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Waterborne Casein-Based Latexes with High Solids Content and Their High-Throughput Coating Optimization

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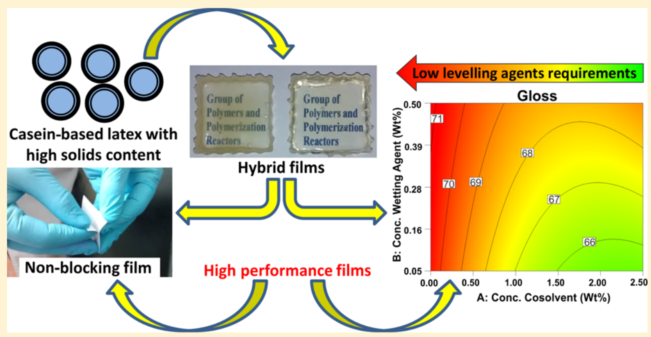
Ⓢ *Supporting Information*

ABSTRACT: Over the past few years casein-based latexes have attracted increasing interest because of their good film-forming properties. This paper investigates the use of acrylic/casein hybrid latexes with a solids content of 35% in a coating application, which involves the evaluation of nonformulated latexes as binders, the high-throughput formulation with different commercial agents (cosolvents, wetting agents, and defoamers) and the formulation optimization using statistic multivariable analysis. Latexes were obtained by emulsifier-free emulsion polymerization of acrylic monomers in the presence of a chemically modified casein containing 10 vinyl bonds per molecule. The optimized clear coats formulated from the hybrid latexes showed a good performance requiring a reduced formulation-agents concentration, which could be an important benefit from an environmental viewpoint. Together the above results demonstrate that the casein biobased latexes represent a promising alternative for the development of a new generation of ecological binders.



1. INTRODUCTION

During the past decade, increasing efforts have been made to replace petroleum-based polymers by renewable and more sustainable materials and to convert biobased feedstocks into industrially applicable polymers.[1−3] Among many employed renewable sources, proteins are one of the most promising candidates since it is possible to design from them new materials for further versatile and valuable applications.[4] In this regard, the synthesis of film-forming casein-based latexes is of particular interest because they have proven to be promising alternatives for the replacement of fully petroleum-based coatings.[5−12]

Acrylic/casein latexes were previously prepared by emulsifier-free emulsion polymerization employing thermal initiators such as potassium or ammonium persulfates.[8] However, the use of this kind of initiators often results in oxidative degradation of casein, producing yellowish products. Li et al.[13,14] reported an efficient synthesis method that overcomes the oxidative problems, which is based in a redox initiation by interaction between an alkyl hydroperoxide and amine groups of casein. Recently, a novel strategy for the synthesis of acrylic/casein nanocomposites with an appropriate control of the synthetic/biopolymer compatibility has been proposed.[15] The synthesis method involves the use of highly methacrylated casein (HMC) in the emulsifier-free emulsion polymerization of acrylic monomers, with the aim of promoting polymer grafting onto the protein backbone. Despite this approach represents an important advance toward the use of these nanocomposites as binders for coatings, the low solids content (maximum 20 wt %) employed limits its industrial implementation. High solids content (≥30 wt %) is of great importance for an effective industrial application of casein-based latexes, because among other factors, it maximizes the reactor production, minimizes transportation and storage costs, improves surface coverage when applied and reduces film-forming and drying times. However, the limited water solubility of casein makes the production of hybrid latexes with high solids content a big challenge.

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The performance of a coating is affected by a wide range of formulation parameters. Among them it can be mentioned the structure and composition of the polymeric binder, and the formulation agents such as cosolvents, thickeners, defoamers, wetting agents and pigments. All of the parameters should be varied in order to develop a correlation between them and the product performance, therefore combinatorial methods appear to be a powerful tool for the optimization of these systems.[16] For a specific coating application there are a considerable amount of variables and choices that make the number of possible combination an overwhelming puzzle. The design of experiments (DoE) is crucial to overcome this problem, extending the coverage and understanding of the variable correlations in the parametric space.[17] Furthermore, in recent years researchers in the field of coatings and polymer formulations have started using high-throughput experimentation (HTE) workflows that allow a not time-consuming and efficient interconnected process to prepare and evaluate coatings. The combination of both tools (DoE and HTE) is demonstrated to be successful for covering a large parametric space in order to get a better understanding of the role of formulation agents in a coatings application.[18]

This work investigates the evaluation of high solids (35 wt %) casein/acrylic latexes as binders for a potential application in water-based paints. In addition, hybrid latexes were formulated by using the combination of DoE and HTE with the aim of optimizing sensitive properties such as gloss, haze, hardness, and chemical resistance. As far as the authors are aware, this is the first article that propose the synthesis of 35 wt % solids latexes of highly compatibilized casein/acrylic particles and their formulation using an HTE technique. Finally, the optimized clear coat formulation was compared with a commercial binder.

2. EXPERIMENTAL SECTION

2.1. Materials. Technical grade casein from bovine milk (Sigma), methyl methacrylate (MMA), butyl acrylate (BA), and glycidyl methacrylate (GMA) (Aldrich) were used as supplied. The employed initiator was *tert*-butyl hydroperoxide (TBHP, Aldrich). Other reagents used were: tetrahydrofuran (THF, Cicarelli) as selected solvent and sodium carbonate (Na_2CO_3, Cicarelli) as buffer to regulate the pH. Formulations of hybrid binders were carried out with the following agents: (i) cosolvents [butyl glycol (BG) and butyl diglycol (BdG) from Helm Chemicals BV], (ii) commercial wetting agents (BYK 348 from BYK and Surfynol CT-211 from Air Products), and (iii) commercial antifoaming agents (BYK 028 from BYK and Tego 825 from Evonik). All the reagents were used as received without any kind of purification. Distilled and deionized water was used throughout the work.

2.2. High Solids Casein/Acrylic Latexes as Binders. Here, 35% solids content modified casein/acrylic latexes were evaluated as binders for paints. The hybrid latexes were synthesized through a two-step procedure which involves the casein methacrylation with a functional monomer, such as GMA, and the later use of this modified protein in the emulsifier-free emulsion polymerization of acrylic monomer redox initiated with TBHP.[15] Shortly, highly methacrylated casein (HMC) containing 10 methacrylic groups per molecule was synthesized by the amine-glycidyl ether reaction at 50 °C for 4 h.[15] A general recipe for the preparation of HMC is presented in the upper part of Table S1. After obtaining HMC, the solution temperature was raised up to 80 °C and BA/MMA (80/20) monomers were loaded. The resulting dispersion was purged with N_2 for 30 min and then the TBHP (0.2% weight based on monomer, wbm) was injected to redox initiate the polymerization with the available casein amine groups. Table S1 also shows the recipe for the synthesis of casein-based latexes. Two latexes of BA/MMA (80/20), in the presence of two different concentrations of HMC, were synthesized. Latex codes are HMC25 and HMC50 for 25% and 50% wbm of casein content, respectively. Table 1 summarizes the characteristics of the casein/acrylic latexes used in terms of solids content, final particle size (measured by dynamic light scattering at a detection angle of 90°), fraction of grafted casein (CGE, determined following a procedure previously reported[19]), and insoluble fraction (IF) of the hybrid materials after Soxhlet extraction with THF.

Table 1. Main Characteristics of the Casein/Acrylic Latexes

experiments	solids (%)	d_p (nm)	CGE (%)	IF (%)
HMC25	34.8	164	67	99
HMC50	34.4	177	78	99

Synthesized latexes presented a high degree of casein/acrylic compatibility. Values of CGE were importantly higher than those achieved when native casein was used.[12] Methacrylation of casein allowed an adequate control of the fraction of grafted casein of 67% (HMC25) and 78% (HMC50), with a reduced amount of ungrafted casein. Also, the high IF values indicate the important compatibility between both components, where most of acrylic polymer contains grafted casein. Furthermore, based on the high vinyl functionality of the protein, it is expected the existence of cross-linked structures in the material. These results suggest that the high values of CGE and IF reached are sufficient to guarantee that almost all of the nanoparticles are compatibilized; i.e., all particles contain acrylic-*graft*-casein copolymer in their composition.

2.3. Characterization of the Casein/Acrylic Hybrid Films. The polymer films were prepared by casting the latexes and then dried at 22 °C and 55% relative humidity.

Film opacity was determined as the area under the absorption spectrum in the UV−visible range (400−800 nm) divided by the sample thickness employing a method proposed elsewhere.[20] Measurements were taken in triplicate for each sample.

Blocking resistance of the films was evaluated following ASTM D 4946-89.[12] The test for each sample was run three times and the results were correlated to rates 0−10 (minimum and maximum blocking resistance, respectively). Minimum film formation temperature (MFFT) of the synthesized latexes was determined employing an optical method as described elsewhere.[21] In short, latex was casted with a cube applicator (120 μm of thickness) on a large metallic table with a temperature gradient across it. The minimum temperature at which the film becomes continuous and clear was considered as the MFFT value.

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC 821. The hybrid films presented two T_g values: one corresponding to the acrylic polymer and the other to the casein. Due to casein showing a glass transition with the beginning of its thermal decomposition,[12] DSC measurements of hybrid films were carried out from −80 to 130 °C at a heating rate of 10 °C/min.

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Tensile tests of the hybrid films were carried out in a universal testing machine (INSTRON 3344), at 23 °C and 50% relative humidity. To this effect, films with dogbone shape of length 9.53 mm and cross section 3.18 × 1 mm^2 were strained with an elongation rate of 25 mm/min. At least five specimens of each sample were tested.

2.4. Clear Coat Formulation. In this study, the effect of cosolvent, wetting agent, and defoamer incorporation on the performance as a "clear coat" (i.e., without pigments) of the hybrid casein/acrylic latexes was studied by means of a combination of DoE and HTE. The main goal was enhancing their performance as coatings using a statistical model to describe the interactions between the hybrid binders and the different components in a formulation of the clear coats. The DoE was carried out with the aid of the commercial software "Design Expert" (version 9).[25] The type of design used was Surface Response, since it offers the possibility of including numerical and categorical factors with high accuracy.[22,23] This setup allows the prediction of clear coat formulations in the space of the variables that have the preferred performance parameters, providing by the parameters fitted in the model. Thirty-five different formulations were prepared for each synthesized hybrid binder (Table S2 in the Supporting Information). Components of formulations were varied according to Table S2, while maintaining constant the amount of hybrid casein/acrylic dispersion. Concentration ranges of cosolvents (BdG and BG), wetting agent (BYK 348 and Surfynol CT-211), and defoamer (BYK 028 and Tego 825) were 0−2.5, 0.05−0.5, and 0.1−1, expressed in weight percent with respect to latex, respectively.

Formulations of Table S2 were carried out with a HTE workflow from Nuplex Resins laboratory. An automatized letdown preparation and mixing was used to obtain the full formulations in a paint robot (SynchronXperimate: Robotic XYZ automated liquid handling systems for bench, integration and custom applications). Then, the formulated dispersions were applied on glass substrates using a barcoater (120 μm of wet film thickness) and dried at 22 °C and 50% of humidity. The coatings were manually tested, by measuring hardness, gloss at 20°, and haze. Film hardness was measured with a Konig pendulum apparatus (Erichsen model 299/300). Gloss at 20° and haze of the coatings were determined with a goniophotometer Rhopoint IQ. It is worth mentioning that film haze is an undesirable phenomenon for optical coatings, where low values of haze indicate good film appearance.

Afterward, all these results obtained were treated as responses from the DoE and fitted into a statistical model that describes the interaction between the formulation variables and the performance responses. The statistical analysis of the responses was carried out with the aid of the software Design Expert. The core of the evaluation was based on the collection of statistical models used to analyze the differences between group means and their associated procedures, well-known as ANOVA (analysis of variances)

The "spot test" was used for evaluating the film chemical resistance. For this purpose, a 50 wt % of ethanol aqueous solution and a coffee infusion (2 g of espresso instant coffee in 50 mL of water) was dropwise added over films, analyzing damage onto film surface after 1 h of exposure. Then this damage was evaluated on a scale of 1 (NOK: a lot of damage) to 5 (OK: excellent).

3. RESULTS AND DISCUSSION

3.1. Evaluation of Nonformulated Casein/Acrylic Latexes As Binders. Table 2 summarizes the results of

Table 2. Properties of Unformulated Films

property	HMC25	HMC50
opacity (AU × nm/mm)	82.1	201.4
antiblocking resistance	10	10
MFFT (°C)	<2	<2
T_g (°C)	−30.1	−30.1
Young's modulus (MPa)	96.2	195.2
tensile strength (MPa)	10.4 ± 0.4	16.3 ± 0.6
elongation at break (%)	380 ± 14.8	119 ± 6.3

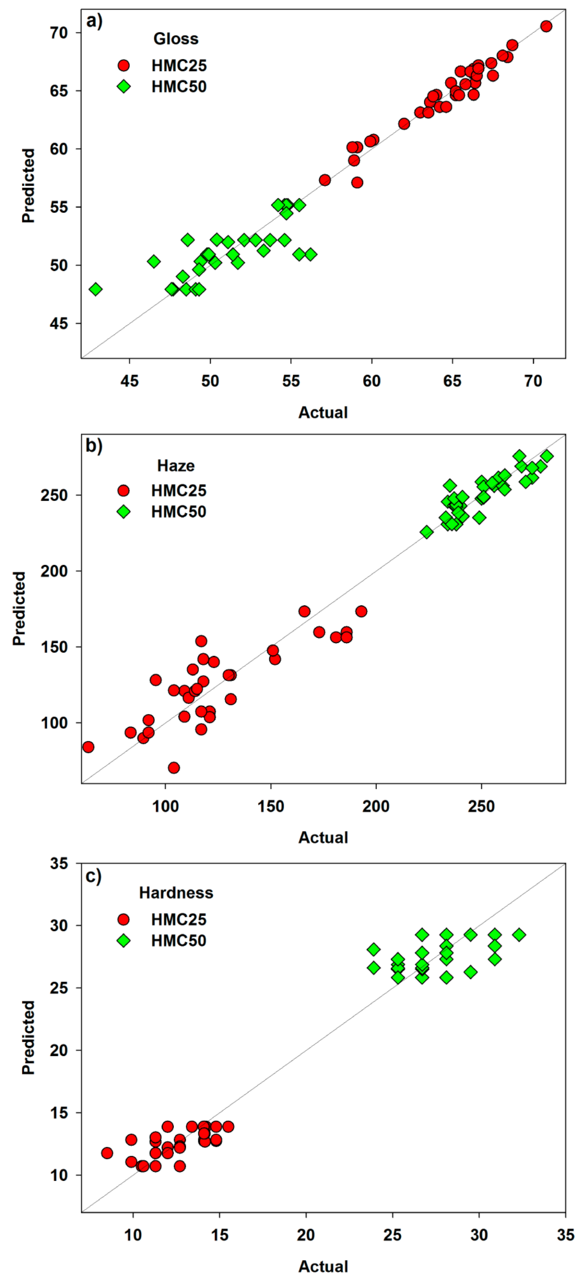

Figure 1. Performance of the statistical model ANOVA for predicting gloss (a), haze (b), and hardness (c).

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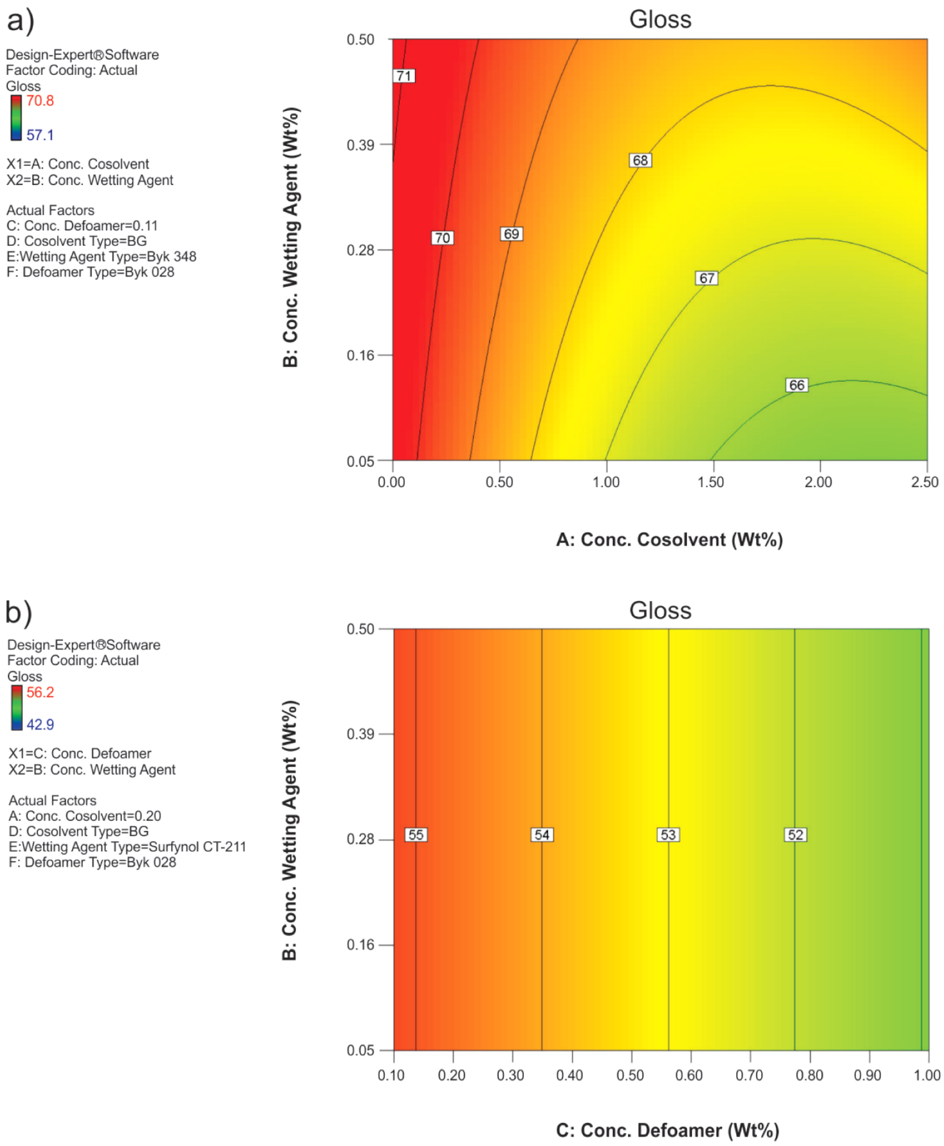

Figure 2. Effect of the cosolvent and wetting agent on gloss of formulated films: (a) HMC25 and (b) HMC50.

opacity, antiblocking, MFFT, T_g, and mechanical properties of the obtained hybrid films without any formulation. Notice that casein content importantly affects film properties. When increasing the casein content, a more opaque hybrid material is obtained. This is a consequence of light scattered from internal irregularities resulting from the presence of two phases, i.e. casein rich acrylic phase and free casein.[12,24]

Both films are completely nonblocking with the maximum antiblocking rate, while presenting a very low MFFT. These results satisfy one of the biggest challenges for waterborne coatings that is to simultaneously attain a low MFFT, to ensure a smooth film formation under applications at room temperature, with a high blocking resistance, which is usually accomplished by polymers with a T_g above the room temperature. This synergetic effect between casein and acrylic is reached since protein in the graft copolymer does not affect the low T_g of the acrylic phase (around −30 °C, Table 2), while a high plasticization effect of water on the casein phase (i.e., the highest T_g component) is present during the film formation.[12] Therefore, film formation at low temperature is promoted for both effects: the low T_g of acrylic phase and the water plasticization on casein phase. After films drying, casein recovered its T_g, improving antiblocking resistance.

On the other hand, when increasing the content of the harder component (i.e., casein), film mechanical properties are significantly affected, resulting a material with higher Young modulus and tensile strength and lower deformation capability (i.e., smaller elongation at break).

3.2. Statistical Evaluation of the Responses and Defining an Optimized Formulation. The responses from the formulation test evaluation of the HTE workflow were studied and fitted into a statistical model based on ANOVA. A detailed description of this statistical model is provided in the Supporting Information. Figure 1 represents the performance of the model obtained analyzing the responses through the ANOVA steps. It can be noticed that there is a good agreement between the values predicted by the ANOVA model and the experimental responses for gloss, haze and hardness.

In general it can be seen that both formulated latexes are capable of forming films with good properties of gloss and haze, in the range of typical values of furniture coatings, suggesting that hybrid binders could be used in this specific application.

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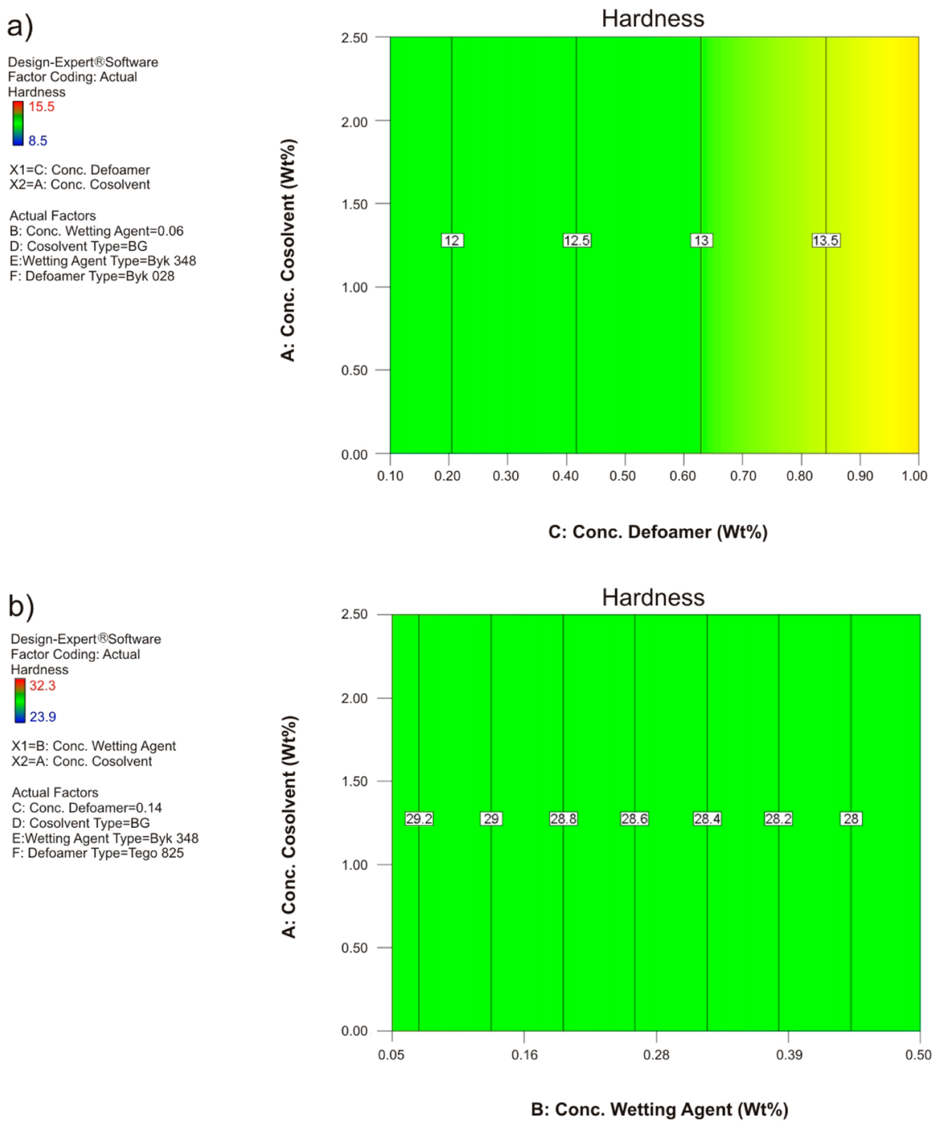

Figure 3. Effect of the additives on hardness of formulated films: (a) HMC25 and (b) HMC50.

Table 3. Optimization of Formulation Performance of Binders HMC25 and HMC50

optimized property	cosolvent (% p/p)	wetting ag (% p/p)	defoamer (% p/p)	predicted value	measured value
		Latex HMC25			
gloss	0.025 (BG)	0.395 (BYK 348)	0.135 (BYK 028)	70.8	74.2
haze	2.5 (BG)	0.05 (Surfynol 211)	0.1 (BYK 028)	70.3	76.6
hardness	0	0.5 (BYK 348)	1.0 (Tego 825)	13.9	17.5
		Latex HMC50			
gloss	0	0.5 (Surfynol 211)	0.1 (BYK 028)	55.7	56.1
haze	0	0.05 (Surfynol 211)	1.0 (BYK 028)	225.7	199.1
hardness	1.125 (BG)	0.005 (BYK 348)	0.515 (Tego 825)	29.7	34.5

Formulated films obtained from HMC25 exhibit higher gloss and better appearance (lower haze) than that of HMC50. Figure 2 shows the parametric curves of gloss property for the hybrid latexes. In such graphic higher gloss values are represented by warm zones while the cold regions point out the lower ones. Note that for both HMC25 and HMC50 higher values of gloss are obtained without requiring the addition of larger amounts of leveling agents (Figure 2). This showed the good performance of the biobased binders for film formation. Hardness is completely dependent on latexes casein content, in agreement with the measured mechanical properties of Table 2, and as it could be observed in Figure 1c, this property was not greatly influenced by the rest of the additives in the formulation. While a slight hardness increment was detected with the addition of defoamer in the formulation of the binder HMC25 (Figure 3a), this resulted independent of the cosolvent and wetting agent concentration. On the other hand, for the formulated latex HMC50, only small differences of hardness are noticeable when wetting agent concentration is varied (Figure 3b).

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Table 4. Chemical Resistance of Formulated Hybrid Binder and Its Comparison with a High-Performance Commercial Binder (Stq Nu)

binder	chemical resistance		gloss (GU)[a]	haze (HU)[b]	hardness (s)
	coffee	ethanol			
HMC25	3.5	2.5	74.25	76.58	17.5
HMC50	4	3	56.12	119.12	34.5
Stq Nu	4	5	70.21	75.2	60.1

[a]GU: gloss unit. [b]HU: haze unit.

One of the advantages of using the ANOVA based statistical models is the possibility of maximizing or minimizing the output of the responses with the ultimate goal of optimizing the formulations for such needs. Table 3 summarizes the optimized formulations (concentration and formulation agent) calculated for each binder. The predicted optimized properties and those experimentally obtained after preparing the optimized formulations are also presented in Table 3.

From Table 3 it could be noted that most of the optimized properties are reached with very low content of additives. Indeed, particles coalescence during film formation mainly occurs in the casein phase (i.e., through the particles shell),[12] where water acts as a good plasticizer; without requiring additional cosolvents. It is worth mentioning that additives were used mainly to improve the film formation and the bulk mechanical properties of the materials are mainly determined by the polymer microstructure. The mechanical behavior of the optimized hardness coatings was compared with that of the nonformulated films, using dynamic mechanic thermal analysis (see Figure S1 of the Supporting Information). The differences between the evolution of elastic modulus (G') of nonformulated and formulated coatings for hardness optimization are not significant. For this reason, important changes in the mechanical behavior are not expected as a consequence of latex formulation.

Then, the clear coats with HMC25 and HMC50 formulated to achieve the maximum hardness were used for testing chemical resistance. Table 4 present the results of coffee and ethanol resistances obtained with the spot test. Also, responses of optimized hybrid formulations were compared with a commercial binder (Stq Nu, Nuplex), which is a furniture coating used for similar purposes than the proposed for these casein-based latexes, and formulated under the same conditions of HMC50. The comparison of spot test results shows that hybrid formulated binder are severely damaged when exposed to ethanol/water solution, while in contact with the coffee infusion hybrid binders reach rate resistance similar to that of Stq Nu.

From Table 4 it can be seen that HMC25 presents values of gloss and haze comparable to those of the commercial resin. Unfortunately degradation in these properties was observed for the hybrid binder with higher protein content. Note also that the hardness values obtained for both dispersions were lower than that measured for the high performance Stq Nu binder. While commercial binder Stq Nu has a decay time (indicator Konig hardness parameter in the assay) of 60.1 s, the hybrid latexes HMC25 and HMC50 presented maximum values of 17.5 and 34.5 s, respectively. It is worth mentioning that Stq Nu binder has certain inherent advantage favoring hardness in comparison to hybrid latexes, which is its T_g of 10 °C with respect to a T_g of −33 °C corresponding to the acrylic phase of hybrid binders.

4. CONCLUSIONS

Recent advances in the design and preparation of acrylic/casein latexes have opened new possibilities for the industrial application of these hybrid materials in the field of water-based coatings. High-solids content hybrid latexes were successfully synthesized via emulsifier-free emulsion polymerization and employing highly methacrylated casein (HMC) to control the acrylic/protein compatibility. The obtained dispersions were evaluated in terms of key film properties, such as MFFT, blocking resistance, opacity, and mechanical behavior, showing good coating performance. With the aim of optimizing the final film properties, hybrid binders were formulated by using tools of DoE and HTE. Some sensitive coating properties as gloss, haze, and hardness were maximized and then compared with a commercial acrylic resin Stq Nu. Results showed that hybrid binders are able to form smooth films at room temperature with excellent appearance requiring minimal additives concentrations, which represent a great advantage from an environmental viewpoint. Despite hybrid films presented some shortcomings, as lower hardness and ethanol chemical resistance in comparison to Stq Nu, a high-performance commercial binder, they represent a promising alternative for the industrial application as coating with reduced carbon footprint.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b02105.

Formulations for the synthesis of methacrylated casein and hybrid latexes are shown in Table S1 and Table S2, respectively. Details of leveling agent types and concentrations used for the DoE are provided in Table S3. Description of the statistical model used for the DoE is presented on page S4. DMTA test conditions are provided on page S6. Storage modulus (G') as a function of temperature for the clear and optimized hardness coatings is shown in Figure S1 (PDF)

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Notes

The authors declare no competing financial interest.

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