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Designing Pickering Emulsions Stabilized by Modified Cassava Starch Nanoparticles: Effect of Curcumin Encapsulation

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Abstract: Curcumin is a hydrophobic bioactive compound, and its incorporation into lipid-based carriers can enhance its bioaccessibility and maintain its stability over time. Pickering emulsions are long-term stability systems, effective for encapsulation, protection, and delivery of bioactive compounds. This study aimed to produce Pickering oil-in-water (O/W) emulsions stabilized by cassava starch nanoparticles (native or modified by heat–moisture treatment (HMT)) with high kinetic stability to encapsulate curcumin. The effect of curcumin incorporation on emulsion features was also assessed, as well as curcumin stability over time. Native starch nanoparticles (NSNPs) were not effective stabilizers in the concentration range of 0.8 to 4 wt%. Otherwise, modified starch nanoparticles (HSNPs) at 4 wt% produced a long-term stability Pickering emulsion, which was used to encapsulate curcumin (0.07 wt%). Confocal laser scanning microscopy (CLSM) showed that HSNPs were located at the droplet's interface. The interfacial tension for HSNPs exhibited initial values from 40 to 33 mN/m, quickly reaching equilibrium. These findings suggest that HSNPs exhibit low surface activity and the stabilization mechanism of emulsion is based on steric hindrance. The stabilization by steric hindrance is supported by the low zeta potential value (−5.39 mV). Stable emulsions showed shear thinning behavior, and the power-law model demonstrated excellent fit to experimental data ($R^2 \geq 0.998$). The addition of curcumin reduced the interfacial tension, droplet size, apparent viscosity, and consistency index, indicating that this bioactive compound can also act at the interface. After 60 days, curcumin degradation was fully avoided. Our findings indicated that HSNP-stabilized Pickering emulsions can protect encapsulated curcumin from degradation.

Keywords: modified starch; HMT; encapsulation; interfacial tension; rheology

Citation: Ramos, G.V.C.; Pinho, S.C.d.; Gomes, A.; Dacanal, G.C.; Sobral, P.J.d.A.; Moraes, I.C.F. Designing Pickering Emulsions Stabilized by Modified Cassava Starch Nanoparticles: Effect of Curcumin Encapsulation. *Processes* **2024**, *12*, 1348. https://doi.org/10.3390/pr12071348

Academic Editor: Urszula Bazylinska

Received: 1 June 2024
Revised: 25 June 2024
Accepted: 26 June 2024
Published: 28 June 2024

1. Introduction

Curcumin, a low-molecular-weight polyphenolic compound, is a powerful natural antioxidant found in *Curcuma longa* L. rhizomes [1–3], being widely used as preservative, flavoring, and natural coloring in beverages and foods [4]. In addition, it has been extensively studied due to its several biological activities, such as anti-inflammatory, antibacterial, antifungal, antitumor, anti-hypocholesterolemic, and antiproliferative activities [3,5]. However, curcumin is hydrophobic and photosensitive and degrades faster when exposed to light and oxygen, which can limit its incorporation in many food products [6].

In recent years, several studies have explored the ability of different systems to protect bioactive compounds [7,8]. Due to their high stabilization and high food safety, in terms of toxicity, Pickering emulsions have been considered ideal options for this purpose [7]. Thus, this type of emulsion can be used to encapsulate hydrophobic nutraceuticals and increase

encapsulation efficiency [9]. Furthermore, many studies have investigated the encapsulation efficiency of these bioactive compounds in different systems [6,10], and Pickering-type systems have shown promising results for protecting and releasing curcumin [7].

The Pickering stabilization system occurs due to a rearrangement of solid particles at the droplet interface to form a dense and thick interfacial layer, generally irreversible due to the high desorption energy [8,11]. Due to long-term stabilization and high food safety, in terms of toxicity, Pickering emulsions can be efficiently used to encapsulate and protect bioactive compounds. Pickering emulsion-based carrier systems improve the physical and chemical stability of the polyphenols over time and provide higher encapsulation efficiency than other emulsified systems [6,9,10].

Solid particles, such as starch, can be used as stabilizers to produce Pickering emulsions. Starch is GRAS (generally recognized as safe), non-allergenic, abundant, and low-cost [12,13]. However, native starch has high hydrophilicity, making it difficult to be used as a stabilizer at the oil–water interface. Therefore, modified starches have been evaluated for this type of application, and the most common methods include octenyl succinic anhydride (OSA) modification [14], hydrolysis [15], milling [16], solventless precipitation [17], modification with acid and nanoprecipitation [18], ultrasound [19], and high-pressure treatments [20].

Physical starch modification by heat–moisture treatment (HMT), treatment with low moisture content (<35%) and high temperatures (T > 90 °C), for a time of 1–16 h [21] or nanoprecipitation (gelatinization followed by precipitation with ethanol) is a safe process and, therefore, presents itself as an interesting option to produce particles capable of stabilizing emulsions [17,18]. Furthermore, several factors affect the stability of starch-based Pickering emulsions, such as the type of starch particles, modification degree, starch source and concentration, type of oils, emulsion composition, pH, and ionic strength [12].

These methods are interesting because HMT makes the granule more rigid and resistant to heating, producing more hydrophobic granules [22], and in the nanoprecipitation method, the nanoparticles produced are amorphous, which improves their flexibility degree and could help in the formation and stabilization of the interfacial layer of an oil droplet, for example [12,17,23]. These properties of HMT nanoparticles were shown in a previous work [23].

Therefore, in this context, the aim of this study was to encapsulate curcumin in a Pickering emulsion stabilized by nanoparticles obtained from cassava starch modified by HMT and nanoprecipitation and to evaluate the bioactive stability for 60 days. A Pickering emulsion without curcumin was used as control.

2. Materials and Methods

2.1. Materials

The ingredients used to prepare the Pickering emulsions included canola oil (Liza/Cargil, Mairinque, SP, Brazil), which was purchased from a local market, type-I cassava starch obtained from Siamar Indústria Alimentícia (Siamar, Neves Paulista, SP, Brazil), and curcumin (*Curcuma longa*) from Sigma Aldrich (Sigma Aldrich, St. Louis, MO, USA). Absolute ethyl alcohol (99.5% PA) was supplied by Exodo Cientifica (Exodo Cientifica, Sumaré, SP, Brazil), and sodium benzoate (99% PA) was sourced from Sigma Aldrich (Sigma Aldrich, St. Louis, MO, USA). The dyes Nile red and Nile blue A were also purchased from Sigma Aldrich (Sigma Aldrich, St. Louis, MO, USA). All reagents used in this study were of analytical grade.

2.2. Starch Nanoparticle Preparation

Native cassava starch was modified by HMT according to Piecyk and Domian [24], with some modifications. The starch moisture content was corrected to 20 wt%, and after 24 h (4 °C), samples were heated to 130 °C for 4 h in an air convection oven (Tecnal, TE-394/3, Piracicaba, SP, Brazil).

Starch nanoparticles (SNPs) were produced following the method described by Ge et al. [17], with modifications. Native and modified cassava starches were dispersed in distilled water (5 wt%) and gelatinized at 95 °C for 30 min. After cooling (25 °C), absolute ethanol (99.5%) was added dropwise at a ratio (v/v) of 1:1 (water:ethanol), under mechanical stirring. The mixture was stirred continuously for 12 h at room temperature. Subsequently, samples were centrifuged (5430R, Eppendorf, Hamburg, Germany) at 3000× g for 15 min and washed twice with absolute ethanol (99.5%). SNPs were lyophilized (LC5500, Terroni, São Carlos, SP, Brazil) and stored in transparent plastic containers, hermetically sealed. Particles were named NSNPs or HSNPs when produced from native or HMT starches, respectively.

2.3. Production of Pickering Emulsions and Curcumin Encapsulation

Oil–water (O/W) emulsions were prepared with 20 wt% of canola oil as the oily phase. SNPs were added to the aqueous phase, and the emulsification process was carried out using a rotor-stator homogenizer (T25, IKA, Staufen, Germany) at 14,000 rpm for 3 min. In addition, sodium benzoate (0.02 wt%) was used as a preservative. The effects of SNP type and concentration (0.8, 2.4, 3, or 4%) (g of SNPs/100 g of emulsion) on the properties of emulsions were evaluated [8].

The emulsion with the lowest instability index (determined according to the methodology described in Section 2.4.1) was selected for the addition of 0.07 g of the curcumin/100 g emulsion [25].

Emulsions containing NSNPs and HSNPs were named EN and EH, respectively, following numbers 0.8, 2.4, 3, or 4 according to particle concentration [23]. The EHC4 sample has curcumin in its formulation.

2.4. Characterization of Pickering Emulsions

2.4.1. Physical Stability

The emulsion was stored in a glass bottle at 20 °C in a BOD incubator (MA 415, Marconi, Piracicaba, SP, Brazil) for 14 days. The physical stability was assessed by visual analysis, as well as by creaming index (CI) and instability index (II) measurements. CI was calculated by Equation (1) [26].

$$CI\ (\%) = \frac{Hs}{Ht}100 \quad (1)$$

where H_s and H_t are the height of the serum layer (if destabilization occurred) and of the fresh emulsion, respectively.

Moreover, a photo centrifuge LUMiSizer (LS 610, LUM GmbH, Berlin, Germany) was used to evaluate emulsion stability under accelerated conditions at 25 °C. Sample aliquots of 0.4 mL were placed in polycarbonate cells (r = 130 mm) and immediately centrifuged at 4000 rpm. This measurement recorded the transmitted light intensity (at 865 nm) as a function of time and position over the sample every 10 s for 60 min. Instability index values (II) were directly obtained from SepView software version 4.1 (L.U.M., Berlin, Germany) [27].

2.4.2. Confocal Laser Scanning Microscopy (CLSM)

The interfacial structure of the Pickering emulsion droplets was observed using confocal laser scanning microscope (Upright, LSM780-NLO, Madrid, Spain). Nile red solution (0.1% *w/v*, in ethanol) was prepared, and 10 µL of this solution/g of lipid was used in the oily phase. To stain SNPs, Nile blue dye was used at a 0.05 mg/mL SNP suspension. A small droplet was placed on a glass slide, covered with a coverslip, and observed under the microscope. Nile red and Nile blue fluorescent dyes were excited at 488 nm and at 633 nm, respectively [28].

2.4.3. Morphology and Droplet Size Distribution

Pickering O/W emulsions were analyzed by optical microscopy (Leica DM. 500/ICC 50W, São Paulo, Brazil). A small droplet was placed on a glass slide, covered with a

coverslip, and observed with a 100× magnification lens. Images were processed using Leica Laz Ez software, version 3.4.0 (Leica, São Paulo, SP, Brazil). This analysis was performed on fresh emulsions and on days 7 and 14.

For each sample, at least 30 microscopic images were taken, and then, the emulsion droplet size was analyzed by observing at least 40 droplets for each micrography. The droplet size distribution was determined using ImageJ v.1.53 (National Institutes of Health and the Laboratory for Optical and Computational Instrumentation, Bethesda, MD, USA) and Mathematica software version 13.1 (Wolfram Mathematica, Oxfordshire, UK). The provided Mathematica Wolfram code snippet applies a sequence of image processing methods to an imported image (Figure 1). First, the image is submitted to edge detection, highlighting the edges using a specified radius and threshold (Figure 1a). Border components are then removed to eliminate noise near the image's edges (Figure 1b). The highlighted edges are dilated to connect any disjointed segments (Figure 1c), and the resulting regions are filled (Figure 1d). Finally, components with circularity greater than 0.9 are selected, effectively filtering out noncircular objects. These operations collectively serve to preprocess the image, enhance edges, remove unwanted particles, and isolate the circular emulsion droplets of interest [29].

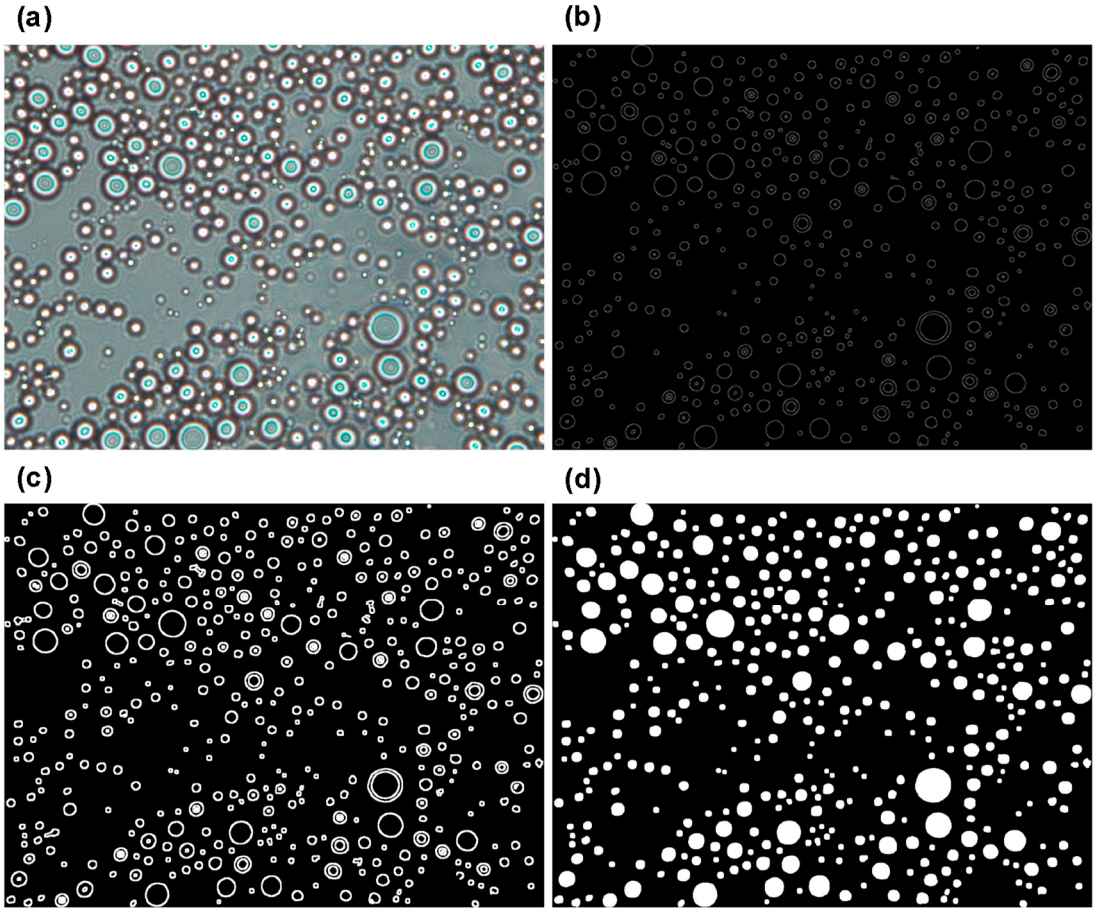

Figure 1. Image processing of Pickering emulsion droplets using Wolfram Mathematica software (**a**–**d**).

The droplet size was expressed as volume-weighted mean diameter (D[4,3]) calculated by Equation (2), where n_i is the number of particles of diameter d_i [28].

$$D[4,3] = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (2)$$

The span was calculated using Equation (3), in which D_i is the diameter, below which i% of the sample is contained (i = 10, 50, 90) [30].

$$Span = \frac{D_{90} - D_{10}}{D_{50}} \quad (3)$$

2.4.4. Dynamic Interfacial Tension

Interfacial tension measurements of the water/oil phases were performed using a tensiometer (Teclis, Tracker-S, Tokyo, Japan) via the pendant droplet method, at 25 °C during 3600 s [31].

2.4.5. Zeta Potential

The zeta potential of samples (pH~7.0) was determined using Zetaplus equipment (Brookhaven Instruments Company, Holtsville, NY, USA) at 25 °C, via electrophoretic mobility. Samples were diluted in deionized water (0.1% *w/v*). Data were obtained by the equipment software [32].

2.4.6. Rheological Behavior (Flow Curves)

The rheological behavior of emulsions was determined at 25 °C using a rotational rheometer (AR 2000, TA Instruments, New Castle, DE, USA) with cone-plate geometry (4°, 60 mm diameter). The flow curves of samples (shear stress or viscosity as a function of the shear rate) were measured by up-down continuous ramp mode in the shear rate range from 0.01 to 100 s^{-1} [33]. The power-law model (Equation (4)) fit the down-curve experimental data by using Rheology Advantage Data Analysis software version 5.3.1 (AR 2000, TA Instruments, New Castle, DE, USA).

$$\tau = k \cdot \gamma^n \quad (4)$$

where τ is the shear stress, k is the consistency index, γ is the shear rate, and n is the flow behavior index.

2.5. Quantification of Encapsulated Curcumin

The quantification of curcumin encapsulated in the Pickering emulsions followed the methodology of Chignell et al. [34]. A 1:10 sample dilution was made in deionized water, and 1 mL of the first dilution was diluted again in 9 mL of DMSO. The curcumin concentration was determined by reading the absorbance in a spectrophotometer (FEMTO, CIRRUS 805T, São Paulo, SP, Brazil) at 430 nm. The absorbance (Abs) was converted into curcumin concentration (c) using a standard curve (Abs = 0.1493 × c + 0.0262, R^2 = 0.9983) at a concentration ranging from 0.5 to 6.0 μg/mL.

2.6. Economic Analysis

Economic analysis was calculated based on the costs of raw materials and the cost of energy in Brazil. The energy expenditure of the equipment was based on the values indicated by the manufacturers. The calculations were made in Excel software version 2016 (Microsoft, São Paulo, Brazil) based on the inputs and energy involved in the production process.

2.7. Statistical Analyses

Experiments were performed in, at least, triplicate. Results were submitted to analysis of variance (ANOVA), and means were compared by the Tukey test ($p < 0.05$), using SAS software version 9.4 (Statistical Analysis System, São Paulo, Brazil).

3. Results and Discussion

3.1. Effect of SNP Type and Concentration on Emulsion Stability

3.1.1. Visual Appearance and Physical Stability

Figure 2a shows the visual appearance of Pickering emulsions, monitored for up to 14 days of storage. All emulsions produced with NSNPs, regardless of nanoparticle concentration, presented phase separation after a few hours of preparation. On the other hand, the sample with the highest HSNP concentration (4%) remained stable for 14 days of storage. Pickering emulsions were monitored by observing the phase separation during storage, through the creaming index (CI%) (Figure 2b). Only the samples that exhibited phase separation, after the homogenization process and during 14 days of storage, are shown in Figure 2b. Emulsions stabilized with NSNPs showed higher CI (70–40%) than emulsions stabilized with HSNPs (CI = 70–0%). The instability index (II) values (Figure 2c), determined using Lumisizer equipment, corroborate the CI results, in which all samples with NSNPs had a higher instability index (0.40–0.89) compared to samples with HSNPs (0.20–0.62) at the same concentration range (0.8–4 wt%). The lower the instability index values (closer to zero), the higher the emulsion stability.

Formulations with SNP concentration $\leq$ 3% showed phase separation, regardless of the type of particle used. This occurs because lower stabilizer concentrations may have been insufficient to fully cover the droplet interface, which explains the greater instability of these formulations. The increase in NSNP concentration to 4 wt% reduced the height of the cream phase. On the other hand, emulsion stabilized by 4 wt% HSNPs did not show any creaming process, indicating that HSNPs were able to form a layer around the droplets covering the entire interfacial area. These results agree with Kamwilaisak et al. [35], who produced Pickering O/W emulsion (30:70 sunflower oil:water) stabilized with rice SNPs crosslinked by citric acid and also observed that the increase in SNP concentration from 0.5 to 4.0% improved emulsion stability.

Some reasons may explain the difference between SNP types and the way they stabilize the oil droplet interface, resulting in systems with distinct stabilities. Studies have shown that HMT-modified starch can present a weaker granule, with roughness and cracks on its surface, due to harsh heat and moisture treatments, in addition to reduction in the granule crystalline area [36,37]. Dewi et al. [37] modified cassava starch by HMT and observed roughness, cracks, and hollows at the center of granules, which was not observed for native cassava starch, in addition to reduction in relative crystallinity from ~36.5 to 28.7% after thermal modification.

The reduction in relative crystallinity and the formation of cavities and holes after modification by HMT are caused by the recombination of amylose and amylopectin chains forming a more compact amorphous region [37]. These authors observed that HMT-modified starch had a rough surface and justified the results by the evaporation of water molecules, inducing the double helix chain of amylopectin to reorganize itself into a denser packing structure, which acts as a barrier to the penetration of water into starch granules. This weakening of the HMT starch granule, as well as the rearrangements of amylose/amylopectin chains, can lead to the production of nanoparticles with smaller sizes. Smaller particles can more easily be adsorbed at the O/W interface, promoting a more efficient physical barrier formation. In our previous study, the HSNPs exhibited sizes ranging from ~60 to 700 nm, while the NSNPs covered a much larger size range, from ~25 to 2000 nm [23].

In addition to smaller size, after nanoprecipitation, HSNP particles have higher surface roughness when compared to the NSNPs' surface [23]. This is due to the rearrangement of laminar aggregates formed by hydrogen bonding interactions during nanoprecipitation, resulting from the high number of hydroxyl groups on the particle surface. The rough surface leads to an increase in the hydrophobic character. The higher particle hydrophobicity enables platelets to be more strongly organized by hydrophobic peaks, forming a dense interfacial monolayer or multilayer film on the surface of their emulsified droplet units.

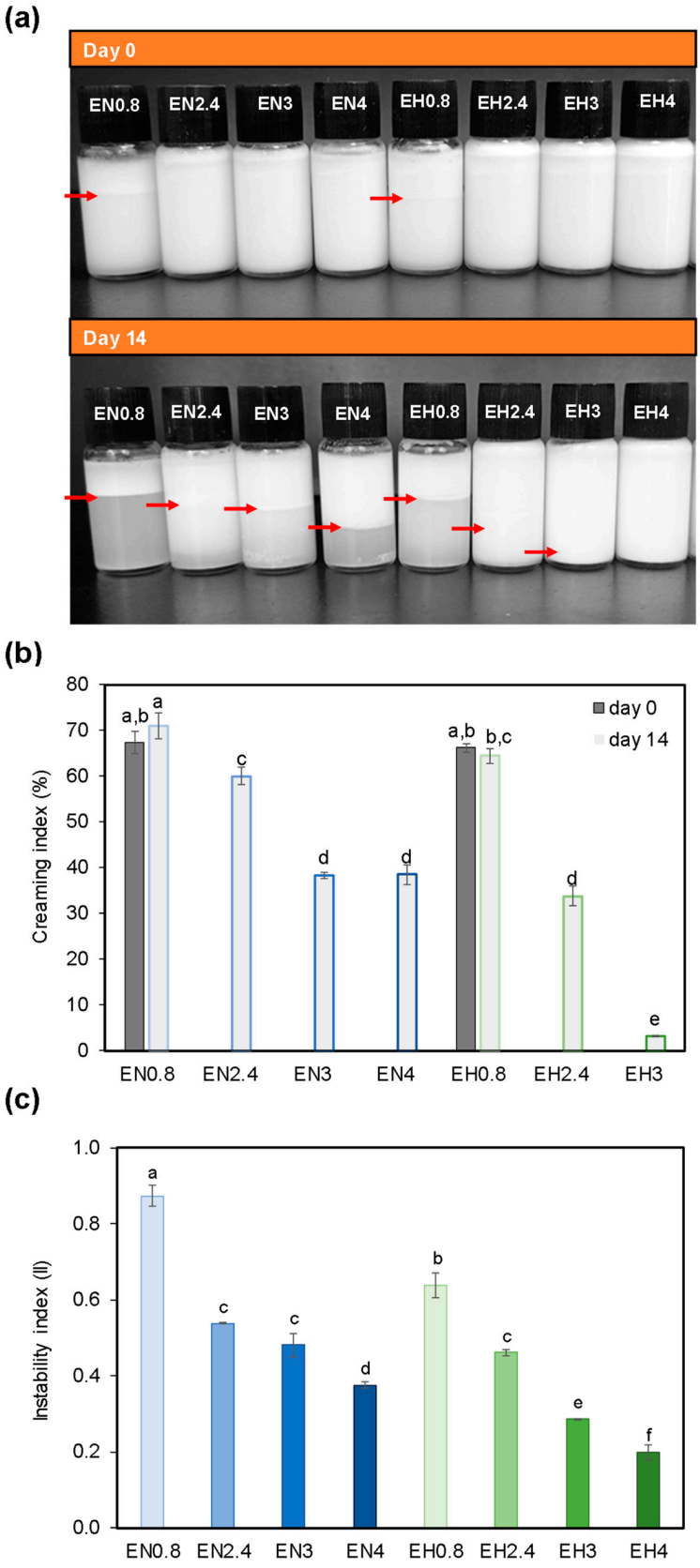

Figure 2. Visual appearance (**a**), creaming index (**b**), and instability index (**c**) of Pickering emulsions stabilized by NSNPs (EN) and HSNPs (EH) at different SNP concentrations (0.8, 2.4, 3, and 4%). Red arrows indicate phase separation. Values followed by the same lowercase letters do not differ significantly ($p < 0.05$).

In fact, it is widely known in the literature that Pickering emulsions use solid particles with intermediate hydrophobicity strongly adsorbed at the interface between two immiscible liquids to provide a steric hindrance against the aggregation of emulsion droplets [38]. Ge et al. [17] studied the effect of the SNP type (corn, tapioca, and sweet potato), obtained by nanoprecipitation, on the stabilization of Pickering emulsions. The authors reported that starches with intermediate hydrophobicity, i.e., almost neutral wettability (θ~90°), were suitable for Pickering stabilization. When highly hydrophilic particles were used, the droplet size became large due to the high number of hydrogen bonds formed with water, and such particles are unlikely to be efficient Pickering stabilizers [17]. This was confirmed by our previous study, which found that HSNP particles exhibited wettability closer to neutral than NSNP particles, with contact angles of 77.3° and 68.4°, respectively [23].

Thus, in this study, the most stable emulsion, the one with the lowest instability index (EH4), was selected to encapsulate the curcumin (EHC4). The microstructure of the EH4 emulsion was investigated (by CLSM) to better understand the stabilization system. Furthermore, these two formulations (with and without curcumin) were characterized in terms of droplet size distribution, interfacial tension, zeta potential, and flow behavior. The quantification of encapsulated curcumin was monitored for up to 60 days.

3.2. Characterization of Stable Pickering Emulsions

The Pickering emulsion with encapsulated curcumin (EHC4) also did not present any creaming for 14 days. However, the addition of curcumin reduced the instability index (II) from 0.20 ± 0.02 (EH4, Figure 2c) to 0.08 ± 0.02 (EHC4), indicating that this bioactive compound significantly improved the emulsion stability.

This fact suggests that curcumin interfered in HSNP adsorption at the droplet interface, resulting in a more compact system formation. Curcumin has two aromatic rings linked by a carbon chain in its structure, and therefore, it is a molecule with hydrophilic parts (hydroxyl/ketone) and hydrophobic parts (aromatic), and despite being a molecule typically insoluble in water, it can be easily allocated in the O/W interface [39].

In fact, some studies have shown that curcumin crystals can even stabilize Pickering emulsions. Zembyla, Murray, and Sarkar [40] produced W/O (5:95 water:soybean oil) emulsions, with curcumin crystals as a stabilizer, varying the concentration of this particle from 0.06 to 1.5 wt%. At the average particle concentration (~0.14%), the authors observed system stability, with maintenance of the size of droplets of emulsions for up to 7 days of storage. These authors also showed that water droplets were surrounded by a dense layer of curcumin particles, through CLSM, confirming the preferential location of polyphenol crystals at the W/O interface.

3.2.1. Microstructure by Confocal Laser Scanning Microscopy

Pickering emulsion stabilized with 4 wt% HSNPs proved to be highly stable, and its microstructure was investigated using CLSM microscopy (Figure 3). The technique allows differentiating SNPs (Figure 3a, blue) from the oil (Figure 3b, red) with dyes of different colors (Nile blue A and Nile red, respectively), allowing visualization of the interaction of materials at the emulsion interface and stabilization. Images clearly show blue halos around a red oil droplet. The micrograph showed that HSNPs were adsorbed at the O/W interface (Figure 3a), with no significant numbers of particles in the continuous phase. The HSNP layer on the surface of emulsion droplets acts as a strong physical barrier (Figure 3c), effectively preventing droplet coalescence through steric hindrance, providing high storage stability.

Ren et al. [41] observed, through CLSM, different droplet sizes and starch/xanthan SNPs present in the droplet interface and in the continuous phase of the emulsion, indicating that some particles are not adsorbed at the interface. These authors also reported that the excess of particles, which were in the continuous phase, formed three-dimensional networks that could effectively capture oil droplets and prevent their movement and aggre-

gation. This behavior was not observed in our work, since particles remained essentially at the droplet interface.

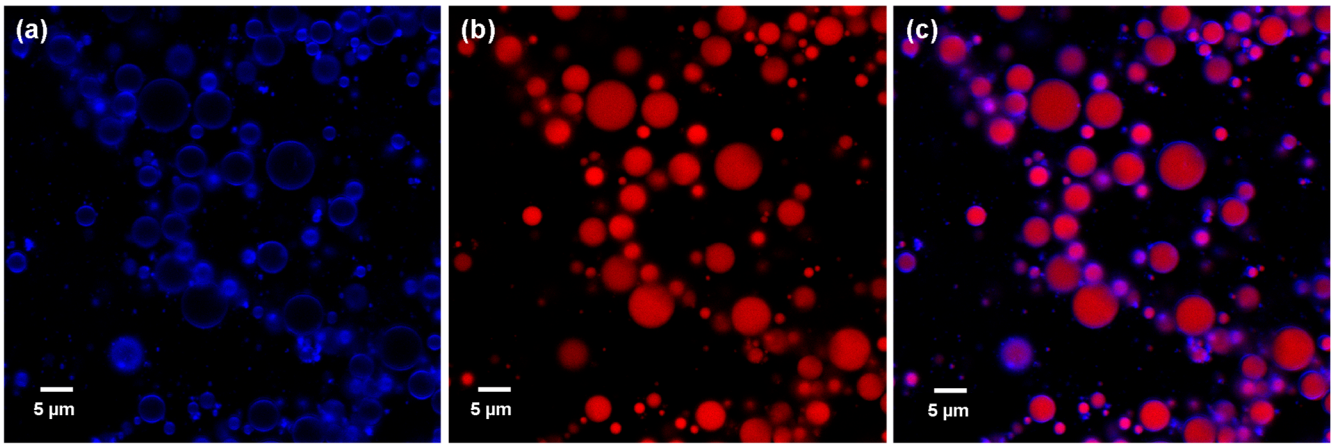

Figure 3. Micrographs obtained by CLSM Pickering emulsion stabilized by HSNPs (4 wt%). (**a**) SNPs stained with Nile blue, (**b**) oil stained with Nile red, and (**c**) HSNPs + oil. Scale bar = 5 µm.

3.2.2. Optical Microscopy and Droplet Size Distribution

Optical microscopy of fresh emulsions and after 14 days of storage (Figure 4) was performed. The micrographs of emulsions (EH4, EHC4) showed small and homogeneous size distribution. Storage did not seem to have influenced the morphology of emulsions during the monitoring period (up to 14 days), which confirms the stability of these emulsions.

The accumulated mass fraction of droplets (Figure 4e,f), the volume-weighted mean diameter values (D[4,3]), as well as accumulated diameters (D_{10}, D_{50}, and D_{90}), and the span (Table 1) of fresh Pickering emulsions were made with the help of Mathematica software.

Table 1. Mean droplet size (D[4,3]) and span of fresh Pickering emulsions produced by HSNPs (4 wt%) without (EH4) and with curcumin (EHC4).

Sample	D[4,3] (µm)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	Span
EH4	9.54 ± 0.18^{a}	3.82 ± 0.23^{a}	9.13 ± 0.23^{a}	15.91 ± 0.04^{a}	1.32 ± 0.06^{a}
EHC4	6.07 ± 0.03^{b}	3.56 ± 0.28^{a}	6.07 ± 0.08^{b}	8.54 ± 0.28^{b}	0.82 ± 0.10^{b}

Values followed by the same lowercase letters in the same column do not differ significantly ($p < 0.05$).

The mean diameter D[4,3] and the span of EH4 emulsion droplets were 9.54 µm and 1.32 (Table 1), respectively. The D[4,3] value was lower than those obtained by Wang et al. [8], who produced Pickering emulsion stabilized with debranched and/or esterified starch, reporting D[4,3] droplet sizes ranging from 31 to 105 µm. It was also lower than the result obtained by Kamwilaisak et al. [35], who determined a mean diameter of 50 µm for the droplet size of a Pickering emulsion (30:70 O:W) stabilized with 4 wt% rice SNPs crosslinked by citric acid.

The EHC4 emulsion showed an appearance and droplet shape similar to the sample without curcumin (EH4), with no changes observed in the storage time. However, the D[4,3] of the curcumin-loaded emulsion was significantly smaller (6.07 µm) (Table 1) than that of the emulsion without curcumin. Feng et al. [42] also reported droplet size reduction from 219 nm to 171 nm when curcumin was incorporated into the O/W emulsion formulation using debranched starch and Tween 80. According to these authors, the addition of curcumin maintained the droplet size unchanged even after 7 days of storage, a phenomenon that did not occur for the same formulation without the bioactive compound.

The span, which refers to the width of the droplet size distribution range within the emulsion, can influence emulsion stability [43]. For Pickering emulsions, this parameter can be associated with the arrangement of solid particles at the oil–water interface. This

rearrangement can be optimized with a narrower span, leading to improved coverage of droplet surfaces and resulting in enhanced stability [43]. The curcumin-loaded Pickering emulsion showed a significantly lower span value (0.82) than the emulsion without the bioactive compound (Table 1). This finding is justified by the fact that smaller particles can lead to narrower spans and more uniform sizes, which could contribute to improve stability, and this result is consistent with the instability index (Section 3.1.1).

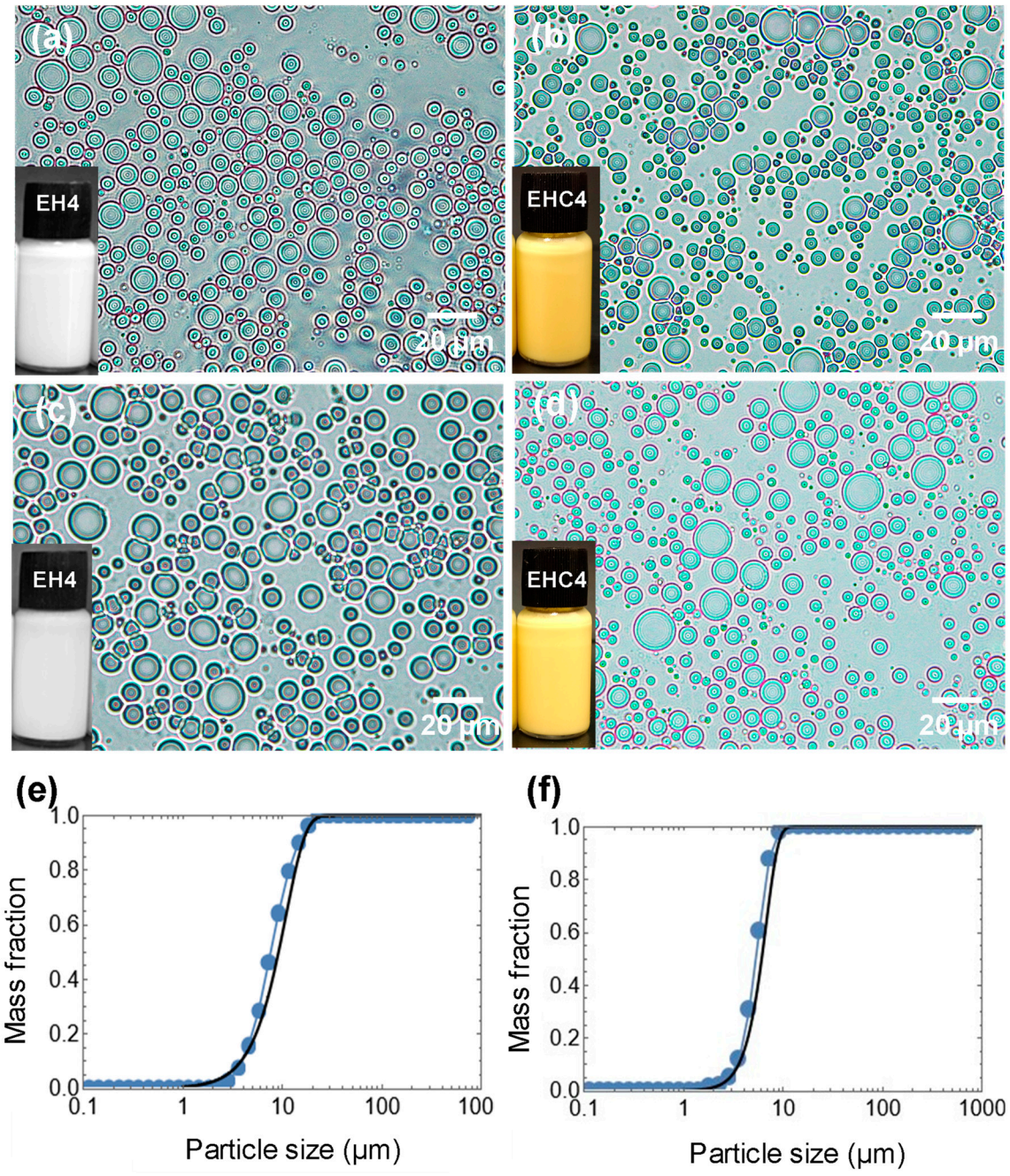

Figure 4. Visual aspect, optical microscopy, and droplet size as a function of the accumulated mass fraction of Pickering emulsions stabilized by HSNPs (4 wt%), without (**a**,**c**,**e**) and with curcumin (**b**,**d**,**f**) on production days 0 (**a**,**b**,**e**,**f**) and 14 (**c**,**d**). Scale bar = 20 µm.

3.2.3. Dynamic Interfacial Tension

The tension (Figure 5) between the water–oil phases with the addition of HSNPs (4 wt%) and curcumin (0.07 wt%) was evaluated to understand the role of each component in the emulsion stability and formation of the interfacial film.

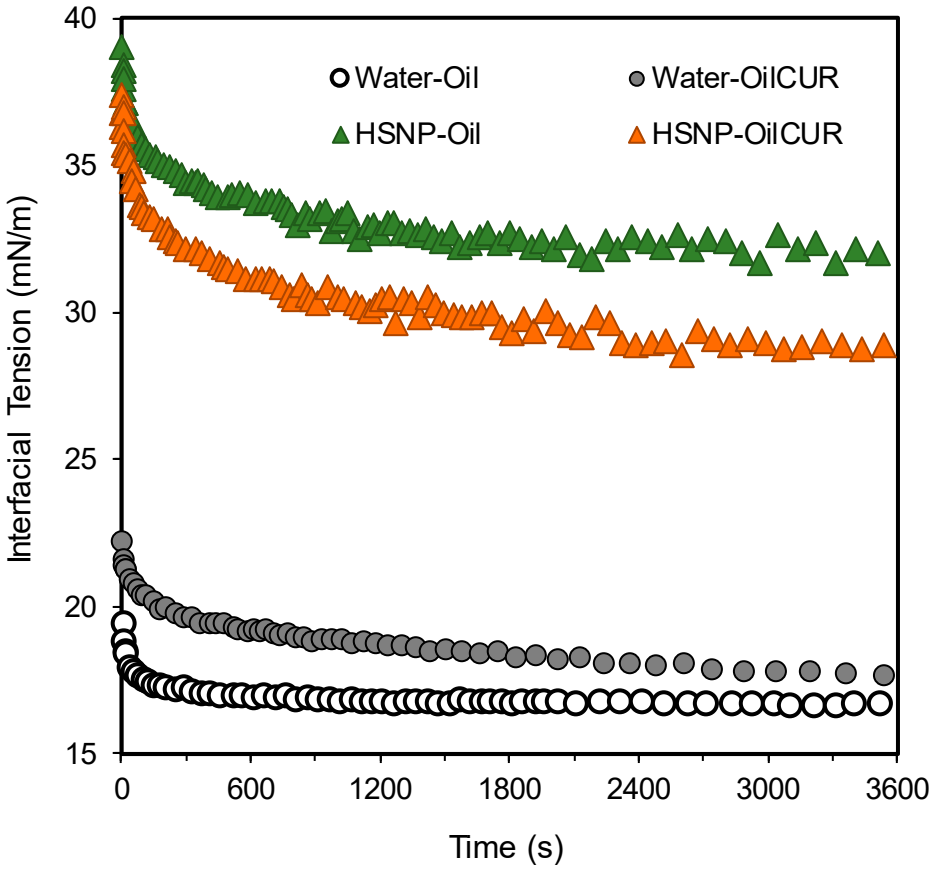

Figure 5. Interfacial tension curves of systems composed of water–oil (white), water–curcumin-loaded oil (gray), HSNP water–oil (green), and HSNP water–curcumin-loaded oil (orange). HSNPs and curcumin were added, when applicable, at concentrations of 4 wt% and 0.07 wt%, respectively.

The water–oil curves showed an initial interfacial tension value of ~20 mN/m. This value increased to ~40 mN/m after the addition of HSNP particles in the aqueous phase. The initial interfacial tension of the HSNP water–curcumin-loaded oil system (Figure 5) was 36 Nm/m, a lower value compared to the HSNP water–oil system (~40 mN/m). However, the opposite phenomenon occurs with curves without stabilizer particles in the system (water–curcumin-loaded oil), in which the addition of curcumin increased the initial interfacial tension in relation to the water–oil curve from ~20 to 22 mN/m. The bioactive molecule, as mentioned earlier, can also interact at the droplet interface and influence the stabilization mechanism. Moreover, curcumin can interact with amylose chains forming in carbohydrate–phenolic complexes. This interaction could explain the decreased tension observed in Figure 5 when both molecules are present [42].

Feng et al. [42] demonstrated, using molecular dynamics simulations, that in the interactions among debranched starch (DBS), curcumin, and water, hydrogen bonds were formed between DBS residues and curcumin molecules, and in systems without curcumin, only unstable hydrogen bonds were formed. Furthermore, these authors reported that, over time, the rearrangement of the two molecules showed a final structure where curcumin was located within the lumen of the DBS helix.

Figure 6 illustrates a schematic representation of the interfacial layer composed solely of HSNPs and a mixture of HSNPs with curcumin, based on the results of our study.

This suggests that curcumin can interact with HSNPs to form carbohydrate–flavonoid complexes. This interaction may alter the adsorption process of HSNPs at the droplet interface. Additionally, free curcumin can adsorb at the oil–water interface due to the presence of hydrophilic and hydrophobic parts in its structure, resulting in the formation of a more compact interfacial layer.

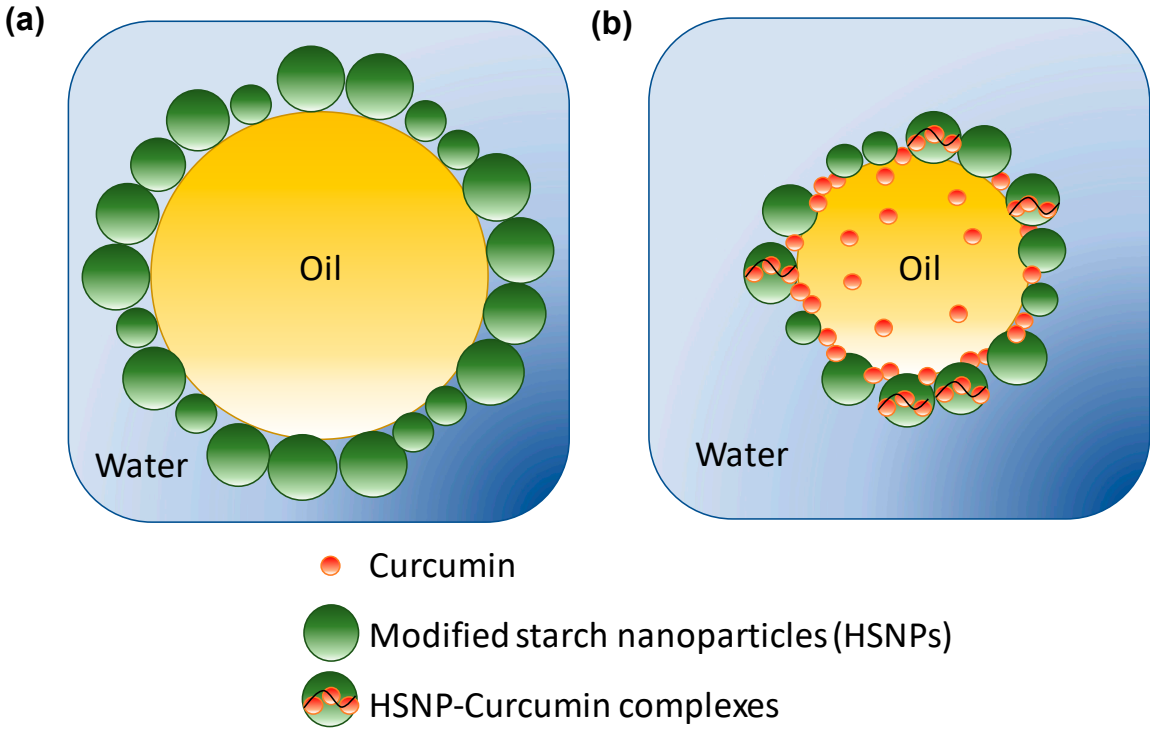

Figure 6. Schematic representation of the interfacial layer of the Pickering emulsion (**a**) without and (**b**) with curcumin.

Typically, the addition of stabilizers in formulations tends to decrease the overall interfacial tension of the system. Han et al. [44] evaluated the interfacial tension of wheat starch in a soybean oil/water system and reported initial reduction in the interfacial tension from 50 to 43 Nm/m. However, this behavior was not observed in our work. Unlike traditional surfactants (such as low-molecular-weight synthetic surfactants), this decrease in tension is not necessarily expected for this type of system. In fact, it could be inferred that the reduction in interfacial tension is not the mechanism responsible for stabilizing the interface of Pickering emulsions; that is, particles do not act as surfactants.

This behavior can also be explained by the fact that polysaccharides are less effective in reducing interfacial tension compared to other molecules, such as proteins or low-molecular-weight surfactants, because they are less able to thermodynamically establish unfavorable contacts between nonpolar groups and water [45]. In addition, due to the low lipophilic properties of some polysaccharides, adsorption at the oil–water interface is a challenge. However, they can envelop the droplet surface and stabilize the emulsion through steric hindrance [46].

The increase in interfacial tension with the addition of HSNPs in systems may also be associated with the phenomenon of competition between SNPs and minor canola oil components. Canola oil is mainly composed of triacylglycerols (94–99%) with a high concentration of oleic acid (61.6%) followed by linoleic acid (21.7%), which are monounsaturated and polyunsaturated fatty acids, respectively. This oil also has minor components such as phospholipids, free fatty acids, tocopherol, sulfur, and iron [47]. Thus, these minor components can compete with SNPs for allocation at the droplet interface, causing an increase in the interfacial tension in relation to the system without particles.

Systems without a stabilizer (HSPN) reached the equilibrium interfacial tension quickly, ~120 s, and for samples containing HSNPs, the analysis time was ~300 s (Figure 5), a similar behavior when comparing systems with or without curcumin, resulting in minor reduction in interfacial tension value (~5 mN/m). These findings suggest that both HSNPs and curcumin exhibit low surface activity, and the mechanism behind emulsion stabilization is based on steric hindrance. Furthermore, the similar kinetic behavior indicates that HSNP particles could migrate to the droplet interface at the same rate, regardless of the presence of the bioactive compound in the emulsion formulation. Liu et al. [48] also reported in their study that interfacial tensions between chitosan and mineral oil decreased over time and reached equilibrium, indicating their spontaneous adsorption at the oil–water interface (~300 s, resulting in about a 2 mN/m reduction in the initial interfacial tension).

The adsorption of colloidal particles at the oil–water interface involves at least three steps: (1) bulk diffusion to the interface, (2) penetration at the interface, and (3) structural rearrangement and formation of viscoelastic films at the interface [49]. The kinetics of the initial interfacial tension decrease is related to the diffusion degree of the emulsifier to the droplet interface [50]. In this work, HSNP particles were able to adhere to the droplet interface; however, there was no reduction in interfacial tension but an increase in this parameter, which may have occurred due to the previously explained mechanisms.

3.2.4. Zeta Potential Determination

The zeta potential (ZP) of emulsions was determined to enable the understanding of interactions at the droplet interface. All samples showed low zeta-potential values (~4.7 mV, Table 2), with no significant difference ($p < 0.05$) from each other (Table 2). These low absolute ZP values discard the possibility of stabilization by electrostatic repulsion, confirming the existence of only the stabilization mechanism based on steric hindrance, a characteristic behavior of Pickering emulsions [51]. This result is consistent with our previous work [23], in which starch particles demonstrated a zeta potential of -3.4 ± 0.6 mV.

Table 2. Zeta potential and power-law model coefficients obtained from flow curves of fresh Pickering emulsions stabilized by HSNPs (4 wt%), without (EH4) and with (EHC4) curcumin.

Sample	Zeta Potential (mV)	n (Flow Index)	K (Pa.s^n)	R^2
EH4	-5.05 ± 0.46 ^{a}	0.75 ± 0.01 ^{a}	0.43 ± 0.02 ^{a}	0.999
EHC4	-4.20 ± 0.11 ^{a}	0.76 ± 0.01 ^{a}	0.29 ± 0.00 ^{b}	0.997

Values followed by the same lower-case letters in the same column do not differ significantly ($p < 0.05$).

In other words, the addition of curcumin to the formulation also did not significantly influence the ZP values (Table 2). These results show that HSNPs remain in the interfacial layer composition as a physical-barrier-type emulsifier, showing no changes in intensities of interactions measured by the emulsion ZP. Differently from our results, Feng et al. [42] produced emulsions with debranched starch (500 mg) and Tween 80 (aqueous phase) and curcumin (10 mg), lecithin, and ethanol (oil phase) and reported zeta-potential values ranging from −15 to −17 mV, with the addition of curcumin in the formulation. This result suggests that the addition of a bioactive compound can intensify the electrostatic repulsion mechanism, resulting in an improvement in the emulsion stability.

Higher absolute ZP values were found by Shao et al. [46] compared to those found in our work. The authors produced Pickering O/W emulsions with medium-chain triglyceride oil (50:50 oil:water) and taro SNPs (3–5 wt%) and reported ZP values of emulsions ranging from −18 to −20 mV in fresh emulsions. Even higher ZP values, from −27 to −31 mV, were shown by Remanan and Zhu [14] for emulsions stabilized by SNPs from quinoa, corn, and potato, with proportions of SNPs to oil at 0.25% *w/v*.

3.2.5. Rheological Behavior

Rheological properties are employed to understand emulsion flow behavior, identify appropriate applications, and assess the stability of the emulsion. Figure 7a shows that

emulsions presented a nonlinear relationship between shear stress and shear rate, which characterizes non-Newtonian fluid behavior. The power-law model was fitted to experimental data with good determination coefficients ($R^2 > 0.997$) (Table 2). Both samples exhibited thinning shear behavior (n < 1), with the apparent viscosity decreasing as the shear rate increased (Figure 7b). This behavior is likely attributed to the deformation and rupture of the oil–water interfacial film or droplet deformation as the shear rate increases [52].

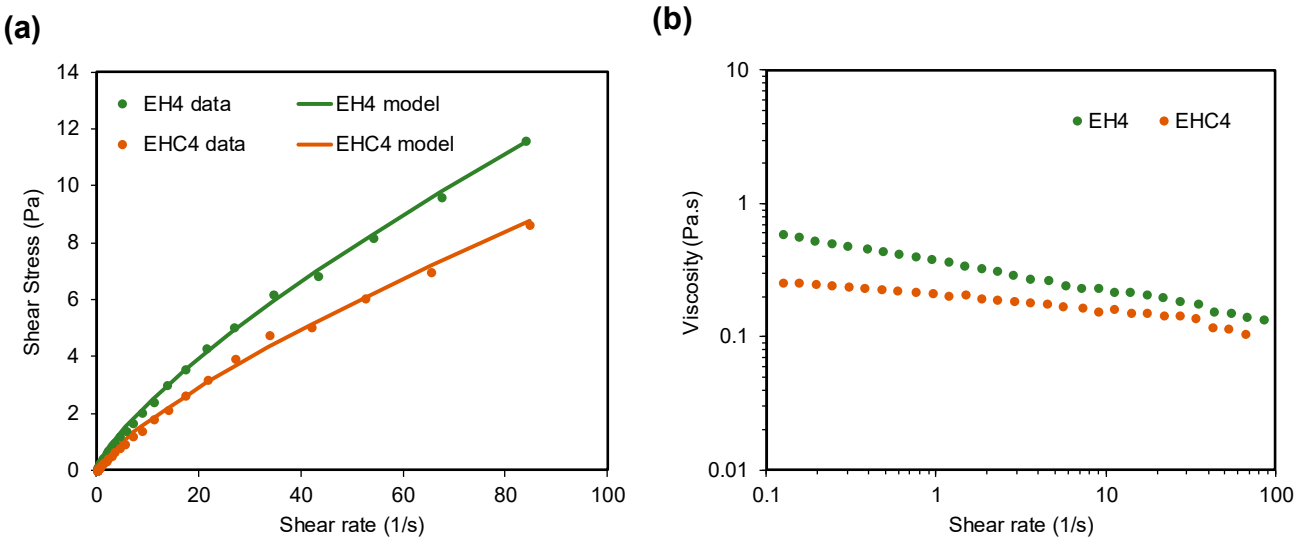

Figure 7. (**a**) Downward flow curves (solid line—power-law model) and (**b**) apparent viscosity as a function of the shear rate of Pickering emulsions stabilized by HSNPs (4 wt%) without (green, EH4) and with curcumin (orange, EHC4).

Curcumin incorporation in the formulation led to a decrease in the apparent viscosity values (Figure 7b) and a reduction in the consistency index (k) from 0.43 to 0.29 Pa·s ^{n} (Table 2). This effect can be attributed to the droplet sizes and broader size distribution (PDI) observed in the emulsion without curcumin (Table 1). A wider range of droplet size allows for greater interaction and hinders flow, leading to higher apparent viscosity. Kamwilaisak et al. [35] produced Pickering O/W emulsions (30:70) with rice SNPs (0.49 wt%) and curcumin (1.6 ppm/ mL oil) encapsulated in the sunflower oil phase and also reported pseudoplastic fluid behavior (n = 0.80), with, however, yield stress values from 0.39 Pa.

Similar results were obtained by Ren et al. [41] when evaluating Pickering emulsions stabilized with xanthan gum/SNPs and also by Wang et al. [8], who used debranched and/or esterified starch. These authors reported good fit to the power-law model, in which the apparent viscosity of all emulsions decreased with increasing shear rate. Qian et al. [53] also observed a decrease in the apparent viscosity of Pickering emulsions stabilized with acetylated starch nanocrystals with the reduction in particles in the formulation.

3.3. Encapsulated Curcumin Quantification

The encapsulated curcumin quantification in emulsion EHC4 was performed after up to 60 days of storage to evaluate the chemical stability of this bioactive compound (Figure 8). The amount of curcumin initially determined in the fresh emulsion was approximately 427.3 ± 18.7 µg/mL, and this value was maintained without significant difference ($p < 0.05$) up to day 60. This demonstrates the effectiveness of our developed Pickering emulsion in protecting the encapsulated bioactive compound during storage.

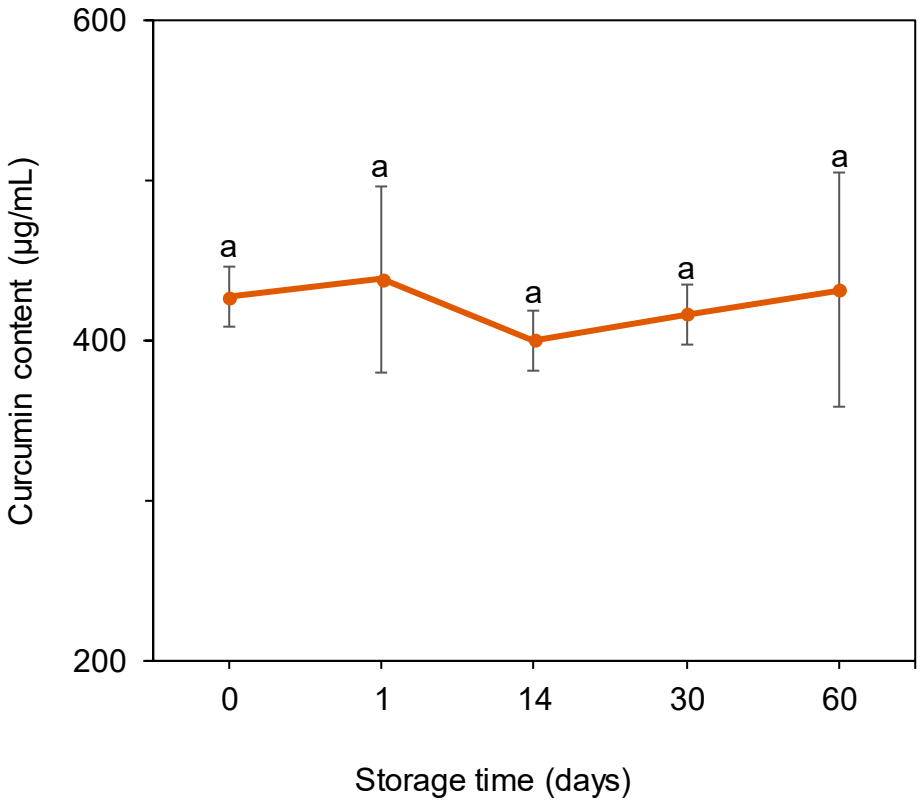

Figure 8. Encapsulated curcumin quantification in Pickering O/W emulsion stabilized with 4 wt% of HSNPs as a function of storage time. Data with the same lowercase letters do not differ significantly ($p < 0.05$).

Different results were found in the literature. Lee et al. [7] produced Pickering emulsions stabilized with waxy maize nanoparticles (1%) and chitin nanofibers (0.2%), 10% oil phase with 335 mg/mL curcumin/g of oil, and reported that residual curcumin quantified after 16 days of storage (20 °C, environment without light) was approximately 50% of that quantified on fresh emulsion. Shah et al. [54] produced Pickering emulsions with chitosan–tripolyphosphate nanoparticles, with 5 and 20% medium-chain triglyceride (MCT) in the formulation, and curcumin was added to the oily phase (MCT) at 0.1 wt%. These authors reported that, for both formulations, curcumin was degraded by 50% after 5 days of storage.

Kharat et al. [10] produced emulsions with encapsulated curcumin, with different types of emulsifiers—caseinate, Tween 80, gum Arabic, or saponin—at critical stabilizer concentrations (1.0, 1.2, and 1.6 wt%) or in excess of 15 wt% and evaluated the effect of stabilizer type and concentration on curcumin quantification (retention) during storage. These authors reported that caseinate, Tween 80, and gum Arabic stabilizers had similar behaviors, with retention of ~75% after 15 days of storage, whereas saponin presented retention of only 15%. Therefore, it could be inferred that the degradation of encapsulated curcumin depends mainly on the type of emulsifier used to coat oil droplets loaded with the bioactive, the formulation used, and the stabilization system produced.

3.4. Potential Applications and Economic Analysis

The curcumin-loaded Pickering emulsion designed in this study has potential applications in the food, nutrition, nutraceutical, cosmetics, and pharmaceutical industries. Its long-term stability, high capacity to protect the bioactive compound over time, and GRAS status make it particularly valuable for these sectors.

The curcumin-loaded Pickering emulsion is a natural and nontoxic material that can function as an edible dye for producing food matrices using 3D printing technology [3]. Its

application in dairy products, such as yogurts, would also be advantageous, as curcumin would act simultaneously as a colorant and bioactive ingredient in the final product. Furthermore, since dairy products are highly susceptible to external conditions, adding the emulsion could improve properties such as texture and shelf life, thereby enhancing the quality and longevity of the food [9]. The emulsion could also be incorporated into mayonnaise, with the aim of reducing the fat content of the food. In fact, within our own research group, this application is being successfully developed.

Encapsulating curcumin in lipid particles not only resolves the challenge linked to its high hydrophobicity but also enhances its bioavailability and bioaccessibility. Previous studies have demonstrated this using excipient food emulsions as vehicles for delivering the desired bioactive compound [2,8]. Integrating the bioactive into a carrier and protective system, like the Pickering emulsion produced in this study, facilitates the beneficial action of curcumin in the human body, including its anti-inflammatory, antitumor, and antibacterial effects. Therefore, a strong application of this system could be as a vehicle for encapsulating and controlling release of functional food ingredients.

The production of SNPs and Pickering emulsions also presents a promising financial alternative. The inputs required for producing SNPs and emulsions are considered low-cost (cassava SNPs, canola oil, and water). Curcumin is the highest value-added ingredient, and its cost depends on the purity of the product used. Therefore, the selection of curcumin purity should be based on the application and the added value of the final product.

Production of both SNPs and emulsions can be carried out using industrial equipment widely used in the food and pharmaceutical industries. However, transitioning from lab-scale to large-scale production is always challenging. A critical step in SNP production is the lyophilization process, which may increase costs and production time. Nonetheless, the estimated production costs of HSNPs are approximately 107.50 USD/kg (Supplementary Material Table S1). On the other hand, the production process of emulsions is relatively straightforward, primarily involving the emulsification process. For instance, the rotor-stator homogenizer equipment can emulsify up to 30 L in a single batch (depending on the model), facilitating scalability to pilot scale. According to the detailed economic study shown in Supplementary Material Table S2, production of our curcumin-loaded emulsion appears feasible compared to existing market products (for example, emulsions with bioactive such as lutein, nanoQ10, and astaxanthin, from the Brazilian company Yosen, are sold at approximately 660.00 USD/L) [55], with an estimated production cost of approximately 8.35 USD/L. Therefore, implementing this process on an industrial scale seems economically viable.

4. Conclusions

A kinetically stable Pickering emulsion was produced using 4 wt% HSNPs. This system effectively encapsulated and protected curcumin from degradation. CLSM confirmed that the starch particles were located at the interface of oil droplets, while interfacial tension and zeta potential analyses indicated that the high stability of this system was based on steric hindrance. The addition of curcumin reduced the interfacial tension and altered the adhesion process of the nanoparticles at the droplet interface, forming a more compact interfacial layer, which resulted in a system with smaller average droplet diameters and improved stability. Furthermore, the incorporation of curcumin reduced the apparent viscosity of the system. Curcumin quantification analysis over time demonstrated that the Pickering emulsion efficiently protected the curcumin, maintaining its stability and, therefore, preserving its functional properties for a period of up to 60 days. These findings show the potential application of the emulsified system developed in this study in pharmaceutical and food products.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/pr12071348/s1: Table S1: Production cost of the stabilizing particles (1 kg); Table S2: Production cost of emulsion (1 L).

Author Contributions: Conceptualization, I.C.F.M.; Validation, G.V.C.R.; Formal analysis, G.V.C.R., A.G. and G.C.D.; Investigation, G.V.C.R.; Resources, P.J.A.S. and I.C.F.M.; Data curation, G.V.C.R.; Writing—original draft, G.V.C.R.; Writing—review & editing, A.G., S.C.P., G.C.D., P.J.A.S. and I.C.F.M.; Visualization, G.V.C.R.; Project administration, I.C.F.M.; Funding acquisition, I.C.F.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by "Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES)"—Finance Code 001.

Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Acknowledgments: The authors thank for the access to equipment and assistance provided by the National Institute of Science and Technology on Photonics Applied to Cell Biology (INFABIC) at the State University of Campinas; INFABIC is co-funded by Research Support Foundation of the State of São Paulo (FAPESP) (2014/50938-8) and National Council for Scientific and Technological Development (CNPq) (465699/2014-6). Thanks to the Laboratory of Process Engineering (LEP) Department of Food Engineering (DEA), Faculty of Food Engineering (FEA), University of Campinas (UNICAMP), for the use of the dynamic tensiometer. P.J.A.S thanks CNPq (30.2482/2022-9) for his research fellowship, and A.G. thanks FAPESP (2019/26348-0) for her post-doc fellowship.

Conflicts of Interest: The authors declare no conflict of interest.

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