Article

Influence of Emulsification Methods and use of Colloidal Silicon Dioxide on the Microencapsulation by Spray Drying of Turmeric Oleoresin in Gelatin-Starch Matrices[†]

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ABSTRACT

Microencapsulated turmeric oleoresin can present improved curcumin stability and be easily applied in hydrophilic systems. Most of the microencapsulation techniques rely on the initial emulsification of the core material in the wall biopolymers and this step affects the encapsulation efficiency and properties of the resulting microcapsules. The objective of this work was to evaluate the effects of different emulsification methods, the use of colloidal silicon dioxide and Tween 80 as additives, and the rheological behaviour of the encapsulating gelatin-starch dispersions on the emulsion stability, encapsulation efficiency, and yield of turmeric oleoresin microcapsules produced by spray drying. The encapsulating matrices were prepared with varied concentrations of modified starch (from 0.22–0.317 g/g (22–31.7 wt%), dry basis) and gelatin (0–0.06 g/g (0–6 wt%), dry basis). The microstructure of the emulsions was evaluated through optical microscopy and small amplitude oscillatory shear rheology. The emulsification of turmeric oleoresin was performed by the following methods: high-shear mixing, using a rotor-stator homogenizer, with and without addition of Tween 80 as a surfactant; and by ultrasound homogenizer with and without the colloidal silicon dioxide (Aerosil 200). The homogenization method presented considerable influence on the emulsion stability and on the average droplet sizes in the emulsion. The concentration of gelatin directly affected the emulsion and microcapsule properties. Ultrasound homogenization and the use of colloidal silicon dioxide resulted in the highest encapsulation efficiency of turmeric oleoresin in the low total-solid formulations. This article is protected by copyright. All rights reserved

Keywords: ultrasound, emulsion stability, silicon dioxide, encapsulation efficiency, gelatin, starch, rheology

INTRODUCTION

Microencapsulation is a process in which a coating wall or an amorphous matrix encloses tiny particles of solid, liquid, or gas, forming microcapsules in order to protect the core material from adverse environmental conditions such as light, moisture, and oxygen, as well as to prevent interactions with other compounds present in a given formulation. Microencapsulation promotes product stability, increases shelf life, and may allow the controlled release of the encapsulated material under specific conditions.[1-3] Most of the microencapsulation techniques involve a previous emulsification of the core material in the solution containing the wall biopolymers. This step exerts great influence on the encapsulation efficiency and properties of the resulting microcapsules. Smaller droplets contribute to the retention of the encapsulated material within the encapsulation matrix during the drying process, reducing the amount of non-encapsulated oil on the surface of dried particles.[4-8] The kinetic stability of the core/wall material emulsion is also important for effective microencapsulation, since the emulsion breakdown within the time elapsed from its preparation up to the actual encapsulation step (e.g. coacervation, drying, ionic gelation, etc.) may give rise to coalescence of the dispersed phase, thus resulting in poor encapsulation efficiency.[9,10]

As a rule, emulsification is achieved by means of high-energy input techniques, most of which are based on mechanical devices that generate intense forces capable of dispersing one phase into another. Emulsification methods include high shear mixing, high-pressure homogenization, microfluidization, and ultrasound homogenization.[11] Ultrasound emulsification is accomplished because of cavitation, a phenomenon by which bubbles collapse at or near the oil-water interface causing disruption and mixing. The ability of ultrasound to promote emulsification depends on the wave frequency used. The generated shear forces from ultrasound are very strong at low frequencies (16–100 kHz) due to the violent nature of the bubble collapse, whereas the shear forces generated at high frequencies are relatively weaker and are not useful for emulsification. The advantages of applying ultrasound for preparing emulsions include: good emulsion stability with no addition (or with only small addition) of surfactants, production of small droplets with narrow size distribution, and lower energy requirements than other emulsification methods.[12] Previous works demonstrated that ultrasound homogenization may produce emulsions with improved textural attributes, higher oxidative stability,[13] increased stability of the encapsulated material, and reduced size of the microcapsules.[8,14]

Surfactants are molecules that have a hydrocarbon chain with a polar group at its terminal portion. The hydrocarbon chain is soluble in oil while the polar grouping is water-soluble. For this reason, surfactants have the property of being located at the interface between the dispersed droplet and the continuous phase.[15] The preparation of emulsions that are kinetically stable over a time period of practical use to the food industry (e.g. a few days, weeks, months, or years) may also require the incorporation of substances known as stabilizers.[16,17]

Turmeric (*Curcuma longa* L.) is a plant of the family *Zingiberaceae*, whose origin dates back from South India and was introduced in Brazil in the 1980s.[18] The pigments that provide turmeric's colour belong to the class diferuloylmethane and are represented mainly by Curcumin [1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiena-3,5-dione]. The Curcumin concentration ranges from 1.5–7.1 % (15–71 mg/g),[19] and the turmeric oleoresin contains 30–45 % (300–450 mg/g) curcuminoid and 15–20 % (150–200 mg/g) volatile oil. Curcumin is a crystalline powder, yellow-orange in colour, insoluble in water and ether, but soluble in ethanol and glacial acetic acid.[20,21]

Native or modified starches are important ingredients for many processed foods. They are widely used in several applications, alone or combined with other gelling agents.[22] Some phenomena affect the properties of the starches. One is gelatinization, which involves the transformation of the granular starch into a viscoelastic paste. Initially, during the heating process of starch dispersion in the presence of excess water, the starch granules start to swell until they break at high temperatures, destroying the molecular order and irreversibly changing their properties. The temperature at which this occurs is called the gelatinization temperature.[23, 24]

Gelatin, a derivative of collagen, is the protein most commonly used for the encapsulation of foods because of its ability to form a film and a gel. It is stable at temperatures lower than 40 °C, in addition to being water soluble, non-toxic, and of low cost. Often, gelatin is used in combination with other encapsulating materials.[25] Repeated amino acid sequences are regularly required for the formation of the triple-helix structure which is characteristic of the gelatin structure, that is responsible for the ability to form gel. The segments in a triple-helix base form cross-linking in a three-dimensional network, which confers mechanical stability to the system at concentrations as low as 1 % (0.01 g/g). Dynamic oscillatory shear testing is a non-destructive means of analyzing the viscoelastic properties of gels and classifying them into strong and weak gels. For an ideal gel which behaves elastically, it is expected that G' (storage modulus) will be higher than G" (loss

modulus) independently of the frequency, whereas G' lower than G" indicates the absence of a gel-like microstructure. It is possible to correlate emulsion stability with the system viscoelastic properties, since formation of a gel network within the continuous phase will slow down the movement of droplets due to gravity or Brownian motion. In general, increasing the viscosity of the emulsion's aqueous phase may also provide better emulsion stability. The rheological properties of emulsions are mainly affected by quality (pH, ionic strength), availability of the solvent, and polymers present in the continuous aqueous phase.[10,26-28]

Colloidal silica or colloidal silicon dioxide is a submicroscopic, white, amorphous powder, with neither odour nor flavour. It is a pharmacotechnical adjuvant used as a desiccant and as a non-stick agent for hygroscopic powders. In addition, it is used for anticaking and anti-humectant, dentifrice polishing, and flow agent.[29] The use of technological adjuvants such as starch, microcrystalline cellulose, β-cyclodextrin, colloidal silicon dioxide, ethyl cellulose, and gelatin were evaluated by Teixeira in spray drying of a vegetable extract.[30] Nevertheless, the use of those adjuvants resulted in very low yields during processing, mainly due to its adherence to the walls of the drying chamber. The only exceptions observed were the products added with colloidal silicon dioxide as technological co-adjuvants.[31-35] Caking, sticking to drying chamber, and loss of the core material from the encapsulating matrix in amorphous dried powders are related to glass transition temperature (T_g). The glass transition causes a drastic decrease in the viscosity and increase in molecular mobility, leading to various time-dependent structural transformations. Addition of high molar mass compounds contributes to an increase in T_g and to maintaining the glassy state in broader temperatures and relative humidity conditions for powder stability.[9,36]

The aim of this work was to evaluate the effects of different emulsification methods, usage of colloidal silicon dioxide and Tween 80 as additives, as well as the influence of the rheological behaviour of the encapsulating gelatin-starch dispersions on the emulsion stability, encapsulation efficiency, yield, and glass transition temperature of turmeric oleoresin microcapsules produced by spray drying.

MATERIALS AND METHODS

Material

Microcapsules were prepared with turmeric oleoresin OS-50 (Agro-Industrial Olímpia Ltda., Olímpia, Brazil), using modified starch (Hi-Cap™ 100, National Starch, Brazil), and bovine gelatin bloom value 240 (Gelita®, Brazil) as wall materials. Polyoxyethylene

monooleate (Tween 80 ®, Labsynth, Brazil) was used as a surfactant, and colloidal silicon dioxide Aerosil 200 USP (Labsynth, Brazil) was employed as a anti-caking agent.

Preparation of Emulsions

The encapsulating materials were dispersed in deionized water at 60 °C according to the following ratios: 22:1, 22:2, 30:1, 12:6, 31.7:0, 31.7:2, and 31.7:6 (g/100 g) of starch:gelatin respectively. The dispersions containing modified starch were further heated to 90 °C to complete starch gelatinization. Turmeric oleoresin was added before the homogenization process in a proportion of 15 g/100 g (15 wt%) of dry mass of encapsulating materials.

Emulsions were homogenized by two different methods: a) using a rotor-stator high-shear homogenizer (Ultra Turrax, T-25, IKA, Germany) at 14 000 rpm for 10 min; b) in an ultrasonic probe (Sonic Ruptor 4000, Omni International, USA) for 3 min at 20 kHz, power input of 210 W, and temperature of ±40 °C controlled by water circulation in a double-jacketed cell.

For emulsions that presented creaming (creaming index, CI > 0, calculated by Equation (1)), Tween 80 was added as an emulsifier (1 g/100 g of total dry mass, 1 wt%). Colloidal dioxide silicon (2 g/100 g of total dry mass, 2 wt%) was also evaluated in combination with ultrasound treatment (Table 1).

Emulsion Stability and Droplet Size

The creaming index (CI), indicative of emulsion stability, was determined by the ratio between the height of the bottom phase (*H*) after the centrifugation process, and the initial height of emulsion in the tube (H_0), according to Equation (1).[37,38] After homogenization, samples of the emulsions (50 mL) were transferred to transparent, graduated, plastic tubes and centrifuged at 50.2 × g (CT-D 5500, Brazil) for 5 min before measurement of *H* and H_0.

$$CI = \frac{H}{H_0} \quad (1)$$

To evaluate the average size of the droplets, 0.1 mL of the emulsion was placed on a glass slide, covered with a coverslip, and observed using an optical microscope (L2000, Bioval, Brazil) coupled with a video camera.[38,39] The scanned images were then analyzed using Image Pro Plus 6.0 software (Media Cybernetics Inc., USA). Droplet sizes were calculated as the average diameter of 30 micelles.

Rheological Behaviour of the Encapsulating Materials

Rheological measurements were carried out in the encapsulating dispersions, without addition of turmeric oleoresin, using an oscillatory rheometer AR2000ex (TA Instruments, USA) with parallel plate geometry and a gap of 800 μm. Samples (1.8 mL) were introduced in the rheometer and left at rest for 5 min before measurements, in order to equilibrate the test temperature (40 °C). Temperature sweeps were performed by reducing the temperature from 40 to 20 °C at a cooling rate of 2 °C/min. The storage and dissipation moduli, G' and G'', were recorded as a function of time at a frequency of 0.1 Hz and strain rate of 0.05.[40] At the end of the temperature sweep, the sample was left to stand in the rheometer at 20 °C for 1 h, in order to allow for biopolymer structural arrangement. Then, a frequency sweep was performed from 0.01 to 10 Hz, at 20 ° C and strain rate of 0.05.

Spray Drying

The emulsions obtained by ultrasonic homogenization with and without colloidal silicon dioxide were subjected to spray drying. The process was performed in a laboratory scale spray dryer (B-290, Büchi, Switzerland) with a 0.7 mm diameter nozzle. The emulsions were maintained under agitation using a magnetic stirrer throughout the drying process. The operational parameters of drying were: feed flow rate of 3 mL/min, drying air flow rate of 420 L/h, 160/90 °C inlet/outlet air temperature and suction at 90 %.

Encapsulation Efficiency

The encapsulation efficiency EE (%) was expressed in terms of curcumin retention. The total curcumin content was determined following the method described by Chauhan et al.[44] A solution of turmeric oleoresin (0.01 mg/mL) in methanol was prepared and analyzed for curcumin content by measuring the absorbance at 425 nm with a spectrophotometer (SP-22, Biospectro, Brazil). 7 mg of microcapsules were taken in a 25 mL standard volumetric flask and the volume was completed using methanol. The solution was homogenized in a vortex for 5 min, followed by centrifugation at 704 × g for 10 min. The supernatant was then taken for measurement of absorbance at 425 nm. The curcumin content was determined using the standard curve.

The curcumin retention in the spray dried powder was calculated by using the following expression:

$$EE\% = \frac{C_F}{C_0} \times 100 \qquad (2)$$

where C_F is the curcumin concentration (mg/g) in the spray dried powder and C_0 is the curcumin concentration (mg/g) in the emulsion, before spray drying.

Encapsulation Yield

Encapsulation yield was determined by the ratio between the final dry mass of the powder obtained after spray drying and the initial dry mass contained in the emulsion. Finally, the efficiency of the process was obtained by multiplying the value of encapsulation efficiency by the encapsulation yield.

Thermal Analyses

For thermal analyses, the glass transition temperature (T_g) was determined for the samples homogenized by ultrasound, with and without silicon dioxide. A differential scanning calorimeter DSC8000 (Perkin Elmer, USA) was used with a temperature varying from -10 °C to 90 °C, with a heating rate of 20 °C/min and using an empty aluminum capsule as reference. The analysis was performed in duplicate and T_g was calculated as the midpoint of the temperature range corresponding to the transition. Nitrogen at 20 mL/min was used as purge gas.

Statistical Analysis

The results of the analytical determinations were expressed as arithmetic means with respective standard deviation, and subjected to analysis of variance (ANOVA), and comparison of the means using Tukey's test at 5 % probability using the Minitab 17 Statistical Software (MINITAB, USA).

RESULTS AND DISCUSSION

Rheological Behaviour of the Encapsulating Materials

The proper balance between the biopolymers is crucial to achieve a strong microstructure that will be effective in protecting the core material in the microencapsulation process.[4] In general, the ratio between biopolymers and the total solid content directly affects the rheological behaviour of hydrocolloid dispersions, and consequently the emulsion stability.[26,41]

Figures 1 and 2 show that gelatin concentration has a relevant role on the formation of a gel with viscoelastic properties, which will then enhance emulsion stability.[42,43] The dispersion of pure starch (Figure 1d) presented values of G" higher than G' along the

complete temperature scan, whereas samples containing gelatin and minimum total solids of 24 % (0.24 g/g) showed G' crossing over G" during cooling (Figures 1b, c, e, and f). This is due to the gelling effect of gelatin molecules, which form an infinite network cross-linked by hydrogen bonding—a thermal reversible gel—in dispersions containing above 1 wt% (0.01 g/g) gelatin and cooled to room temperature.[44] In samples containing the same concentration of starch, the higher the gelatin concentration, the higher the gelling temperature upon cooling. On the other hand, when comparing dispersions with the same concentration of gelatin (Figures 1b and e) it is possible to see that increasing starch concentration did not cause a great increment on the viscoelastic moduli. It has been reported that addition of polysaccharides such as maltodextrin or starch to collagen[45] or gelatin[44] above certain concentrations may lead to thermodynamic incompatibilities between the biopolymers, resulting in structures less elastic than those obtained with the pure protein at the same concentration.

The same conclusions are supported by the mechanical spectra presented in Figure 2, in which G' and G" curves indicate that the samples behaved as if they were between the end of the plateau zone and the beginning of the transition zone. According to Hsieh et al.,[46] such behaviour indicates that the systems simultaneously have relaxation times that correspond to short (between entanglements) and long (beyond entanglements) range interactions that involve the flexile molecular chains. The short-range relaxation occurs at high frequencies, in a time scale corresponding to the transition zone, where diffusive movements of parts of the concatenation give rise to a power-law dependence of G' and G" on frequency. On the other hand, in the plateau zone, which appears at intermediate frequencies, the gel behaves as a permanently cross-linked system because in these conditions the test time scale is shorter than the typical network lifetime.[46] The plateau zone is wider if many non-covalent interactions are involved in the network formation, whereas a narrower plateau is detected when fewer non-covalent interactions occur; in the extreme case of absence of non-covalent interactions, the plateau zone may even vanish.[47] Figure 2 suggests that the wider plateau zone corresponds to the blend S22/G2 (Figure 2b), while the narrower one was presented by pure starch (Figure 2d). In addition, samples containing higher concentrations of gelatin showed higher values of G', indicating a prominent elastic behaviour (Figures 2b, e, f). The blend S22/G2 presented rather stable mechanical properties indicating that, even when the biopolymers are not completely thermodynamically compatible, at appropriate proportions synergy between them is promoted and the properties of both biopolymers act in order to stabilize the gel structure.

Emulsion Stability

The creaming index (CI) is related to emulsion stability, in such a way that the lower the CI the more stable the emulsion will be.[38] The measurements of CI (Table 1) showed that the method of emulsification directly influenced the emulsion stability, and the competition for water seems to have an important role on the stability of the two phases. Considering the rotor-stator homogenization without surfactant, the sample S31.7/G0 presented no creaming (CI = 0), which means that, considering the conditions applied, 31.7 wt% (0.317 g/g) of modified starch was enough to provide a stable emulsion. In addition, the sample S30/G1 presented slightly higher CI (0.03), suggesting that concentrations of modified starch above 30 % of the total mass of the solution provide a considerably stable emulsion. This fact is explained by the properties presented by the modified starch, such as having excellent emulsion stabilizing properties,[48-52] being a strong surface-active due to the long amylopectin chain. This is due to the fact that the droplets are protected against flocculation by a steric stabilization mechanism.[53] On the other hand, the sample S31.7/G6, that had the high solid content and gelatin concentration, also presented a low CI (0.02) and higher values of storage modulus (Figure 2f) as well. The higher stability of emulsions containing higher concentrations of solids could be explained based on polymer-induced depletion forces.[54-57] When depletion interactions are stronger, emulsion creaming is inhibited due to the viscoelastic character of the interconnected regions of emulsion droplets into a gel-like network.[43] Nevertheless, finding the appropriate proportion of gelatin and starch seems to be important for the emulsion stabilization, in view that the sample S31.7/G2 resulted in an unstable emulsion with a high value of CI (0.93). In a previous study, Tesch and Schubert[26] showed that the higher the viscosity of an emulsion, the lower the probability of creaming. This happens because emulsions with higher viscosity present an increase in the drainage time of the continuous phase, when compared to low-viscosity emulsions. In addition, the collision rate between the emulsion droplets, which promotes creaming, is not affected by the emulsion viscosity. Knowing those facts it is possible to correlate the CI of this sample with its viscoelastic properties, considering that incompatibility of the biopolymers and competition for water makes the gel weaker, breaking down the emulsion structure.[26,28,58-60]

Taking into account the homogenization with surfactant, sample S31.7/G2 presented a very low CI, showing that for this formulation, the emulsifier helped to stabilize a previously unstable emulsion. In addition, using the emulsifier, samples S22/G2 and S31.7/G6 had a decrease in their CI, with sample S31.7/G6 showing no creaming. The decrease in CI is due to

the non-polar groups of Tween 80 that interact with the oil, while its ionic groups interact with the dispersed biopolymers, therefore increasing the emulsion stability.[59] On the contrary, the samples S22/G1 and S30/G1 presented an increase in CI, which could be explained considering that the addition of Tween 80 in a low concentration increased even more the water competition between the gelatin and starch in these samples, bringing down the emulsion stability.[60,61]

When ultrasound homogenization was applied, all the samples presented a considerable decrease in their CI, showing that this method can successfully emulsify and increase emulsion stability of formulations that are not stable when homogenized through other methods.[62,63] In spite of starch and gelatin being incompatible polymers that tend to compete for the water present in the medium and destabilize the emulsion, low-frequency ultrasound promotes cavitation with high levels of power applied in the system, leading these polymers to interact in a more intensive way and providing greater stability to the emulsion.[8] During sonication, liquid mixing happens due to local perturbations of the interface between the polymers and also because bubble implosion is much faster than dilation.[16, 64, 65]

The use of colloidal silicon dioxide associated to homogenization by ultrasound probe prevented creaming in all the blends, except for sample S31.7/G6. It is worth noting that, initially, the use of the colloidal silicon dioxide was not aimed at the improvement of emulsion stability, since colloidal silicon dioxide is usually applied as an anti-wetting and anti-caking agent in dried products.[32-36] However, the fact that this additive was able to provide such an increase in the emulsion stability is promising for industrial applications. Christensen et al.[66] observed small droplets in a wet emulsion that were subjected to drying and their study was a precursor to application of colloidal silicon dioxide for improving emulsion stability in pharmaceuticals. The lag between emulsification of a core material in the encapsulant dispersion and the subsequent spray- or freeze-drying is a critical step in which emulsion stability is essential to the production of microcapsules with high encapsulation efficiency, uniformity, and high yield.[38,67,68]

Emulsion Droplet Size

All the samples that had a CI below 0.3 also had an average particle size (Table 2) smaller than 3 μm. In addition, the sample S31.7/G2, which presented the highest droplet size as well as the highest particle size dispersion (8.26 ± 3.53 μm), was also the most unstable emulsion (CI = 0.93). These facts indicate a correlation between emulsion droplet size and CI.[69-71] A similar result was obtained by Dickinson,[72] who observed that stable emulsions

presented droplet sizes of no more than 10 μm. For samples with less than 2 % (0.02 g/g) gelatin, droplet size was influenced by different proportions of the biopolymers used, with significant differences ($p < 0.05$). A similar result was obtained by Malacrida et al.[73] for modified starch and gelatin blends.

The use of Tween 80 or ultrasound homogenization decreased the diameter of the emulsion droplets. This effect was observed with the use of Tween 80 in the samples S22/G1 and S31.7/G2, whereas with the use of ultrasound homogenization the samples S22/G1, S22/G2, S31.7/G0, and S31.7/G2 presented significant ($p < 0.05$) decreases on the emulsion droplet size. It was expected that the average droplet size generated in samples homogenized by ultrasound would be smaller than the droplet size generated in samples homogenized by a rotor-stator system.[15,16] Nevertheless, the use of ultrasound and Tween 80 resulted in droplets of similar size for the same formulations, although ultrasound homogenization provided smaller droplet size dispersion. This can be explained due to the cavitation process created by high energy input during ultrasound homogenization.[63-65,74]

Thermal Analyses

Thermal analyses in microencapsulated material are important because it is known that the rate of oxidation of sensitive compounds in a dry matrix is enhanced above Tg. This happens due to the crystallization process, which forces the encapsulated materials from the system to the surface, increasing the interaction of microencapsulated compounds with oxygen.[73] The glass transition temperature (T_g) of the spray dried powders varied between 48.8–66.2 °C for water contents ranging from 0.73–2.49 g_{water}/100 g (Table 3). There were no significant differences between values of T_g, although it is possible to observe a trend of higher glass transition temperatures in samples containing colloidal silicon dioxide. This is an indication that the use of colloidal silicon dioxide as an additive could be better studied as an adjuvant to improve emulsion stability and to prevent glass transition related changes in the resulting powders, including structural collapse, stickiness, and caking.[32,35,36,66] Cortéz-Rojas and Oliveira[75] observed that the use of colloidal silicon dioxide as a carrier agent for drying phytopharmaceutical formulations resulted in highly amorphous powders, as indicated by the large, non-defined peaks with abundant noise in the X-ray diffractograms, which are typical of amorphous materials. According to these authors, as the colloidal silicon dioxide is a non-water-soluble compound that presents a very high T_g value (higher than 900 °C), the prevalence of an amorphous structure in formulations containing this carrier would be expected. On the other hand, it is important to note that the water content of the dried

microcapsules containing colloidal silicon dioxide were generally lower than those dried without these additives. Since water exerts a plasticizing effect, the lower T_g values observed in samples without colloidal silicon dioxide could also be attributed to the higher water contents. The values found for T_g of the blends exceeded the reference values for modified and native starch. In the literature, the T_g for native starch is approximately 39.3 °C,[76] and for gelatin, approximately 30.6 °C. This demonstrates the advantages of combining two or more biopolymers to obtain improved calorimetric results.[76,77]

Encapsulation Efficiency (EE) and Yield

The results presented in Table 5 indicate that, without silicon dioxide, the EE increased with the increase of total solids in the emulsion, as well as with the increase in the proportion of gelatin in relation to modified starch. The values of EE varied from 34 % (S22/G1) to 70 % (31.7/G6) for the formulations without silicon dioxide. The positive effect of gelatin in the encapsulation efficiency observed for the spray-dried microcapsules of turmeric oleoresin was not observed in previous studies in which the microcapsules were freeze-dried. Studying microencapsulation of β-carotene using native "*pinhão"* starch, modified "*pinhão"* starch, and gelatin by freeze-drying, Spada et al.[77] noted that the addition of gelatin did not significantly affect the encapsulation efficiency of β-carotene, with modified starch presenting 93.41 % and native starch 64.95 % of encapsulation efficiency. Malacrida et al.[73] observed that curcumin retentions differed significantly between freeze-dried capsules produced with varied proportions of gelatin and modified starch: comparison among samples with the same percentage of modified starch (30 g/100 g) showed that increasing the concentration of gelatin from 1 to 3 g/100 g resulted in a significant decrease in curcumin retention from 71.6 to 63.8 %; nevertheless, when the amount of total solids was lower, the increase in the proportion of gelatin in relation to modified starch did not result in a significant decrease in curcumin retention. These results indicate that the encapsulation efficiency of the same wall matrix may follow different trends depending on the drying method used to produce the microcapsules.

When the colloidal silicon dioxide was added to the emulsions to be dried, the opposite effect was observed. Samples S22/G1 and S22/G2 had the lowest EE without silicon dioxide; however, in the presence of this carrier, these samples presented a great increase in their EE (Table 4). Their EE was statistically comparable to the EE determined without silicon dioxide for the sample S31.7/G6, which had at least 13.7 % more solids than samples S22/G1 and S22/G2. That shows that it is possible to obtain higher values of EE and yield with

emulsions that have low total solids. The study performed by Tonon et al.[5] showed that without silicon dioxide, lower total solids content led to the formation of less stable emulsions with larger droplets, a fact also noted in this study, resulting in lower encapsulation efficiency. In addition, it is important to highlight that the application of silicon dioxide also improved the emulsions' stability,[69] lowering their CI and the final moisture of the dried powders of these two formulations. This important result is not only in accordance with previous studies which relates the emulsion stability before the drying process with EE,[6,7,70,71,78] but also indicates that the properties of the colloidal silicon dioxide go beyond the anti-caking and anti-humectant properties, making it a good alternative for stabilizing food emulsions.

CONCLUSIONS

Results presented in this study show that the proportion and the concentration of the biopolymers and the gelatin concentration affect not only the gel properties but the emulsion stability and its droplet average size. In addition, the homogenization method had a significant influence on these parameters, with the use of ultrasound homogenization providing the best results for the emulsion properties and for the spray dried power. In addition, the use of the additives Tween 80 and colloidal silicon dioxide improved emulsion stability.

Formulations with higher solid contents and gelatin concentrations presented higher encapsulation efficiencies. However, the use of colloidal silicon dioxide not only increased the encapsulation efficiency for formulations with lower solids concentration, but also increased the emulsion stability and decreased the final moisture of spray dried powders ($p < 0.05$). Hence its use can be an alternative for obtaining good results in emulsion stability and in the process of microencapsulation using blends which have a low total solid concentration.

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Figure Legends:

Figure 1. Temperature dependence of G' (filled symbols) and G" (non-filled symbols) of the encapsulant dispersions at different formulations: (a) 22:1; (b) 22:2; (c) 30:1; (d) 31.7:0; (e) 31.7:2; and (f) 31.7:6 (g/100 g) of modified starch:gelatin, respectively.

Figure 2. Frequency dependence of G' (filled symbols) and G" (non-filled symbols) of the encapsulant dispersions at different formulations: (a) 22:1; (b) 22:2; (c) 30:1; (d) 31.7:0; (e) 31.7:2 and (f) 31.7:6 (g/100 g) of modified starch:gelatin, respectively.

Table 1. Creaming index (CI) of emulsions of turmeric oleoresin stabilized by gelatin/modified starch blends prepared with different homogenization methods

Sample	Starch ($g\ kg^{-1}$)	Gelatin ($g\ kg^{-1}$)	CI[1]			
			Rotor-stator homogenization	Rotor-statorhomogenization with Tween 80	Ultrasonic homogenization	Ultrasonic homogenization with colloidal silicon dioxide
S22/G1	220	10	0.09 ± 0.00^{DEF}	0.26 ± 0.05^{BC}	0.01 ± 0.01^{F}	-
S22/G2	220	20	0.25 ± 0.01^{BCD}	0.20 ± 0.04^{BCD}	0.16 ± 0.01^{CDE}	-
S30/G1	300	10	0.03 ± 0.01^{EF}	0.10 ± 0.01^{F}	0.02 ± 0.01^{F}	-
S31.7/G0	317	-	-	-	-	-
S31.7/G2	317	20	0.93 ± 0.00^{A}	0.01 ± 0.00^{F}	0.29 ± 0.13^{BC}	-
S31.7/G6	317	60	0.02 ± 0.01^{F}	-	-	0.30 ± 0.07^{B}

[1]Mean values ± standard error (n = 2)

*Different letters in superscript in each column indicate significant differences (Tukey test, $p < 0.05$)

Table 2. Droplet size of emulsions of turmeric oleoresin stabilized by gelatin/modified starch blends prepared with different homogenization methods

Sample	Starch ($g\ kg^{-1}$)	Gelatin ($g\ kg^{-1}$)	Droplet size (μm)[1]		
			Rotor-stator homogenization	Rotor-stator homogenization with Tween 80	Ultrasonic homogenization
S22/G1	220	10	2.77 ± 1.12^{B}	1.58 ± 0.37^{CDEF}	1.40 ± 0.24^{DEF}
S22/G2	220	20	2.33 ± 0.77^{BC}	1.87 ± 0.41^{CDE}	1.27 ± 0.28^{EF}
S30/G1	300	10	1.78 ± 0.68^{CDE}	1.76 ± 0.38^{CDE}	1.30 ± 0.26^{EF}
S31.7/G0	317	-	2.23 ± 0.43^{BCD}	-	0.89 ± 0.16^{F}
S31.7/G2	317	20	8.26 ± 3.53^{A}	1.77 ± 0.52^{CDE}	1.62 ± 0.27^{CDEF}
S31.7/G6	317	60	1.63 ± 0.42^{CDEF}	1.83 ± 0.38^{CDE}	1.02 ± 0.25^{EF}

[1]Mean values ± standard error (n = 30)

*Different letters in superscript in each column indicate significant differences (Tukey test, $p < 0.05$)

Table 3. Glass transition temperature (T_g) and water content of spray dried turmeric oleoresin powders stabilized by gelatin/modified starch blends prepared with and without colloidal silicon dioxide

Sample	Starch (g kg^{-1})	Gelatin (g kg^{-1})	Samples dried without colloidal silicon dioxide		Samples dried with colloidal silicon dioxide	
			T_g[1] (ºC)	Water content[1] (g/100g wb)	T_g[1] (ºC)	Water content[1](g/100g wb)
S22/G1	220	10	59.5 ± 1.6$^{\beta}$	2.47 ± 0.00^{A}	55.9 ± 7.8$^{\beta}$	1.03 ± 0.08^{BCD}
S22/G2	220	20	61.7 ± 8.5$^{\beta}$	2.49 ± 0.02^{A}	63.9 ± 5.2$^{\beta}$	1.18 ± 0.12^{BCD}
S30/G1	300	10	57.2 ± 0.2$^{\beta}$	2.46 ± 0.11^{A}	60.5 ± 2.8$^{\beta}$	0.95 ± 0.29^{CD}
S31.7/G0	317	-	51.5 ± 7.0$^{\beta}$	2.43 ± 3.5^{ABCD}	66.2 ± 3.5$^{\beta}$	1.75 ± 0.88^{D}
S31.7/G2	317	20	51.3 ± 0.7$^{\beta}$	1.77 ± 0.17^{A}	59.8 ± 0.9$^{\beta}$	0.73 ± 0.01^{ABCD}
S31.7/G6	317	60	48.8 ± 5.9$^{\beta}$	1.85 ± 0.04^{ABC}	55.2 ± 3.5$^{\beta}$	2.08 ± 0.03^{AB}

[1]Mean values ± standard error (n = 2)

[*]Different letters or symbols in superscript in each column indicate significantdifferences (Tukey test, $p < 0.05$)

Table 4. Encapsulation efficiency (EE) and yield ofturmeric oleoresin encapsulated in different proportions ofmodified starch/gelatin,with and without use of colloidal silicon dioxide

Sample	Starch (g kg^{-1})	Gelatin (g kg^{-1})	Samples dried without colloidal silicon dioxide		Samples dried with colloidal silicon dioxide	
			EE (%)[1]	Yield (%)	EE (%)[1]	Yield (%)
S22/G1	220	10	34.87 ± 3.99^{F}	48.19	70.33 ± 0.93^{AB}	68.04
S22/G2	220	20	40.43 ± 1.96^{EF}	45.39	76.45 ± 3.58^{A}	59.32
S30/G1	300	10	47.37 ± 2.30^{DE}	37.99	53.62 ± 1.15^{D}	40.39
S31.7/G0	317	-	51.71 ± 1.62^{CD}	25.52	66.21 ± 0.59^{AB}	35.17
S31.7/G2	317	20	55.51 ± 4.59^{DE}	68.46	68.52 ± 1.03^{ABC}	56.51
S31.7/G6	317	60	70.64 ± 0.31^{AB}	71.59	59.41 ± 7.10^{BCD}	9.33

[1]Mean values ± standard error (n = 2)

[*]Different letters in superscript in each column indicate significant differences (Tukey test, $p < 0.05$)

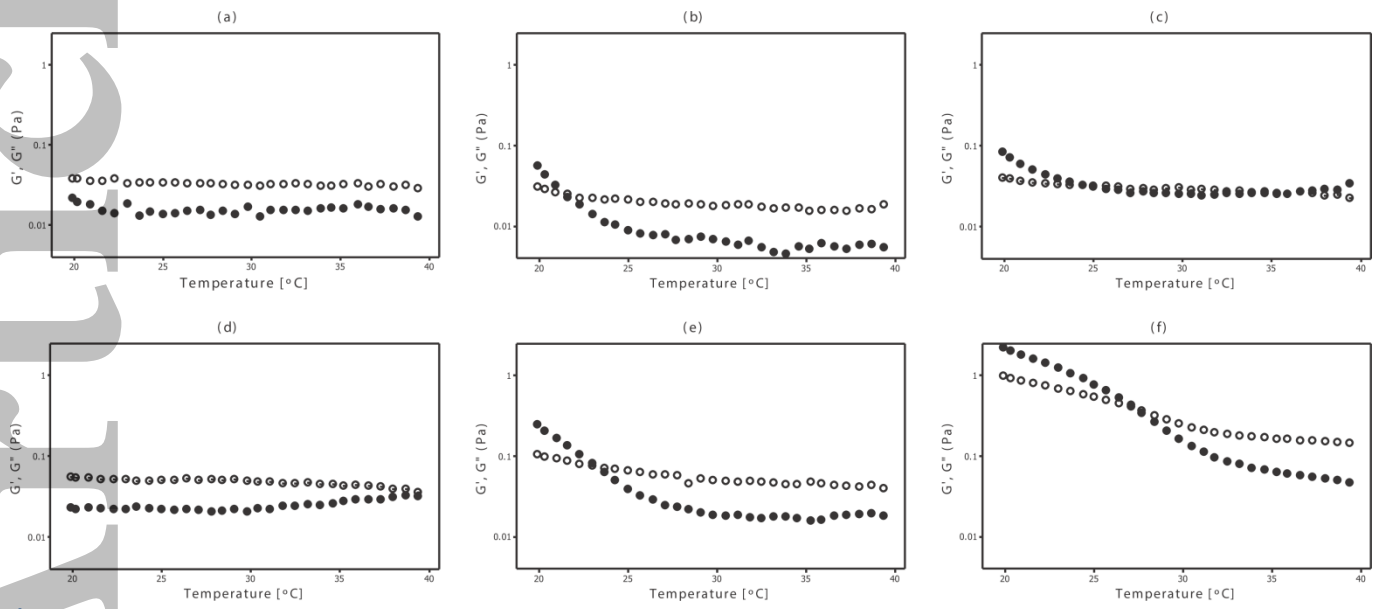

Figure 1

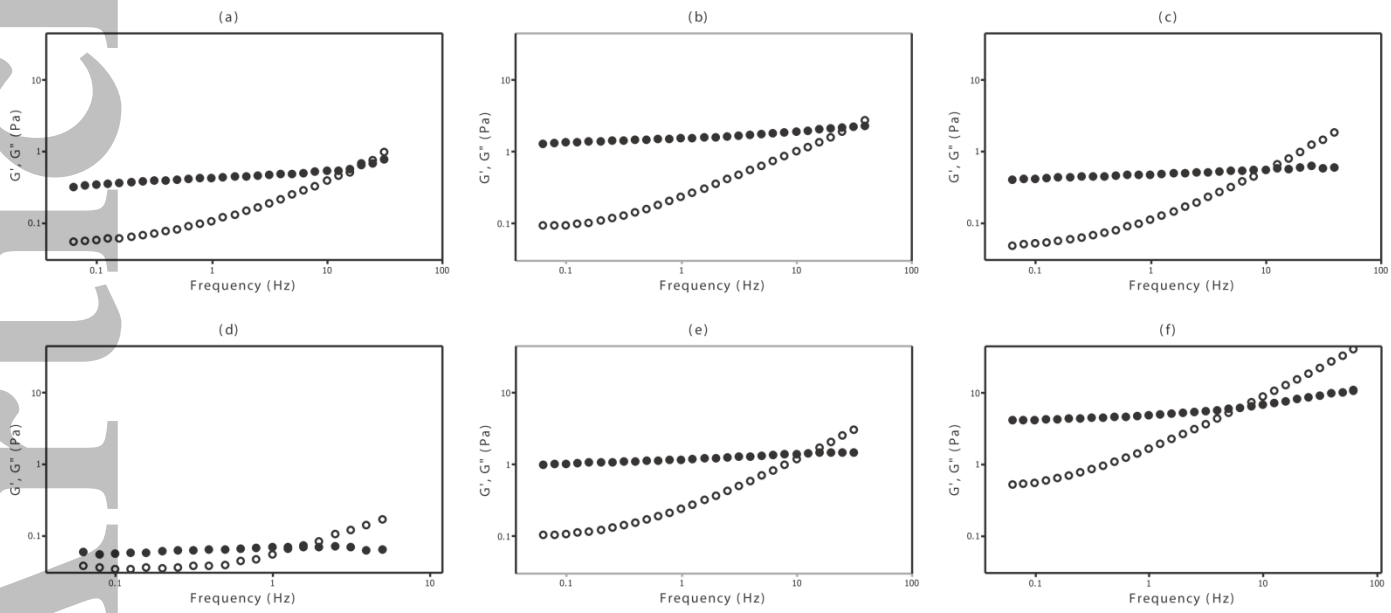

Figure 2