Revista Mexicana de Ingeniería Química

Vol. 8, No. 2 (2009) 187-196

INTERRELATIONSHIP BETWEEN THE STRUCTURAL FEATURES AND REHYDRATION PROPERTIES OF SPRAY DRIED MANZANO CHILLI SAUCE MICROCAPSULES

INTERRELACIÓN ENTRE LAS CARACTERÍSTICAS ESTRUCTURALES Y LAS PROPIEDADES DE REHIDRATACIÓN DE MICROCÁPSULAS DE SALSA DE CHILE MANZANO OBTENIDAS MEDIANTE SECADO POR ASPERSION

C. Pérez-Alonso[1*], M. F. Fabela-Morón[1], A. Y. Guadarrama-Lezama[1], J. F. Barrera-Pichardo[1], L. Alamilla-Beltrán[2] and M.E. Rodríguez-Huezo[3]

[1]*Facultad de Química, Universidad Autónoma del Estado de México, Paseo Tollocan esq. Paseo Colón s/n, CP 50120 Toluca, Estado de México, México.*
[2]*Departamento de Graduados e Investigación en Alimentos, ENCB-IPN, Carpio y Plan de Ayala s/n, CP 11340 México, D.F., México.*
[3]*División de Ingeniería Química y Bioquímica, Tecnológico de Estudios Superiores de Ecatepec, Av. Tecnológico s/n, CP 55210 Ecatepec, Estado de México, México.*

Received 2 of December 2008; Accepted 10 of June 2009

Abstract

Manzano chilli sauce microcapsules (MCHS) were obtained by spray drying using Gum Arabic (GA100%), whey protein concentrate (WPC100%) and a blend of these biopolymers (GA50%-WPC50%) as wall materials in 2:1 and 4:1 wall to core material ratios (WCMR). Water vapor adsorption isotherms data of microcapsules were obtained at 35 °C and fitted to GAB's model. The monolayer water content values of the microcapsules varied from 9.97 to 14.32 kg H_2O/100 kg dry solids, and were used for determining the surface fractal dimension (D_s). D_s values ranged between 2.04 to 2.30 for the 2:1 WCMR and 2.17 to 2.43 for the 4:1 WCMR, respectively. Microcapsules topology was determined by Scanning Electronic Microscopy (SEM). Microcapsules with WPC100% exhibited smoother and more regular shaped topology than those with GA100% which tended to exhibit surface flaws and dents, while those made with the biopolymers blend exhibited an intermediate morphology. Rehydration times of the microcapsules were function of water activity (a_w) and WCMR. The higher the WCMR, the higher the rehydration time required.

Keywords: fractal dimension surface, sorption isotherms, water activity, microencapsulation, topology, structural features.

Resumen

Se obtuvieron microcápsulas de salsa de chile manzano (MCHS) mediante secado por aspersión usando como agentes encapsulantes, goma Arábiga (GA100%), concentrado de proteína de suero de leche (WPC100%) y una mezcla de ambos biopolímeros (GA50%-WPC50%), con relaciones de material de pared a material encapsulado (WCMR) de 2:1 y 4:1. Se obtuvieron isotermas de adsorción de las microcápsulas a 35 °C, las cuales se ajustaron al modelo de GAB. El contenido de humedad en la monocapa de las microcápsulas varió entre 9.97 y 14.32 kg H_2O/100 kg s.s., y estos valores se utilizaron para determinar la dimensión superficial fractal (D_s). Los valores de D_s se encontraron entre 2.04 a 2.30 para la WCMR 2:1 y de 2.17 a 2.43 para la WCMR 4:1. La topología de las microcápsulas se determinó por microscopía electrónica de barrido (SEM). Las microcápsulas con WPC100% presentaron superficies suaves y regulares, con GA100% defectos superficiales caracterizadas por pliegues poco tersos, y la mezcla GA50%-WPC50% una morfología intermedia en comparación con los biopolímeros puros. Los tiempos de rehidratación de las microcápsulas fueron función de WCMR y de la actividad de agua (a_w). A mayor WCMR, mayor fue el tiempo de rehidratación requerido.

Palabras clave: dimensión superficial fractal, isotermas de adsorción, actividad de agua, microencapsulación, secado por aspersión.

* *Corresponding author. E-mail: cpereza@uaemex.mx*
Tel. (+52)7222173890 Fax (+52)7222175109

Publicado por la Academia Mexicana de Investigación y Docencia en Ingeniería Química A.C.

1. Introduction

Spices form a major class of ingredients used in most food products today. Among the major spices, Mexico has a high production of chillies. Manzano chilli (*Capsicum pubescens*) is a spice used to elaborate sauces, which are highly consumed in Mexico due to their characteristic flavor. These products offer additional benefits to the consumers due to their nutritional content, because they aid the metabolic functions of the organism, have analgesic and anti-inflammatory properties, and are attributed as preventing some types of cancers (Eshbaugh, 1979; Long-Solís, 1998). Capsaicin, which is the main active principle in chilli, is responsible of pungency in sauces. Due to the presence of unsaturated bonds in the molecular structure of capsaicin contained in manzano chilli, it is susceptible to degradation by environmental factors (air, light, temperature, oxygen, moisture, etc.) (Beristain *et al*., 2001). Microencapsulation is a technique that allows the preservation of foods and other products, by rendering free flowing stable powders, easily mixable with other dry ingredients, and where the core material natural characteristics are protected against deleterious environmental factors (McNamee *et al.,* 1998; Madene *et al*., 2006; Ré, 2006). A possible approach for protecting the active ingredients contained in chilli sauces is to transform them into microencapsulated powders by spray drying. By doing this, the water content is substantially decreased, so that the rate of spoilage mechanisms related to high water contents is diminished, resulting in products with superior physicochemical and sensory properties, and an increased shelf life.

Biopolymers used as wall materials for lipid encapsulation by spray drying include gum Arabic (Shaikh *et al*., 2006), maltodextrins (Watanabe *et al*., 2002), whey protein concentrate (Hogan *et al*., 2001) and mesquite gum (Beristain and Vernon-Carter, 1994; Beristain *et al*., 2002). The selection of wall material may influence the emulsion stability during its formation and upon the drying process affecting the characteristics of the resulting microcapsules (Ré, 1998; Gharsallaoui *et al*., 2007). Wall materials for microcapsules by spray-drying should preferrably comprise biopolymers that possess good surface activity (which will affect emulsification/encapsulation efficiency), are highly soluble and exhibit low viscosity at high concentrations (because usually wall to core material ratios are high in microcapsules, and because spray drying requires high solids concentration to be economically feasible), and form dense adsorbed layers around the lipid being encapsulated (so as to minimise diffusion of pro-oxidant agents). Polymeric membranes that form the wall of microcapsules are semipermeable, that determine the behavior of liberation of core contained into the capsule and the morphology of microcapsules (Shahidi and Han, 1993; Park *et al.,* 2001).

The thermodynamics of water sorption in dried foodstuffs has drawn interest because it provides a more thorough interpretation of the sorption isotherm phenomenon and helps to understand better the sorption mechanism. Sorption isotherms are useful thermodynamics tools in determination of water interactions and components of the foods, operation conditions and processing like drying, mixing, packing and storage. Stability is greatly influenced by the moisture sorption characteristics of the product (Ayranci *et al.*, 1990; Beristain *et al*., 2002; Pérez-Alonso *et al*., 2006).

During and after drying, physical properties of microcapsules change mainly because of the loss of its moisture content. Attempts have been made to characterize these physical properties changes in terms of such parameters as the changes in volume, area and shape, these changes in the surface are directly related to the structure of the drying material (Moreau and Rosenberg, 1998; Kerdpiboon and Devahastin, 2007). A noninteger dimension called surface fractal dimension, D_s, has been widely used to characterize particle surface roughness. It is an operative measure of the surface and structural irregularities of a given solid that present self-similarity. The value of D_s varies from 2 for a perfectly smooth surface to 3 for a very rough surface (Tang *et al.,* 2003). Doulia *et al*. (2000) proposed the use of fractal theory as an alternative to describe complex mechanisms involved in drying: moisture gradients into the particles may cause mechanical tension which, in turn, will cause irregularity of the particle not only along the process but also as final product.

Studies leading to the description of morphological changes of particles along spray drying, including evaluation of ruggedness of these particles in terms of the fractal dimension of the product, may give an insight of the complex phenomena of morphology development during spray drying (Alamilla-Beltrán *et al*., 2005). The fractal theory has been used to describe the microstructure changes and mechanical property changes of foods and drugs, these changes can be evaluated through Scanning Electronic Microscopy (SEM) coupled a fractal analysis to monitor changes of some properties; i.e., shrinkage in function of its shape, area and volume to describe microestructural changes in processing applications (Quevedo *et al*., 2002; Kerdpiboon and Devahastin, 2007).

The aim of this work was to obtain spray-dried microcapsules of manzano chilli sauce using different biopolymers as wall materials and different wall to core material ratios and determine their: (a) water vapor adsorption isotherms; (b) surface fractal dimension, (c) surface topology by Scanning Electron Microscopy, and (d) rehydration times.

It is hoped that by doing this, an interrelationship between formulations, structural

features and rehydration properties can be established, contributing to the knowledge for obtaining spray dried products with enhanced functional properties.

2. Materials and methods

2.1. Materials

Manzano chilli, garlic, mustard and vinegar were acquired in a supermarket in the Toluca, State of Mexico, Mexico. Whey protein concentrate with 80% of protein in d.b. (WPC; Hilmar™ 8000, Hilmar Ingredients, Hilmer, CA, USA), gum Arabic (GA; Drogueria Cosmopolita S.A. de C.V., Mexico, city) were used as wall materials. Salts analytic grade of LiCl, $KC_2H_3O_2$, K_2CO_3, $MgNO_3.5H_2O$, $NaNO_2$, NaCl y KCl, were purchased in Sigma Aldrich Co. (Toluca, State of Mexico, Mexico). Water used in the experiments was bidistilled.

2.2. Manzano chilli sauce (MCHS) preparation

Manzano chillies and garlic were manually cleaned by removing all foreign matter, disinfected with a sodium hypochloride solution (0.02 M), cut into small squares, and deseeded. 500 g of manzano chilli was mixed with 30 g of mustard, 1 g of garlic and 83 g of vinegar and blended (O/4655 classic blender, Osterizer Inc., USA) until a homogeneous mixture was obtained. The manzano chilli mixture was passed through a Tyler # 9 (2000 μm) sieve in order to obtain the manzano chilli sauce (MCHS).

2.3. Preparation of the oil-in-water emulsions and spray-drying

Three different types of oil-in-water emulsions (O/W) were prepared using wall to core material ratios (WCMR) of 2:1 and 4:1, consisting of gum Arabic (GA100%), whey protein concentrate (WPC100%) and a blend of both biopolymers (GA50%-WPC50%) as wall materials. The required amount of MCS was added dropwise to the required amount of wall materials solution using the Ultra-Turrax T50 homogenizer (IKA®-WERKE Works Inc., Wilmington, N.C., USA) at speed of 5200 rpm during 5 min. All the emulsions had a volumetric dispersed phase (ϕ) of 0.10. The biopolymers solutions were maintained in an iced water bath in order to keep the emulsion temperature below 30ºC (Koberstein-Hadja and Dickinson, 1996). The O/W emulsions with 30% (for the 2:1 WCMR) and 50% (for the 4:1 WCMR) solids content were fed at a rate of 40 ml/min to a 8K2SRMA series 193 spray-dryer (Confad Industry, Mexico, city, Mexico) operated with an atomization pressure of 4 bar, an inlet air temperature of 170 °C and an outlet air temperature 85 ºC.

2.4. Sorption isotherms of microcapsules

Microcapsules of MCHS were put into petri dishes, so that they covered completely and homogeneously the dishes surface. The dishes were then introduced into glass desiccators, containing P_2O_5 as a desiccant, at room temperature for 3 weeks in order to reduce to moisture content (~2%) of the powders. The adsorption isotherms were determined at 35 ºC using the gravimetric method described by Lang *et al*. (1981). Approximately 1.0 g samples of each microcapsule were put into small glass desiccators of 10 cm diameter which contained saturated solutions of different salts (LiCl, $KC_2H_3O_2$, K_2CO_3, $MgNO_3.5H_2O$, $NaNO_2$, NaCl y KCl) that provided water activities (a_w) in the range of 0.108–0.821 (Labuza *et al*., 1985; Domínguez-Domínguez *et al*., 2007). Filter paper (Whatman No. 1), placed above the saturated salt solutions, in a perforated plate used as support for the powders and for allowing moisture transmission. Five desiccators of each powder were placed into forced convection drying ovens (Riossa model E-51, Mexico) at 35 ±0.1 ºC. The powders were weighed with an Ohaus electronic balance (model AP210, Pine Brook, NJ, USA) every five days until equilibrium was achieved. Equilibrium was assumed when the difference between two consecutive weightings was less than 1 mg/g of solids. The time to reach equilibrium varied from 20 to 25 days. Moisture content of the humidified systems was determined by difference in weight after drying in a vacuum oven (FELISA, Mexico City, Mexico) at 60 °C in the presence of magnesium perchlorate desiccant. The water activity was measured with an Aqualab water activity meter with temperature compensation (model series 3 TE, Decagon Devices, Inc., Pullman, WA, USA). The Guggenheim-Anderson-De Boer (GAB) equation was used in modeling water sorption (Rizvi, 1986):

$$M = \frac{M_o C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

where M is the equilibrium moisture content (kg water/100 kg dry solids); M_o is the monolayer water content (kg water/100 kg dry solids), a_w is the water activity, and C is the Guggenheim constant, given by:

$$C = c' \exp\left(\frac{h_m - h_n}{RT}\right) \quad (2)$$

where c' is the equation constant; h_m is the total heat sorption of the first layer (kJ/mol); h_n is the total heat of sorption of the multilayers (kJ/mol); R is the universal gas constant (kJ/mol K); T is the absolute temperature (K), and K is the constant correcting properties of the multilayer molecules with respect to the bulk liquid, and given by:

$$K = k' \exp\left(\frac{h_1 - h_n}{RT}\right) \quad (3)$$

where *k'* is the equation constant; h_l is the heat of condensation of pure water (kJ/mol). The parameters were estimated by fitting the mathematical model to the experimental data, using non-linear regression with Polimath software version 5.1. Goodness of fit was evaluated using the relative percentage difference between the experimental and predicted values of moisture content, or mean relative deviation modulus (*E*), defined by the Eq. (4) (Lomauro *et al*., 1985; Aguerre *et al*., 1989; McLaughlin and Magee, 1998). It is generally assumed that a good fit is obtained when $E < 5\%$.

$$E = \frac{100}{N}\sum \frac{|M_i - M_{Ei}|}{M_i} \quad (4)$$

where M_i is the moisture content at observation *i*; M_{Ei} is the predicted moisture content at that observation and *N* is the number of observations.

2.5. Surface fractal dimension (D_s)

Surface fractal dimension of microcapsules was determined through water vapor sorption isotherms, using the modified Frenkel-Halsey-Hill theory (Tang *et al*., 2003). Values of monolayer moisture content (M_o) calculated from the fits of adsorption isotherms of microcapsules at different ratios of wall material to core material (2:1 and 4:1), was calculated moisture content (*M*) using the GAB model. Tang *et al*. (2003) derived an expression for D_s from an analysis of multilayer adsorption to a fractal surface:

$$\ln\left(\frac{M}{M_o}\right) = B + A\ln\left(a_w\right) \quad (5)$$

where *B* is the intercept, *A* is an exponent of potency law which depends of D_s and the adsorption mechanism (δ). Linearization of Eq. (5) permits to obtain *A* from the slope, and this parameter provides an estimation of the adsorption mechanism taking place:

$$\delta = 3(1+A) - 2 \quad (6)$$

If $\delta \geq 0$, the adsorption mechanism is by superficial tension, capillary condensation or porosity, and D_s is determined as follows (Pfeifer and Cole, 1990; Pfeifer, 1991):

$$A = D_s - 3 \quad (7)$$

If $\delta < 0$, the adsorption mechanism occurs by van der Waals forces, and the relation between *A* and D_s is expressed as follows (Wu and Suchsland, 1996):

$$A = \frac{D_s - 3}{3} \quad (8)$$

Finally the number of layers adsorbed (*n*) is determined by:

$$n = \left(\frac{M}{M_o}\right)^{\frac{1}{(3-Ds)}} \quad (9)$$

2.6. Morphology of microcapsules by scanning electronic microscopy (SEM) analysis

A JSM-5800LV model scanning electron microscope (Jeol Co. Ltd., Tokyo, Japan) was used to investigate the microstructural properties of the spray-dried encapsulated powders. The samples were placed on the SEM stubs using a two-sided adhesive tape (Ted Pella, Redding, California, USA). The samples were subsequently coated with aurum using a magnetron sputter coater (Denton Vacuum Model, USA), at 100 militorrs and 15 mA. The coated samples were then analyzed using SEM operating at an accelerating voltage of 15 kV. The micrographs representing the microstructure of the encapsulated powders were taken by the instrument's software installed on a PC connected to the system.

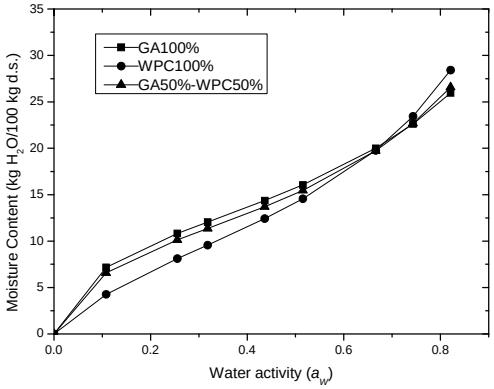
2.7. Rehydration time

The rehydration capability of the powders was evaluated according to Martinelli *et al*. (2007). Samples of 1.0 g microcapsules were storaged at different water activities (a_w) between 0.108 and 0.821 and at 35 ºC until to reach equilibrium state, after were completely dissolved in 40 mL of bidistilled water. It was measured with chronometer Casio (model HS20, Argentina) the initial time when the powder touched water until complete disolution of microcapsules.

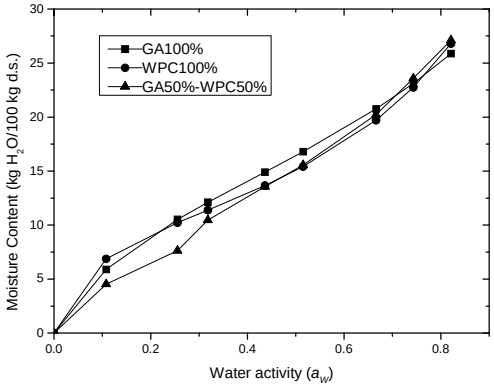
3. Results and discussion

3.1. Sorption isotherms

Sorption isotherms at 35ºC of microcapsules of manzano chilli sauce are shown in Fig. 1. The experimental data were described very well with the GAB model (Tables 1 and 2), as the mean relative deviation modulus (% E) was <5% in all cases independently of the ratio of wall to core material employed. The adsorption isotherms of all the microcapsules had a typical sigmoid shape that is known as type II isotherm, and is characteristic of several materials such as apple pectin, soy protein, whey protein, sodium caseinate (Weisser, 1985); powder of juice lemon, gum Arabic and biopolymers blends (Martinelli *et al*., 2007). Sorption isotherms presented interweaving at different water activities values (a_w). For example, the GA50%-WPC50% microcapsule presented interweaving with the GA100% microcapsule (both at a 2:1WCMR) at a_w value of ~0.58, while the WPC100% and GA100% microcapsules interwove at a_w value of ~0.78. This means that above these a_w values, the microcapsules had an enhanced water adsorption capability. Microcapsules at 4:1 WCMR also presented interweaving. Interweaving between the GA100% and WPC100% microcapsules occurred at a_w value of ~0.65 while that between GA50%-WPC50% and GA100% microcapsules occurred at a_w value of ~0.42.



a)



b)

Fig. 1. Sorption isotherms of MCHS microcapsules at 35 ° C, with wall to core material ratios of: a) 2:1 and b) 4:1.

Table 1. Estimated parameters of the GAB equation for manzano chilli sauce microcapsules at 35 °C with a 2:1 wall to core material ratio.

Wall materials	M_0 (kg H_2O/100 kg d.s.)	C	K	$\%E$
GA100%	11.11	17.51	0.717	2.44
WPC 100%	10.48	6.20	0.803	3.40
GA50%-WPC50%	10.31	15.69	0.762	3.92

GA = Gum Arabic, WPC = Whey Protein Concentrate.

Table 2. Estimated parameters of the GAB equation for manzano chilli sauce microcapsules at 35 °C with a 4:1 wall to core material ratio.

Wall materials	M_0 (kg H_2O/100 kg d.s.)	C	K	$\%E$
GA100%	14.32	8.83	0.612	2.79
WPC 100%	9.97	18.62	0.778	4.14
GA50%-WPC50%	12.85	5.91	0.718	3.77

GA = Gum Arabic, WPC = Whey Protein Concentrate.

The value of the monolayer (M_o) is of particular interest, because it indicates the amount of water that is strongly adsorbed in specific sites and is considered as the optimum value at which the food is more stable (Martinelli *et al*., 2007; Gabas *et al.*, 2007). Microcapsules GA100% exhibited higher monolayer moisture contents of 11.11 and 14.32 kg H_2O/ 100 kg d.s. for the 2:1 and 4:1 WCMR, than for the WPC100% and GA50%-WPC50% microcapsules (9.97-12.85 kg H_2O/ 100 kg d.s.). These results can be probably explained in terms of the location of water in gum Arabic microcapsules. Strong internal hydrogen bonding occurs in the molecules of carbohydrates. Under such forces, the carbohydrate molecules organize themselves in crystal lattices that include as many hydrogen bonds as possible. As a result of this organization, various molecules of water are included in a crystalline structure (Kim *et al.,* 1996). Iglesias and Chirife (1982) reported M_o values in the range of 4 to 11 kg H_2O/ 100 kg d.s. for several foods, which included whey protein concentrate, starch, starch gel, and sucrose, among others.

The parameter C in the GAB equation lacks of any physical meaning, and may be considered as the result of mathematical compensation among parameters. Nevertheless, it provides an important insight about the degree of the interaction taking place between the adsorbent-adsorbate molecules. The values of C for all of the microcapsules ranged from 6.2 to 17.5 for the 2:1 WCMR and from 5.9 to 18.6 for the 4:1 WCMR. These results are similar to those reported for microcapsules made with mesquite gum and gum Arabic (Pérez-Alonso *et al*., 2006) and fell within the range of 4.1 to 17.6 reported for the same foods mentioned above for M_o (Iglesias and Chirife, 1982).

The value of K provides a measure of the interaction of the molecules in the multilayers with the adsorbent, and tends to fall between the energy value of the molecules in the monolayer and that of liquid water. A value of K below 1 indicates a less structured state of the adsorbate in the multilayers or GAB layers (Martinelli *et al*., 2007). The values of K in all of the microcapsules ranged from 0.612 to 0.803.

The δ parameter provides an estimation of the mechanism by which water adsorbed in the microcapsules. As can be observed in Tables 3 and 4, the values of δ for all of the microcapsules was ≥0, so that the sorption mechanism was due to capillary condensation or porosity. Tang *et al.* (2003) found similar results for powders of bovine serum albumin obtained by spray drying.

3.2. Surface fractal dimension (D_s)

Fig. 2 shows a plot of Ln [Ln (a_w)] versus Ln (M/M_0) for the GA 100% microcapsules in a 2:1 WCRM at 35 °C. A high correlation coefficient (R^2 = 0.9991) existed between Ln [Ln (a_w)] versus Ln (M/M_0), and this trend occurred for all the microcapsules studied. The values of parameter A were obtained from the slope of the Ln [Ln (a_w)] versus Ln (M/M_0) plots (Tables 3 and 4). The values of parameter A fell in

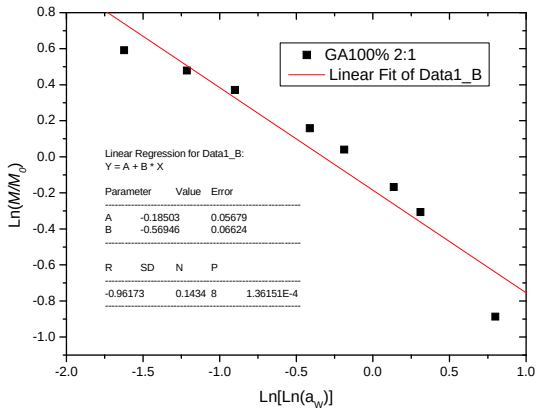


Fig.2. Linear fit of the water vapor adsorption isotherms for GA100% with 2:1 wall to core material ratios of ratio at 35 °C.

between 2.7884 to 3.8658. These A values were used in conjunction with δ (computed with Eq. 6) for calculating D_s using Eq. (7). The values of D_s were: 2.30 (GA100%), 2.04 (WPC100%), 2.20 (GA50%-WPC50%) for the 2:1 WCMR and 2.43 (GA100%), 2.17 (WPC100%), 2.25 (GA50%-WPC50%) for the 4:1 WCMR (Table 3). D_s is a mathematical parameter that provides information regarding the external microstructural features of solids (topology). When D_s has a value of 2.0 the solid has a smooth topology, but as the value of D_s approaches to 3.0, solid surface topology is considered as rough. From this point of view, all our microcapsules had a relatively smooth topology which was from highest to lowest as follows: WPC 100% > GA50%-WPC50% > GA100%. n represents the number of water adsorbed layers on the microcapsules, and is a function of moisture content. Pfeifer (1991) obtained D_s values between 2.06 to 2.51for porous silica solids which fall within our D_s value range.

The values of n varied from 0.39 to 3.37 for the 2:1 WCMR and from 0.21 to 3.31 for the 4:1 WCMR (Tables 3 and 4). Tang *et al.* (2003) that when n fall in between 1.0 and 2.0, i.e., around monolayer coverage, correct values of D_s were obtained. At higher coverages, i.e., n > 2.0, the adsorbed molecules form multilayers the value of D_s tends to increase, and may be incorrect.

3.3. Morphology of microcapsules by SEM analysis

SEM micrographs of the microcapsules at 2:1 and 4:1 WCMR at a_w = 0.515 are shown in Figs. 3 and 4. Independently of the WCMR used to form the microcapsules, those made with WPC 100% showed a smoother surface topology than those made with GA50%-WPC50% and GA100%. The latter ones are characterized by showing multiple dimples in their surface (Figs. 3a, 4a). The microcapsules made with a mixture of WPC and GA showed intermediate topology (Figs. 3b, 4b). Thus, surface topology of the microcapsules was highly dependent on the nature of the biopolymers used as encapsulating agents (Morr and Ha, 1993; Krishnan *et al*., 2005 a, b). Surface topology is clearly interrelated with D_s. Surface topology tended to be less smooth as D_s increased from a value of 2.0 towards 3.0. Our results are in agreement with other morphological studies made on microcapsules obtained by spray-drying and using biopolymers as wall materials (Buffo *et al*., 2002; Alamilla-Beltrán *et al.*, 2005; Shu *et al*., 2006; Jafari *et al.,* 2007).

3.4. Rehydration times

One of the main drawbacks of powdered products is the difficulty found when trying to rehydrate them. A functional powder food should be wetted quickly and thoroughly, sink into the liquid (water) rather than float on the surface and disperse or dissolve within a short period time without lump formation. Fig. 5 a and b show the plots of water activity against rehydration times of the microcapsules made with 2:1 and 4:1 WCMR, respectively. The necesary time

Table 3. Surface fractal dimension for manzano chilli sauce microcapsules with a 2:1 wall to core material ratio.

Wall materials	A	R^2	δ	D_s	n
GA100%	-0.6976	0.9991	3.0929	2.30	0.53-3.37
WPC 100%	-0.9553	0.9929	3.8658	2.04	0.39-2.84
GA50%-WPC50%	-0.7999	0.9961	3.3996	2.20	0.57-3.26

GA = Gum Arabic, WPC = Whey Protein Concentrate.
D_s = surface fractal dimension, n = number of adsorbed layers, R^2 = correlation coefficient.

Table 4. Surface fractal dimension for manzano chilli sauce microcapsules with a 4:1 wall to core material ratio.

Wall materials	A	R^2	δ	D_s	n
GA100%	-0.5695	0.9249	2.7084	2.43	0.21-2.83
WPC 100%	-0.8255	0.9934	3.4764	2.17	0.64-3.31
GA50%-WPC50%	-0.7473	0.9965	3.2420	2.25	0.25-2.72

GA = Gum Arabic, WPC = Whey Protein Concentrate.
D_s = surface fractal dimension, n = number of adsorbed layers, R^2 = correlation coefficient.

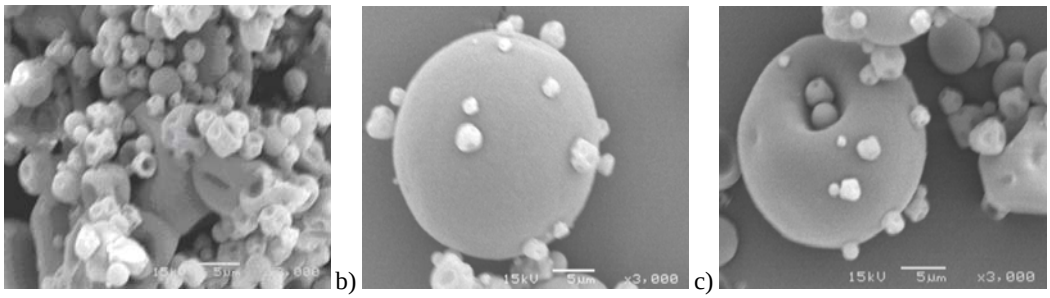


Fig. 3. Topology of the microcapsules with a 2:1 wall to core material ratio: a) GA 100%, b) WPC 100%, c) GA50%-WPC50% at a_w = 0.515.

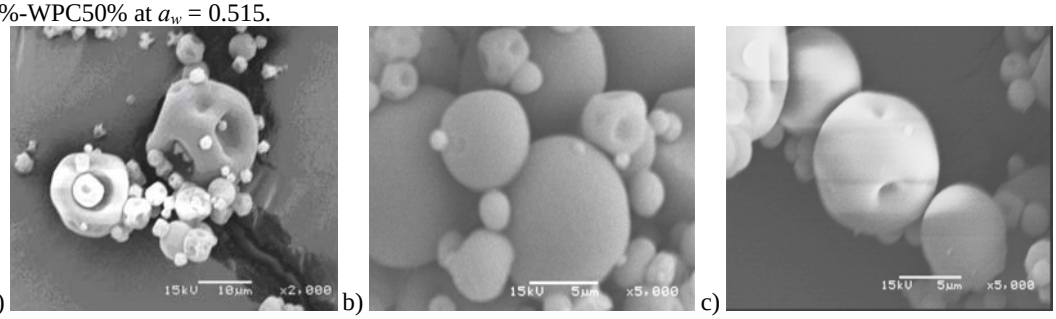


Fig. 4. Topology of the microcapsules with a 4:1 wall to core material ratio: a) GA 100%, b) WPC 100%, c) GA50%-WPC50% at a_w = 0.515.

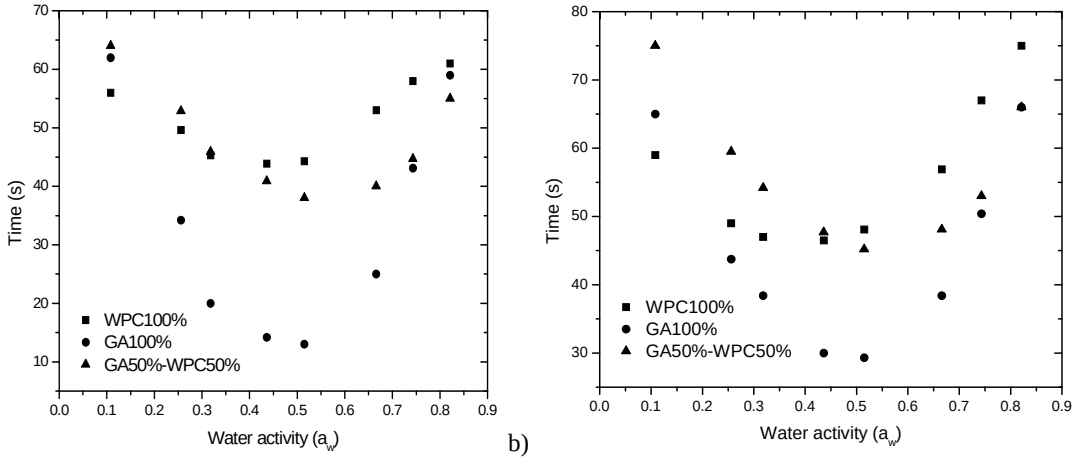


Fig. 5. Topology of the GA100% microcapsules with a 4:1 wall to core material ratio: a) a_w = 0.108, b) a_w = 0.743.

to the manzano chilli sauce microcapsules were dispersed in water after the dry process was of 12-45 s at a_w values between 0.4-0.5, i.e., monolayer coverage conditions. The GA100% microcapsules at 2:1 (12 s)and 4:1 (25 s) WCMR showed lower rehydration than their WPC100% (43 s for 2:1 WCMR and 47 s for 4:1 WCMR) and GA50%-WPC50% % (38 s for 2:1 WCMR and 45 s for 4:1 WCMR) counterparts. Thus, rehydration times were shorter the less smooth were the surface topologies of the microcapsules. This phenomenon may be due to the dimples and flaws present in the surface of the microcapsules that exhibited larger D_s values. The more flawed the microcapsule surface, the easier the penetration of water into the microcapsules interior, which on turn facilitates water adsorption in specific sites.

Figs. 5 a and b show SEM micrographs for the GA100% microcapsules for a 4:1 WCMR at a_w's of 0.108 and 0.743, respectively. A similar behavior was shown at the same water activities for the WPC 100% and GA50%-WPC50% microcapsules. Rehydration times were much longer at a_w's below 0.4 or above 0.5 (Fig. 5 a and b). At a_w of 0.108 the microcapsules show a topology that is very similar to that shown by the microcapsules at a_w between 0.4-0.5. However, in the former the surface coverage is well below the monolayer value, so that more time is required for achieving this state (Fig. 6a). When a_w is 0.743 the microcapsule original structure is completely lost (Fig. 6b) due to the dissolution of the wall material, which leads to extensive fusing of the microcapsules, which hinders rehydration (Rodríguez-Huezo *et al.*, 2004).

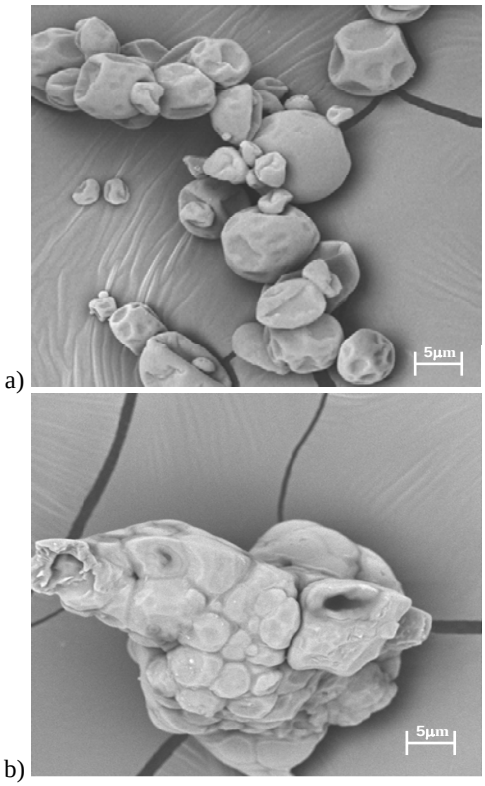


Fig. 6. Rehydration times of the microcapsules at 35 ° C with wall to core material ratios of: a) 2:1 and b) 4:1.

Conclusions

The surface fractal dimension provided a quantitative indicator for establishing surface topology the microcapsules. Higher surface fractal dimension values were obtained for microcapsules with 4:1 than 2:1 wall to core material ratios. The surface fractal dimension was useful tool for characterizing the surface topology smoothness of the microcapsules. Rehydration times of the manzano chilli sauce microcapsules were affected by water activity and wall material composition and by wall to core material ratios. Best rehydration conditions occurred for water activities in between 0.4-0.5 which corresponded to monolayer coverage conditions. The less smooth the topology of the microcapsules, the quicker their rehydration time.

Acknowledgments

The authors wish to thank the financing of this research to the Universidad Autónoma del Estado de México through grant 2398/2006 and PROMEP/103.5/05/1696 to finance this work.

References

Aguerre, R. J., Suárez, C. and Viollaz, P. E. (1989). New BET type multilayer sorption isotherms. Part II: Modelling water sorption in foods. *Lebensmittel-Wissenschaft und Technologie 22*, 192–195.

Ayranci, E., Ayranci, G. and Dogantan, Z. (1990). Moisture sorption isotherms of dried apricot, fig and raisin at 20 ºC and 35 ºC. *Journal of Food Science 55*(6), 1591-1593.

Alamilla-Beltrán, L., Chanona-Pérez, J. J., Jiménez-Aparicio, A. R. and Gutiérrez-López, G. F. (2005). Description of morphological changes of particles along spray drying. *Journal of Food Engineering 67*, 179-184.

Beristain, C. I., García, H. S and Vernon-Carter, E. J. (2001). Spray-dried encapsulation of cardamom (*Elettaria cardamomum*) essential oil with mesquite (*Prosopis juliflora*) gum. *Lebensmittel-Wissenschaft und Technologie 34*, 398-401.

Beristain, C.I. and Vernon-Carter, E.J. (1994). Utilization of mesquite (*Prosopis juliflora*) gum as emulsion stabilizing agent for spray-dried encapsulated orange peel oil. *Drying Technology 12*, 1727-1733.

Beristain, C. I., Azuara, E. and Vernon-Carter E. J. (2002). Effect of water activity on the stability to oxidation of spray-dried encapsulated orange peel oil using mesquite gum (*Prosopis juliflora*) as wall material. *Journal of Food Science 67*, 206-211.

Buffo, R.A., Probst, K., Zehentbauer, G., Luo, Z. and Reineccius, G.A. (2002). Effect of aglomeration on the properties of spray dried encapsulates flavors. *Flavors and Fragance Journal 17*, 292-299.

Domínguez-Domínguez, S., Domínguez-López, A., González-Huerta, A. and Navarro-Galindo, S. (2007). Cinética de imbibición e isotermas de adsorción de humedad de la semilla de Jamaica (*Hibiscus sadariffa* L.). *Revista Mexicana de Ingeniería Química 6*, 309-316.

Doulia, D., Tiza, K. and Gekas, V. (2000). A knowledge base for the apparent mass diffusion coefficient (D_{eff}) of foods. *International Journal of Food Properties 3*(*1*), 1-14.

Eshbaugh, W. H. (1979). Biosystematic and evolutionary study of the *Capsicum pubescens* complex. In: *Research Report 1970 Projects*, National Geographic Society, S.143-162, Washington, USA.

Gabas, A.L., Telis, V.R.N., Sobral, P.J.A. and Telis-Romero, J. (2007). Effect of maltodextrin and Arabic gum in water vapor sorption thermodynamic properties of vacuum dried pineapple pulp powder. *Journal of Food Engineering 82*, 246-252.

Gharsallaoui, A., Roudaut, G., Chambón, O., Voilley, A. and Saurel, R. (2007). Applications of spray-drying in microencapsulation of food ingredients: An overview. *Food Research International 40*, 1107-1121.

Hogan, S.A., McNamee, B.F., O´Riordan, E.D. and O´Sullivan, M. (2001). Microencapsulating

properties of whey protein concentrate. *Journal of Food Science 66*, 675-680.

Iglesias, H.A. and Chirife, J. (1982). *Handbook of food isotherms.* Academic Press. New York , USA.

Jafari, S. M., He, Y. and Bhandari, B. (2007). Encapsulation of nanoparticles of d-limonene by spray drying: Role of emulsifiers and emulsifying techniques. *Drying Technology 25*, 1069-1079.

Kerdpiboon, S. and Devahastin, S. (2007). Fractal characterization of some physical properties of a food product under various drying conditions. *Drying Technology 25*, 135-146.

Kim, Y. D., Morr, C. V. and Schenz, T. W. (1996). Microencapsulation properties of gum arabic and several food proteins; spray-dried orange oil emulsion particles. *Journal of Agricultural and Food Chemistry 44*, 1314-1320.

Krishnan, S., Bhosale, R. and Singhal, R. S. (2005a). Microencapsulation of cardamom oleorresin: Evaluation of blends of gum arabic, maltrodextrin and modified starch as wall materials. *Carbohydrate Polymers 61*, 95-102.

Krishnan, S., Kshirsagar, A.C. and Singhal, R. S. (2005b). The use of gum arabic and modified starch in the microencapsulation of a food flavoring agent. *Carbohydrate Polymers 62*, 309-315.

Koberstein-Hadja, A. and Dickinson, E. (1996). Stability of water in oil in water emulsions containing faba bean proteins. *Food Hydrocolloids 10*, 251-254.

Labuza, T. P., Kaanane, A. and Chen, J. Y. (1985). Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. *Journal of Food Science 50*, 385–391.

Lang, K. W., McCune, T.D. and Steinberg, M.P. (1981). A proximity equilibration cell for rapid determination isotherms. *Journal of Food Science 46*, 936-938.

Lomauro, G. J., Bakshi, A. S. and Labuza, T. P. (1985). Evaluation of food moisture sorption isotherms equations. Part I: Fruit, vegetables and meat products. *Lebensmittel- Wissenschaft und Technologie 18*, 111–117.

Long-Solís, J. (1998). *Capsicum y cultura: la historia del chile* (2nd Ed.). Fondo de Cultura Económica, México, D.F.

Madene, A., Jacquot, M., Scher, J. and Desobry, S. (2006). Flavour encapsulation and controlled release – a review. *International Journal of Food Science and Technology 41*, 1–21.

Martinelli, L., Gabas, A.L., and Telis-Romero, J. (2007). Thermodynamic and quality properties of lemon juice powder as affected by maltodextrin and gum Arabic. *Drying Technology 25*, 1-21.

McLaughlin, C.P. and Magee, T.R.A. (1998). The determination of sorption isotherm and the isosteric heats of sorption for potatoes. *Journal of Food Engineering 35*, 267-280.

McNamee, B. F., O´Riordan, E. D. and O´Sullivan, M. (1998). Emulsification and microencapsulation properties of gum Arabic. *Journal of Agricultural and Food Chemistry 46*, 4551-4555.

Morr, C.V. and Ha, E. (1993). Whey protein concentrates and insolates: processing and functional properties. *Critical Reviews in Food Science Nutrition 33*(6), 431-476.

Moreau, D.L. and Rosenberg, M. (1998). Porosity of whey protein-based microcapsules containing anhydrous milkfat measured by gas displacement pycnometry. *Journal of Food Science 63*, 819-823.

Park, S. J., Shin, Y. S. and Lee, J. R. (2001). Preparation and characterization of microcapsules containing lemon oil. *Journal of Colloid and Interface Science 241*, 502-508.

Pérez-Alonso, C., Beristain, C. I., Lobato-Calleros, C., Rodríguez-Huezo, M. E. and Vernon-Carter, E. J. (2006). Thermodynamic analysis of the sorption isotherms of pure and blended carbohydrate polymers. *Journal of Food Engineering 77*, 753-760.

Pfeifer, P. and Cole, M.W. (1990). Fractals in surface science: scattering and thermodynamics of adsorbed films II. *New Journal Chemistry 14* (33), 221-232.

Pfeifer, P. (1991). Structure analysis of porous solids from presorbed films. *Langmuir 7*, 2833-2835.

Rodríguez-Huezo, M.E., Pedroza-Islas, R., Prado-Barragán, L.A., Beristain, C.I. and Vernon-Carter, E.J. (2004). Microencapsulation by spray drying of multiple emulsions containing carotenoids. *Journal of Food Science 64* (7), E351-E359.

Quevedo, R., López, G. R. Aguilera, J.M. and Cadoche, L. (2002). Description of food surfaces and microestructural changes using fractal image texture analysis. *Journal of Food Engineering 53*, 361-371.

Ré, M.I. (1998). Microencapsulation by spray-drying. *Drying Technology 16*, 1195–1236.

Ré, M.I. (2006). Formulating drug delivery systems by spray drying. *Drying Technology 4*, 433-446.

Rizvi, S. S. H. (1986). Thermodynamic properties of foods in dehydration: Engineering properties of foods, (1st ed.). Marcel Dekker, Inc., USA.

Shahidi, F. and Han, X. (1993). Encapsulation of food ingredients. *Critical Reviews in Food Science Nutrition 33*, 501-547.

Shaikh, J., Bhosale, R. and Singhal, R. (2006). Microencapsulation of black pepper oleoresin. *Food Chemistry 94*, 105-110.

Shu, B., Yu, W., Zhao, Y. and Liu X. (2006). Study on microencapsulation of lycopene by spray-drying. *Journal of Food Engineering 76*, 664–669.

Tang, P., Chew, N.Y., Chan, H.K. and Raper, J.A (2003). Limitation of determination of surface fractal dimension using N_2 adsorption isotherms and modified Frenkel-Halsey-Hill theory. *Langmuir 19*, 2632-2638.

Watanabe, Y., Fang, X., Minemoto, Y., Adachi, S., & Matsuno, R. (2002). Suppressive effect of saturated L-ascorbate on the oxidation of linoleic acid encapsulated with maltodextrin or gum arabic by spray-drying. *Journal of Agricultural and Food Chemistry 50*, 3984-3987.

Weisser, H. (1985). Influence of temperature on sorption equilibria. In: *Properties of water in foods,* (D. Simatos and J.L Multon, eds.), Pp. 95-118. Martinus Nijhoff Publishers. Dordrecht, Netherlands.

Wu, Q. and Suchsland, O. (1996). Prediction of moisture content and moisture gradient of overlaid particleboard. *Wood and Fiber Science 28*(2), 227-239.