalized casein (c), and functionalized casein and CTA (d). The value above CGE bar corresponds to the mass of grafted casein in pphm.

g/mol for Hyb-FC$_{10}$-CTA). These observations are in agreement with previous results obtained in conventional emulsion polymerizations of MMA with the incorporation of *i*OMP as CTA (Ronco *et al.*, 2013). Comparing latexes synthesized with the same content of native casein, those produced with *i*OMP as CTA exhibited higher CGE (Fig. 3b). Probably, *i*OMP radicals generated by transfer reaction to CTA, exhibit higher mobility in a lower viscosity medium (polymer particles of reduced molecular weights) and, as a consequence, a greater probability to induce grafting by abstraction of hydrogen from casein chains. However, significant lower AGE values were obtained, also due to the mentioned decrease of acrylic copolymer molecular weights, produced by

transfer reaction to the CTA. This observation is supported by the average number of acrylic grafting points per casein molecule (calculated from the mass of grafted casein and acrylic with the assumption that the average chain length of grafted acrylic branches coincides with that of the free acrylic), which resulted 0.4 and 2.9 for samples Hyb-NC$_{10}$ and Hyb-NC$_{10}$-CTA , respectively. Therefore, in hybrid latexes produced with CTA, acrylic chains grafted to casein are much shorter, resulting in a lower weight fraction of grafted acrylic, despite of the higher number of acrylic grafting points. Moreover, it was observed an improvement in the degree of compatibility of the acrylic-casein latexes synthesized with CTA, when native casein was replaced by the functionalized one (Fig. 3d).

C. Properties of the hybrid materials

As expected, all latexes showed a pseudoplastic behavior typically observed in this kind of colloids (Fig. 4). These viscosity measurements were fit with the Power Law model according to Eq.(3):

$$\eta = m\,\dot{\gamma}^{\,(n-1)} \qquad (3)$$

where, η is the viscosity (cP), $\dot{\gamma}$ is the shear rate (s^{-1}), n and m (cP.s) are the model parameters. The fit parameters are presented in Table 2.

Generally, latexes with higher casein content exhibited a more pseudoplastic behavior (see n value, Table 2) and higher viscosities in the shear rate range studied. Fig. 4a shows viscosity results for latexes produced with different content of native casein. This effect could be related to the amount of free casein in the continuous phase of the latex, since with a greater amount of biopolymer in solution, a higher viscosity is obtained. Note that latexes synthesized with native casein presented higher amount of free casein when protein in the formulation was increased. In addition, comparing analogous latexes synthesized with the same amount of casein (Fig. 4b), those produced with functionalized casein exhibited lower viscosities, due to their reduced content of free casein (higher CGE).

In an application where the recycling process is crucial, the adhesive removal is a key. The removal capacity of dry latex films in alkaline solution showed that higher compatibilities between materials favored their removal (Fig. 5). Note that latexes synthesized with functionalized casein, with and without CTA, exhibited an improved removal capacity compared to those with native casein, at the same content of protein. According to previous work (Picchio *et al.*, 2016), this type of hybrid nanoparticles present core-shell morphology, with a core of acrylic polymer (insoluble in alkaline solution) and the outer shell formed by casein. When the grafted protein is low it could occur a phase separation of the components during film formation, and the free casein could segregate into the film, leaving the surface enriched with acrylic particles. On the other hand, an increase in compatibility, by chemical bonding of acrylic and casein components, limited molecular mobility and restricted phase separation. Therefore, in samples with

Table 2: Parameters of Power Law model fits for different hybrid latexes.

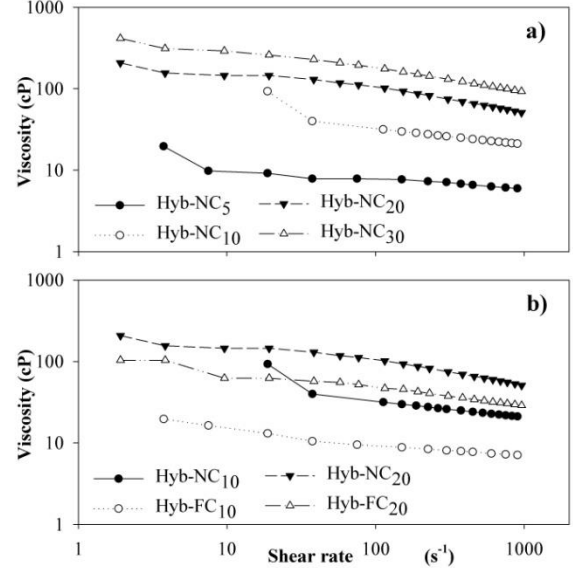| Experiment	n	m (cP.s)
Hyb-NC$_5$	0.86	15.7
Hyb-NC$_{10}$	0.81	77.2
Hyb-NC$_{20}$	0.70	400.5
Hyb-NC$_{30}$	0.72	624.4
Hyb-FC$_{10}$	0.88	16.1
Hyb-FC$_{20}$	0.79	125.6

Figure 4: Viscosity of acrylic-casein latexes synthesized with variable content of native casein (a), and comparison of viscosities for analogous latexes with 10 and 20 pphm of native casein (closed symbol) or functionalized casein (open symbol) (b).

high CGE, most of casein is grafted to the acrylic polymer, covering the hybrid nanoparticles surface. Consequently, compatibility between the adhesive film and the alkaline solution increases, due to the hydrophilic character of protein, favoring the film removal capacity.

IV. CONCLUSIONS

Hybrid acrylic-casein latexes containing different biomaterial concentration were synthesized by surfactant-free emulsion polymerization, with the aim of producing new hybrid adhesives. When increasing the concentration of protein, the polymerization rate and final monomer conversion were favored, independently of using native casein or functionalized casein.

However, the degree of compatibility achieved between casein and the acrylic copolymer during the synthesis, significantly influenced the application properties of the produced hybrid latexes. Materials synthesized with native casein presented lower grafting degree, which reduced the removal capacity in alkaline condition of films obtained from latex casting. Nevertheless, this property markedly improved by increasing the compatibility between both materials, through the use of functionalized casein instead of native one, with the best results obtained when including CTA in the polymerization recipe. In addition, the decrease in the amount of
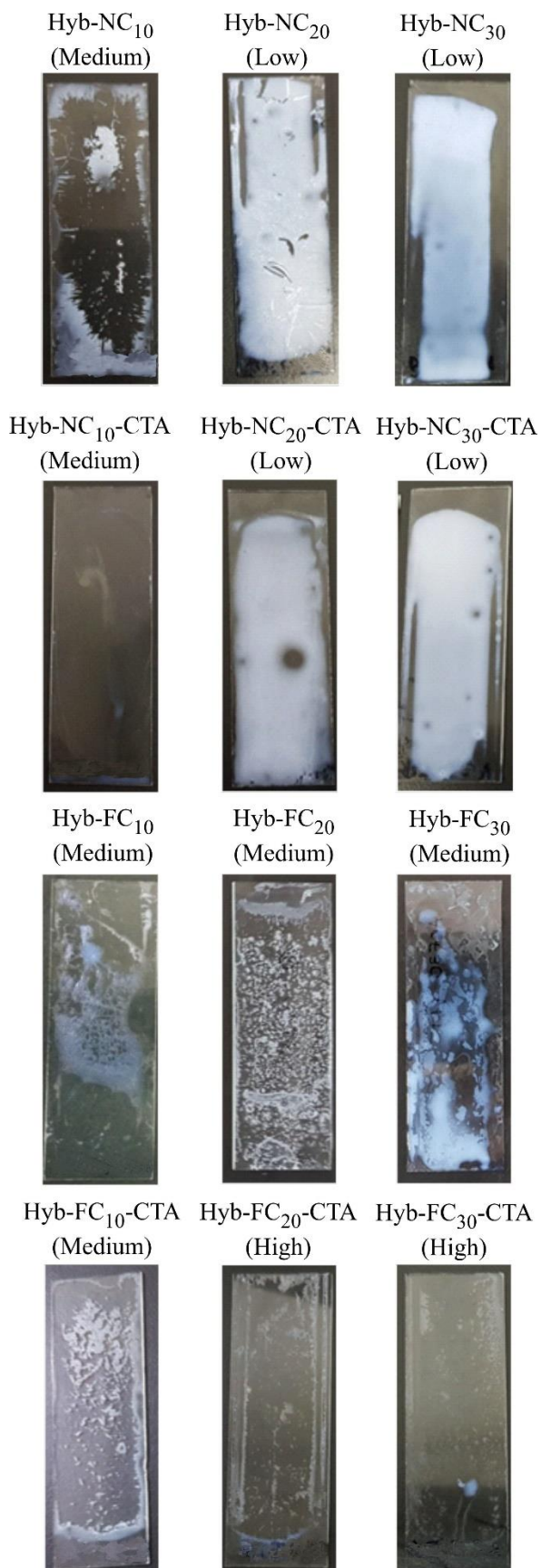
Figure 5: Removal capacity of dry latex films in alkaline solution.

free casein when employing modified protein, reduced latex viscosity.

These results stand out the versatility and convenience of the employed strategy to produce hybrid acrylic-casein latexes with controlled microstructure and nanomorphology for their potential application as adhesives more easily removable.

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