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Turmeric oleoresin encapsulated by spray drying in maltodextrin/gelatin and starch/gelatin blends: storage stability and water sorption

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ABSTRACT. Turmeric oleoresin is a widely used a flavoring agent and a food color with relevant nutraceutical properties. It is obtained by organic solvent extraction of turmeric (*Curcuma longa* L.). Microencapsulation is a good alternative to transform liquid food flavorings free-flowing powders and to improve stability of protection of compounds of interest. Thus, the aim of this study was to assess microencapsulation by spray drying of turmeric oleoresin using blends of maltodextrin-gelatin and starch-gelatin, evaluating its sorption isotherms and the storage stability at different temperatures. Turmeric oleoresin encapsulated was stored at - 20, 25 and 60°C, in the absence of light, and at 25ºC in the presence of light, and analyzed over a period of 35 days for curcumin and total phenolic contents and color. The encapsulation efficiency was 72.3% for capsules with starch-gelatin blends and 52.1% with maltodextrin-gelatin blends. Besides the greater encapsulation efficiency, starch-gelatin blends also showed greater stability during storage and retention of curcumin and phenolic compounds. Encapsulated materials were more stable during storage at - 20ºC and less stable at 25°C in the presence of light. Water adsorption of turmeric oleoresin microcapsules were well described by GAB model and the microcapsules produced with starch-gelatin blends showed high hygroscopic behavior.

Keywords: *Curcuma longa* L.; microencapsulation; polymer blend; curcumin; sorption isotherm.

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Introduction

Microencapsulation is a powerful technique to improve characteristics of compounds of interest, such as stability under harsh conditions, products lifespan and controlled release of the encapsulated core (Ferreira & Nicoletti, 2020; Ferreira & Nicoletti, 2021; Pereira et al., 2018). One compound of interests to have its properties protected and enhanced are the pigments in the turmeric oleoresin (Ferreira, Malacrida, & Nicoletti, 2019; Ferreira, Malacrida, & Telis, 2016). The pigments that provide turmeric oleoresin`s (*Curcuma longa* L.) colour and phenolic content belong to the class curcuminoid-diferuloylmethane and are represented mainly by Curcumin [1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiena-3,5-dione]. Even though turmeric oleoresin has antioxidant properties, its phenolic compounds are highly susceptible to degradation by oxygen, light, pH, enzymes and heat (Goëlo, Chaumun, Gonçalves, Estevinho, & Rocha, 2020; Jayaprakasha, Rao, & Sakariah, 2005). Using protective polymers blends of starches, proteins and gums it is possible to create wall or microcapsule to protect a valuable core from harsh conditions (Pereira et al., 2018). The process of microencapsulation by spray drying using polymer blend is specially used for hydrophobic compounds, such as turmeric oleoresin, increasing core protection and promoting water solubility of the oil (Ferreira et al., 2019; Sri, Seethadevi, Prabha, Muthuprasanna, & Pavitra, 2012).

Modified starches are important ingredients for many processed foods, and special for microencapsulation alone or combined with other gelling agents (Ferreira et al., 2016). Octenyl succinic anhydride modified starch is a chemically modified starch that has hydrophilic and lipophilic surface properties and is often used as a stabilizer and encapsulation agent (No, Mun, & Shin, 2019). Maltodextrin is a hydrolyzed starch commonly used as carrier agent in spray-drying process acting as an encapsulating material, promoting the stability on the core material properties, such as protection against oxygen degradation, improved solubility, increasing the products shelf-life (Madene, Jacquot, Scher, & Desobry, 2006; Telis & Martínez-Navarrete, 2009; Zuanon et al., 2019). Gelatin, a derivative of collagen, is commonly used in combination with other encapsulating

materials in encapsulation processes. Due to its repeated amino acid sequences, gelatin presents a triple-helix structure that is responsible for the ability to form gel and its emulsifying properties (Dib Taxi, Menezes, Santos, & Grosso, 2003; Ferreira et al., 2019; Gómez-Guillén, Giménez, López-Caballero, & Montero, 2011).

Water sorption isotherms can be used to predict moisture changes that occur during storage and to estimate stability during shelf life, which is crucial for microencapsulated food powders (Busch et al., 2017; Telis & Martínez-Navarrete, 2009). The use of vegetable dried powders is directly correlated with their stability in storage, taking into consideration the water sorption behavior of the final powder (Viganó et al., 2012). Highly hygroscopic powders may be go through to water plasticization, glass transition-related changes, stickiness, caking, mechanical collapse, color and chemical degradation (Adhikari, Howes, Bhandari, & Troung, 2004; Díaz, Lugo, Pascual-Pineda, & Jiménez-Fernández, 2019).

The aim of this study was to study the effect of blends of maltodextrin/gelatin and modified starch/gelatin as encapsulant materials on the characteristics and stability of turmeric oleoresin microencapsulated by spray drying. In addition, a water sorption study of the powder of turmeric oleoresin with maltodextrin/gelatin and starch/gelatin was carried out, which has not been present on the literature until now.

Material and methods

Turmeric oleoresin OS-50 (Agro-Industrial Olimpia Ltda., Brazil) was used as core material. The encapsulant materials included modified starch HiCap® 100 (National Starch and Chemical Industrial Ltda, Brazil), a n-octenyl succinic anhydride-modified starch from waxy maize, maltodextrin DE 10 Mor-Rex® 1910 (Corn Products, Brazil) and bovine gelatin bloom value 240 (Gelita®, Brazil).

Preparation of homogenized emulsions

Modified starch was suspended in distilled water and heated in water bath (80°C) for 30 min. to obtain gelatinized starch. The gelatin was dissolved in distilled water at 60°C. The solution, containing 30 % (w w^{-1}) of modified starch and 1% (w w^{-1}) of gelatin, was cooled to room temperature, mixed and turmeric oleoresin was added into the solution at a 15 % level (based on the weight of carrier materials). The mixtures were emulsified in a shear homogenizer Ultra Turrax (T - 25, IKA, Germain) operating at 18,000 rpm for 10 min.

Samples containing 26 % (w w^{-1}) maltodextrin and 0.6 % (w w^{-1}) gelatin were prepared as described above, except that it was not necessary to heat the suspension. Optimization of encapsulant materials proportions was determined in previous studies (Malacrida, Ferreira, Zuanon, & Telis, 2015; Malacrida, Ferreira, & Telis, 2013).

Spray-drying of homogenized emulsions

Spray-drying process was performed in a laboratory scale spray-dryer (B-290, Buchi, Switzerland) with a 1.5 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 6 mL $min.^{-1}$, drying air flow rate of 420 L h^{-1} and 170 / 80°C inlet / outlet air temperature. The yield percentage of the encapsulation process was determined as ratio of powder mass obtained after drying with the total solid in solution before spray-drying.

Encapsulation efficiency

The total curcumin content was determined following the method described by Chauhan, Singh and Agrawala (1999). A solution of turmeric oleoresin (0.01 mg ml^{-1}) in methanol was prepared and analyzed for curcumin content by measuring the absorbance at 425 nm with a spectrophotometer (SP-22, Biospectro, Brazil). Seven milligrams of microparticles 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 x 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 encapsulation efficiency was expressed as the curcumin retention in the spray-dried powder in relation to theoretical curcumin concentration in the emulsion.

Characterization of spray-dried materials

Moisture determination: Moisture content of encapsulated powders was determined gravimetrically by oven drying at 105ºC for 6 hours (Association of Official Analytical Chemists [AOAC], 2005).

Curcumin content: Curcumin content was determined as previously described.

Total phenolic content: Total phenolic content was determined by Folin-Ciocalteu method (Singleton & Rossi, 1965). One hundred milligrams of microparticles 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 centr;ifugation at 704 x g for 10 min. In a test-tube were added 0.5 mL of the supernatant, 8 mL of distilled water and 0.5 mL of Folin-Ciocalteau reagent. After 3 min. at room temperature, one mL of aqueous sodium carbonate solution (20 %) was added. After 1h reaction at room temperature, the absorbance was read at 760 nm against a reagent blank using a UV-vis spectrophotometer (SP-22, Biospectro, Brazil). Total phenolic were calculated on the basis of the calibration curve of Gallic acid.

Color: The color attributes (Hunter L, a and b values) were measured using a colorimeter (ColorFlex EZ, HunterLab, USA) equipped with D65 illuminant and a 10º observation angle. The total color difference was calculated from Hunter L, a and b values.

Solubility: Solubility was determined according to the method used by Cano-Chauca, Stringheta, Ramos, and Cal-Vidal (2005), where 100 mL of distilled water were transferred into a beaker and the powder sample (1 g) was carefully added with high velocity magnetic agitation up to 5 min. The solution was filtered through a filter paper an aliquot of 25 mL of the filtered solution was transferred to Petri dishes previously weighed and oven-dried at 105ºC for 5h. Solubility (%) was calculated by the weight difference.

Particle morphology: Morphology and surface appearance of turmeric oleoresin encapsulated were examined using a Scanning Electron Microscope - SEM (Zeiss, model 960, Germany). The powders were attached to SEM stubs using adhesive tape and coated with gold under vacuum (Sputer Coater, model SCD 050, Brazil). SEM carried out at 20 kV with work distance of 12 mm. The scanned images were collected digitally using Digital Image Transfer 1.0 (PUC, Brazil).

Temperature and light stabilities

Encapsulated materials were submitted to temperature and light stability tests. The tests were performed at temperatures of freezer (-20 ± 1.5°C), oven (60 ± 1°C) and room temperature (25 ± 0.1°C) in the absence of light. Light stability test was performed at room temperature (25 ± 0.1°C) in presence of light (3400 lx). Samples (10 g) of encapsulated materials were packed in low density polyethylene bags, sealed and stored at these temperatures for a period of 35 days. Stabilities were monitored by analyzing curcumin and total phenolic retentions and color parameters each 7 days. The percentage retention of curcumin and total phenolics was calculated by the formula (analyte at X storage time) / (analyte at zero storage time) x 100.

Sorption isotherms

The sorption isotherms of turmeric oleoresin encapsulated were determined by the gravimetric method as described by Spiess and Wolf (1983) Samples of about 0.6 g of the powers were conditioned at 25°C using saturated salt solutions to give different relative humidity in the range of 11.2 - 75.5 %. The sample weights were controlled until a constant value was attained, where the equilibrium was assumed to be reached. The equilibration process took about 3 - 4 weeks to be completed.

Sorption isotherms data were modeled according to Guggenheim-Anderson-de Boer (GAB) (Equation 1) and Brunauer-Emmett-Teller (BET) (Equation 2) models, using STATISTICA 5.0 (StatSoft Inc., USA). The goodness of fit was evaluated by the determination coefficient (R^2) and the mean relative deviation modulus (E) (Equation 3).

$$X_e = \frac{X_m C_{GAB} K_{GAB} A_W}{[(1-K_{GAB}A_W)(1+K_{GAB}(C_{GAB}-1)A_W)]} \quad (1)$$

where X_m is the monolayer moisture content (g water/dry solids), C_{GAB} and K_{GAB} are the GAB model constants and A_w is the water activity.

$$X_e = \frac{X_m C_{BET} A_W}{[(1-A_W)(1+(C_{BET}-1)A_W)]} \quad (2)$$

where X_m is the monolayer moisture content (g water/dry solids), C_{BET} is the BET model constant and A_w is the water activity.

$$E = \frac{1}{100}\sum_{i=1}^{N}\frac{|V_e - V_p|}{V_e} \quad (3)$$

where N is the population of experimental data, Ve is the experimental value and Vp is the predicted value.

Statistical analysis

Data of analytical determinations were subjected to analysis of variance and differences between means were tested by Tukey test at 5% probability using MINITAB 16 (Minitab Inc., USA). The parameters of the models were estimated using STATISTICA 5.0 (StatSoft Inc., USA).

Results and discussion

Encapsulation process

Encapsulation efficiency (*EE*) for capsules with MG was 52.1% and 72.3% for capsules with SG. In a study of the influence of emulsification methods and spray drying parameters on the microencapsulation of turmeric oleoresin, Ferreira et al. (2019) found *EE* from 3 to 77%. Ferreira et al. (2016) studied encapsulation of turmeric oleoresin using modified starch-gelatin blends, reporting *EE* from 53 to 76 % with the use silicon dioxide and *EE* from 34 to 70% without silicon dioxide. Malacrida et al. (2015) reported 92% yield and 71.6% curcumin retention for turmeric oleoresin encapsulated in modified starch/gelatin (30:1) by freeze drying. Thus, it can be seen that the type of drying has little effect on curcumin retention but significantly changes the yield of the process.

During spray drying, even when the drying parameters (inlet air temperature, air flow and feed flow rate) varied, it was observed that large amount of the emulsion were adhered on the drying chamber, resulting in low yields of powder: 24.6% for MG and 40% for SG microparticles. Low yields are usually reported for a laboratory-scale spray dryer apparatus (Ameri & Maa, 2006). In addition to the drying conditions, the composition of the encapsulant material also interferes with the spray drying performance. Zuanon, Malacrida and Telis (2017) found yield of 61.75 - 65.07% for turmeric oleoresin encapsulated in gelatin-collagen, Ferreira et al. (2016) obtained yield from 9 to 71 % for turmeric oleoresin encapsulated in starch/gelatin using the same spray dryer model and similar drying conditions.

Scanning electron micrographs (SEM) of the encapsulated materials are shown in Figure 1. Microparticles produced with MG presented rounded shapes with a toothed surface, irregular depressions and concavities. Although the microparticles had irregular depressions or concavities, no cracks or pores were found on the surfaces. It was also observed a small tendency to form agglomerates (Figure 1A). Microparticles produced with SG (Figure 1B) presented more spherical and smoother surfaces than MG, although irregular depressions and concavities were also observed. Heterogeneous particle sizes from very small (< 2 µm) to large (> 20 µm) were also observed. Large particles with a toothed surface and concavities may indicate that the solidification of the encapsulating material during drying occurred before the expansion of the microparticles (Jafari, He, & Bhandari, 2007). The smoother surface of microparticles with SG indicates better miscibility and compatibility of encapsulating agents. Similar particle morphology was reported: using maltodextrin as encapsulant material, in works of curcumin encapsulation using polysaccharide-based systems (Goëlo et al., 2020) and investigating the influence of emulsification and spray drying parameters (Ferreira et al., 2019); using starch as encapsulant material for production of microparticles with cross-linked gelatin (Dang et al., 2017) and using phosphorylated starch (García-Tejeda, Salinas-Moreno, Hernández-Martínez, & Martínez-Bustos, 2016).

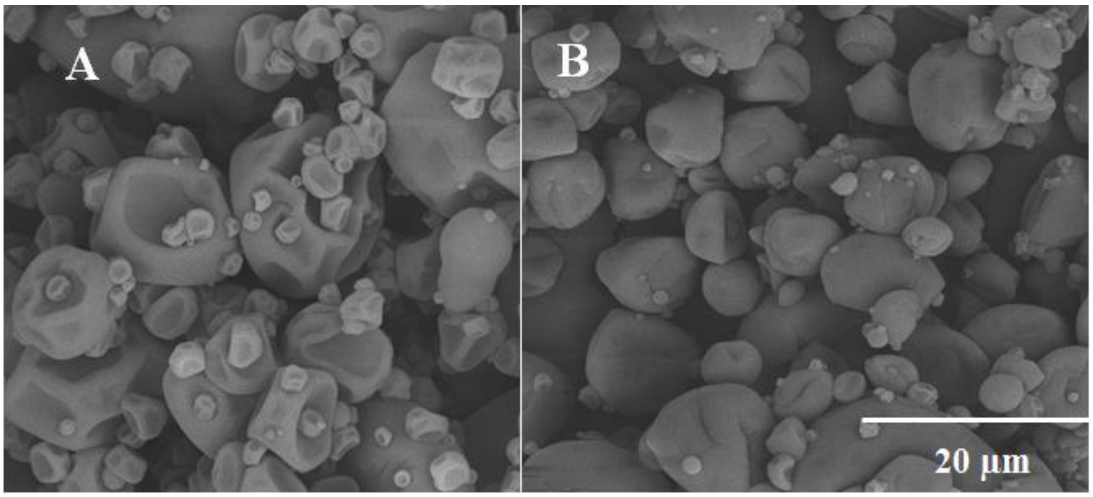

Figure 1. Scanning electron photomicrographs (1000 x magnification) of turmeric oleoresin encapsulated by spray drying using maltodextrin and gelatin (A) and modified starch and gelatin (B) as encapsulant materials.

Table 1 shows the physicochemical properties of turmeric oleoresin encapsulated. MG encapsulated materials presented higher moisture percentages than those obtained with SG. These results are corroborated by studies of curcumin encapsulation by spray drying using blends starch/gelatin and maltodextrin/gelatin (Ferreira et al., 2016, 2019). It is common for materials encapsulated with maltodextrin to have higher moisture, due to the presence of hydrophilic groups in its chemical structure that can easily bind to water molecules from the ambient air after spray drying.

Regarding the curcumin content, phenolic compounds and color parameters, sample produced with SG showed values significantly higher. The protection of phenolic compounds achieved using starch is attributed to its structural and chemical properties (Błaszczak, Misharina, Fessas, Signorelli, & Górecki, 2013; Misharina, 2004). The modified starch molecule has amphiphilic characteristic, ie good ability to hydrophobic interaction. Its high molecular weight and branched structure allows it to stabilize emulsions and other dispersed systems by steric impediment even at low concentrations (Sweedman, Tizzotti, Schäfer, & Gilbert, 2013). These characteristics allowed a greater interaction with the turmeric oleoresin resulting in microparticles with high retention of curcumin and phenolic compounds.

Visually the encapsulated materials showed differences in their initial coloration. The use of SG as encapsulant material gave powders with a more intense yellow color than MG. This visual difference was confirmed by the significantly lower initial value ($p < 0.05$) of the parameter b (yellow) in the sample containing MG.

Table 1. Characterization of turmeric oleoresin encapsulated with maltodextrin and gelatin (MG) and modified starch and gelatin (SG) by spray drying.

	MG	SG
Moisture content (% wb)	3.80 ± 0.03^a	2.00 ± 0.02^b
Curcumin content (mg g^{-1})	2.30 ± 0.10^b	5.60 ± 0.10^a
Phenolic content (mg g^{-1})	100.1 ± 1.74^b	$400.7 \pm 0,45^a$
Color parameters		
L (lightness-darkness)	94.9 ± 0.00^a	92.1 ± 0.00^b
a (redness-greenness)	-2.2 ± 0.01^b	0.3 ± 0.01^a
b (blueness-yellowness)	31.4 ± 0.05^b	45.1 ± 0.01^a
Solubility (%)	94.5 ± 1.39^a	93.6 ± 1.29^a

[1]Means ± standard error (n = 3) with different letters in superscript in each row are significantly different (Tukey test, $p < 0.05$).

No significant differences were observed in solubility, with both samples having high solubility values (> 90%). In spray drying, the high temperature can disrupt the structural organization of the starch granules and facilitate the entry of water resulting in microparticles of high solubility. High values of solubility also were presented in turmeric oleoresin microencapsulated by spray drying using gelatin-collagen (96.8%), maltodextrin/gelatin (84 – 98 %) and maltodextrin, gum arabic and modified starch (85.35 - 99.25%) (Cano-Higuita, Malacrida, & Telis, 2015; Rudke et al., 2019; Zuanon et al., 2017).

Stability of microencapsulated materials during storage

Stabilities of encapsulated materials for the curcumin content, total phenolic compounds and color were evaluated under different storage conditions during 35 days. Comparing the encapsulant material biopolymers, SG presented lower losses of curcumin at all temperatures (Table 2). Only storage at -20°C did not cause significant losses of curcumin ($p < 0.05$) after 35 days. Stability of curcumin decreases with increasing storage temperature and the greatest losses of this compound were observed during storage in the presence of light. After 35 days, curcumin losses were 50.6% for MG and 11% for SG in the presence of light.

In addition to presenting lower losses of curcumin, the encapsulated materials with SG were more stable during the storage time. Significant decreases ($p < 0.05$) were observed after 21 days of storage at 25°C (89.8% of retention), and 14 days at 25°C in the presence of light (92.1% of retention) and at 60°C (94.1% of retention). Meanwhile, MG encapsulated materials showed significant losses within the first 7 days of storage at 25° C in the absence (81.9% of retention) and presence of light (57.9% of retention).

The same behavior noted for curcumin retention was observed for stability of phenolic compounds, where it decreased with increasing storage temperature. Higher losses were observed during the light stability test at 25ºC of the MG encapsulated materials with a 61.1% reduction after 35 days of storage. SG encapsulated materials showed higher efficiency in the phenolic compounds retention at 25ºC in the presence and absence of light.

In general, the SG matrix was able to protect the bioactive compounds (curcumin and phenolic compounds) more efficiently than the MG matrix during stability tests at 25ºC, 60ºC and 25ºC + light. The morphology of the capsules (Figure 1) may have great influence in the microparticles stability. MG capsules presented more irregular surface, it will have higher surface area to interact with oxygen, potentializing curcumin and phenolic degradation. Since SG capsules have more regular surface, it is expected less interaction with oxygen, and higher values of phenolic content and curcumin retentions.

Turmeric oleoresin microencapsulated with modified starch / gelatin (30:1) by freeze-drying showed lower stability to temperature and light tests (Malacrida et al., 2015). Curcumin retention was 97.5 % (-20ºC), 85.5 % (25ºC), 77.2% (60ºC) and 53.4% (25ºC + light). This indicates that turmeric oleoresin encapsulated by spray drying has greater stability than the encapsulated by freeze drying. The specific structures of the matrices after drying promotes higher retention of curcumin in spray-dried samples. As seen in Figure 1, no pores could be seen in the capsules surface. Freeze-drying results in capsules with more heterogeneous and porous matrices, larger particle sizes and which probably had a higher amount of oleoresin on the surface, thus more exposed to degradation. In a study of production and storage of betalain particles by spray drying using blends of maltodextrin/modified starch, on assays of stability at 25ºC with light, Zuanon et al. (2019) reported the same behavior in function of storage time as found in this study, with a significant decrease of core retention after 15 days.

Table 2. Retentions of curcumin and phenolic compounds after 35 days of storage at different temperatures of turmeric oleoresin encapsulated with maltodextrin and gelatin (MG) and modified starch and gelatin (SG) by spray drying.

Temperature	Retention (%)[123]	
	MG	SG
	Curcumin	
-20 ºC	98.6 ± 2.08 ^{Aa}	98.3 ± 2.64 ^{Aa}
25 ºC	70.3 ± 5.19 ^{Bb}	94.8 ± 0.90 ^{Ab}
60 ºC	66.3 ± 5.66 ^{Bc}	94.0 ± 0.73 ^{Ab}
25 ºC + light	49.4 ± 2.30 ^{Bd}	89.0 ± 1.57 ^{Ac}
	Phenolic compounds	
-20 ºC	100.5 ± 1.47 ^{Aa}	99.8 ± 3.75 ^{Aa}
25 ºC	95.7 ± 2.42 ^{Bb}	98.9 ± 1.13 ^{Aa}
60 ºC	90.0 ± 2.84 ^{Ab}	90.6 ± 3.68 ^{Ab}
25 ºC + light	38.9 ± 4.77 ^{Bc}	100.5 ± 0.33 ^{Aa}

[1]Mean values ± standard error (n = 3). [2]Mean values with different capital letters in superscript in each row are significantly different (Tukey test, $p < 0.05$). [3]Mean values with different lowercase letters in superscript in each column are significantly different (Tukey test, $p < 0.05$).

Changes in color parameters of turmeric oleoresin encapsulated are shown in Table 3. In general, it was observed that the samples encapsulated with MG showed an increased in the L parameter and those encapsulated with SG had a decrease in the parameter L, indicating darkening and bleaching of the samples, respectively.

Table 3. Color parameters variations and total color difference of turmeric oleoresin encapsulated during storage at different temperatures.

	MG	SG
Temperature -20°C		
ΔL	-0.4 ± 0.01	-0.6 ± 0.01
Δa	0.2 ± 0.03	1.3 ± 0.02
Δb	1.5 ± 0.08	-0.1 ± 0.06
ΔE	1.5	1.4
Temperature 25°C		
ΔL	1.0 ± 0.01	-2.6 ± 0.02
Δa	-1.4 ± 0.02	4.8 ± 0.02
Δb	-4.9 ± 0.07	9.6 ± 0.03
ΔE	5.2	4.1
Temperature 60°C		
ΔL	0.4 ± 0.00	-0.4 ± 0.03
Δa	-1.4 ± 0.01	1.6 ± 0.06
Δb	3.1 ± 0.05	-0.1 ± 0.01
ΔE	5.0	4.7
Temperature 25°C + light		
ΔL	1.3 ± 0.01	-1.3 ± 0.02
Δa	2.4 ± 0.02	7.3 ± 0.02
Δb	-14.2 ± 0.06	-12.7 ± 0.05
ΔE	14.4	14.7

[1]Mean values ± standard error (n = 3).

Total color difference (ΔE) shows the overall difference between the initial sample and the samples stored in the different temperatures. ΔE varied little among the different matrices during the 35 days of storage. The greatest variations in the color parameters were observed in samples stored at 25°C + light, however, a significant color difference was observed after storage of the samples at all temperatures. Variations in parameter b were more significant during storage with the presence of light for the two encapsulating matrices. The decrease in the yellow color in the samples coincided with the greatest losses of curcumin. What it suggests that the degradation of curcumin occurred mainly due to the exposure to light of the pigments present on the surface of the microparticles.

For $\Delta E < 1.5$ is expected no visual color difference of the sample, $1.5 < \Delta E < 5$ it is expected small visual difference on the powder color and for $\Delta E > 5$ there are large differences in coloration (Obón, Castellar, Alacid, & Fernández-López, 2009; Young & Whittle, 1985). Results in Table 3 show that, although the temperature has affected the color stability, samples were more susceptible to color changes caused by presence of light during storage. The increase in the storage temperature from 25 to 60°C did not affect the total color variation of the samples that showed similar values at both temperatures. Regarding to color, storage at low temperature (-20°C) showed the least effect after 35 days.

Other works reported total color difference of 6 (collagen-gelatin), 15.75 (maltodextrin/modified starch), 10.13 (gum arabic) and 7.69 (gum Arabic/maltodextrin/modified starch) in turmeric oleoresin encapsulated by spray drying after 35 days of storage at 25°C + light (Cano-Higuita et al., 2015; Zuanon et al., 2017). Turmeric oleoresin encapsulated by freeze drying using MG and SG showed higher ΔE values after storage of 35 days at -20, 25 + light and 60°C (Malacrida et al., 2013; 2015), demonstrating that spray drying results in more stable capsules to color variation at these temperatures. This confirms that light plays an important factor in degradation of turmeric oleoresin compounds. In the future, more effort/studies should be carried aiming to increase the turmeric microparticles resistance to light degradation.

Sorption behavior

Equilibrium moisture content of turmeric oleoresin encapsulated with MG and SG and stored at different water activities are shown in Table 4. The equilibrium moisture increased with increasing water activity and the samples encapsulated with SG reached higher values in the different water activities.

Experimental data of the sorption isotherms were fitted to GAB and BET models. The estimated parameters are presented in Table 5. Both GAB and BET models showed a good fit to experimental data with high R^2 values and satisfactory mean relative deviation modulus (E). The GAB model, however, fitted better to the experimental data, presenting R^2 values close to 1 and E values lower than the BET model adjustments.

Table 4. Equilibrium moisture content of turmeric oleoresin encapsulated with maltodextrin and gelatin (MG) and modified starch and gelatin (SG) by spray drying.

Aw	Equilibrium moisture content (g/g dry matter)	
	MG	SG
0.112	0.0242 ± 0.0009	0.0267 ± 0.0010
0.225	0.0358 ± 0.0013	0.0393 ± 0.0002
0.320	0.0468 ± 0.0013	0.0547 ± 0.0002
0.432	0.0627 ± 0.0010	0.0714 ± 0.0010
0.529	0.0762 ± 0.0014	0.0943 ± 0.0015
0.645	0.0991 ± 0.0012	0.1371 ± 0.0046
0.755	0.1324 ± 0.0025	0.1985 ± 0.0006

[1]Mean values ± standard error (n = 3).

Monolayer moisture content (X_m) is considered as the safe moisture for dried food products during storage and it indicate the amount of water that is strongly adsorbed to the specific sites at the food surface (Labuza, 1980; Tonon et al., 2009). It is an important value to ensure food stability. According to Table 5, the values of X_m were 4.6 and 5.2% in the materials encapsulated with MG and SG, respectively. Thus, the encapsulated materials showed moisture (Table 1) below the monolayer moisture content. Using blends of starch-maltodextrin as encapsulant material, Zuanon et al. (2019) reported similar sorption isotherms for belalanin extract, confirming that the encapsulant material have more influence on the water sorption behavior than the hydrophobicity of the encapsulated material.

Table 5. Estimated GAB and BET parameters for turmeric oleoresin encapsulated with maltodextrin and gelatin (MG) and modified starch and gelatin (SG) by spray drying.

Model	Sample	Parameters			R^2	E (%)
		X_m	C_{GAB}	K_{GAB}		
GAB	MG	0.046	6.995	0.888	0.999	2.18
	SG	0.052	5.472	0.993	0.999	3.25
		X_m	C_{BET}			
BET	MG	0.343	0.463		0.997	8.03
	SG	0.172	1.287		0.999	3.55

Sorption isotherms adjusted to the GAB model are shown in Figure 2. In Aw>0.450, the sample produced with SG had the highest hygroscopic behavior. Maltodextrin has a large number of ramifications with hydrophilic groups that facilitate the adsorption of moisture from the environment and generally presents higher hygroscopicity than starch (Tonon, Brabet, & Hubinger, 2009). This behavior was not verified in the present work since the microparticles produced with SG absorbed more water in Aw above 0.1 than those produced with MG. The interaction with gelatin may have reduced the available hydrophilic groups of maltodextrin, contributing to its becoming less hygroscopic than SG.

Adsorption process for biopolymers involves adsorption but also structural changes of the polymer matrix due to swelling, highlighting, also, the conformation and topology of molecule and the hydrophilic/hydrophobic sites adsorbed at the interface (Pérez-Alonso, Beristain, Lobato-Calleros, Rodríguez-Huezo, & Vernon-Carter, 2006).

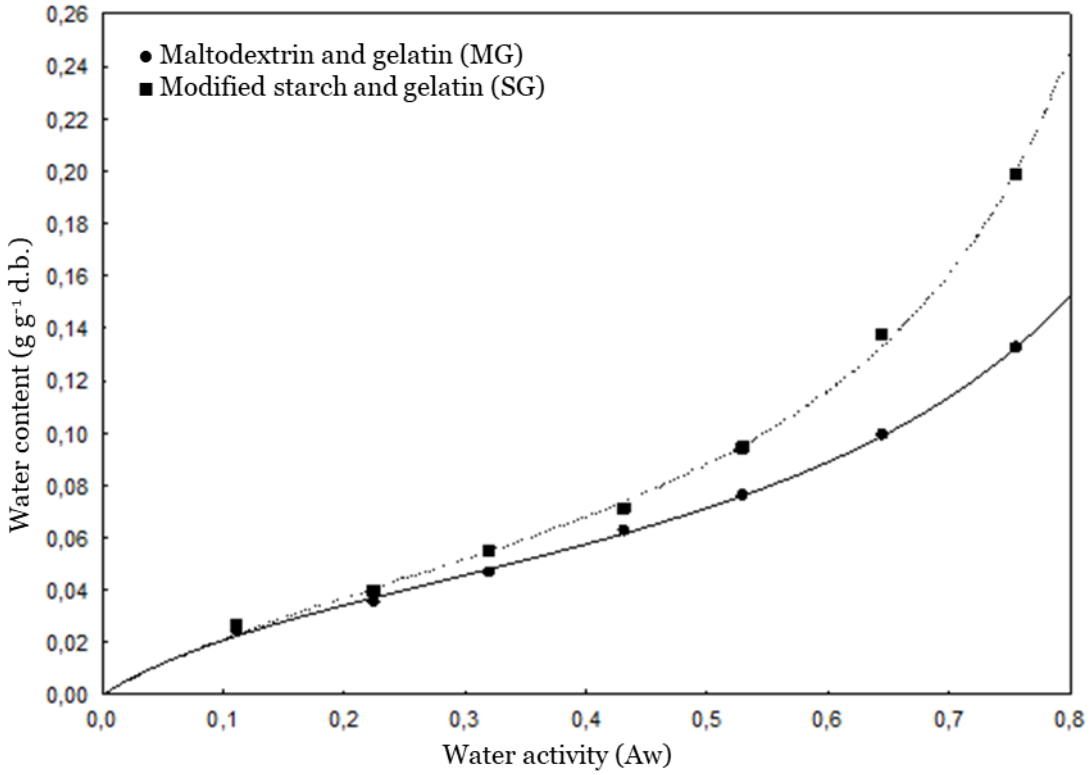

Figure 2. Sorption isotherms (GAB model) of turmeric oleoresin encapsulated with maltodextrin and gelatin (MG) and modified starch and gelatin (SG) by spray drying.

Conclusion

The use of the modified starch and gelatin mixture as encapsulant material yielded microparticles with better physicochemical characteristics: less moisture, higher retention of curcumin and phenolic compounds and more intense color. Process yield was low yield for the two polymeric matrices. In the stability tests, the presence of light during storage was the parameter that most affected the stability of the encapsulated materials independent of the polymeric matrix. Encapsulated materials were more stables when stored at freezer temperature (-20ºC). The microparticles produced with SG showed better stability with respect to

curcumin and phenolic compounds retentions and color. Therefore, considering the conditions of encapsulation tested, the results obtained indicate that the use of SG as encapsulant material is more suitable for the encapsulation of turmeric oleoresin. Water adsorption of turmeric oleoresin microparticles produced with MG and SG were well described by GAB model and the microparticles produced with SG showed high hygroscopic behavior.

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