Powder Technology 253 (2014) 89–97

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Morphologic and stability cassava starch matrices for encapsulating limonene by spray drying

Mónica Ordoñez [b], Aníbal Herrera [a,*]

[a] Post Harvest Laboratory, Agronomy Department, National University of Colombia, Universidad Nacional de Colombia, Bogota, Colombia
[b] Masters in Food Science and Technology, Science Department, National University of Colombia, Universidad Nacional de Colombia, Bogota, Colombia

ARTICLE INFO

Article history:
Received 19 January 2013
Received in revised form 11 August 2013
Accepted 3 November 2013
Available online 13 November 2013

Keywords:
Cassava starch
Whey protein
Gum Arabic
Spray drying
Limonene

ABSTRACT

The following mixtures of encapsulating matrices were evaluated in this study: gum Arabic (GA), Whey protein concentrate (WPC), cassava starch (Y) and gum Arabic (GA) in proportions of 50:50 and 17:83 and cassava starch (Y) and whey protein concentrate (WPC) in proportions of 50:50 and 17:83. Encapsulation efficiencies above 40% were found using gas chromatography, and a morphological characterization of each matrix was performed using scanning electron microscopy (SEM). Smooth surfaces were found, indicating the effectiveness of the encapsulation process and of the matrices studied, both before and after accelerated aging at 40 °C and 75% relative humidity (RH). X-ray diffraction allowed the evaluation of the phase change of the encapsulating matrices before and after spray drying and during the accelerated-aging test for each of the studied matrices.

1. Introduction

Employed to produce a variety of materials, particle encapsulation is a standard process in the food industry that consists of encapsulating particles in a protective layer, covering, or containment material to protect a sensitive ingredient or nucleus from adverse reactions. This process prevents the loss of volatile ingredients and helps control their release. Encapsulation acts as a storage tool for functional molecules that are sensitive to external conditions (temperature, light, oxygen, and humidity), reducing the transfer of the nucleus to the medium, modifying the physical characteristics of the material to facilitate its manipulation, and prolonging its useful lifetime during storage [1–4].

Starch and its derivatives are widely used in the food industry to contain and protect volatile compounds, acting as containment materials for encapsulating aromas, replacing fats, and stabilizing emulsions. Indeed, these applications have been widely reported [2,5–12].

New starch-based materials known as microporous starches improve flavor retention, contribute to the controlled release of compounds in the head-space of packaging, or facilitate the selective absorption of impurities and bitter compounds [5].

Starch is a semi-crystalline biopolymer comprised mostly of two types of polysaccharides, amylose and amylopectin; 70% of the mass of a starch granule is considered amorphous, and approximately 30% is crystalline. The molecular size of amylose is highly variable and it tends to form helical structures that can include other molecules, such as fatty acids and hydrocarbons. Amylopectin, unlike amylose, has very little tendency for retrogradation and does not age even when the concentration is very high [7,9,10]. The form and surface of granules are considered important functional physical characteristics, particularly when starch is used as a carrier of colorings and on the surface of flavorings and condiments [11].

Another substance used as a containment material is gum Arabic, a highly branched polymer exuded from acacia, which is composed of units of galactose, rhamnose, arabinose, and glucuronic acid. Gum Arabic is one of the most commonly used containment materials in the microencapsulation of oils and flavors, as it has emulsifying properties, a low protein content, and high solubility/low viscosity in aqueous solutions in comparison with other gums, properties that facilitate the drying process [13]. Gum Arabic has been known for many years as an effective containment material due to the stability of its emulsions and its ability to retain volatile compounds. Nonetheless, this polymer shows some disadvantages for generalized use due to its high cost and limited availability [2], a situation that justifies the search for alternatives to this food industry compound [14].

Whey proteins also exhibit effective properties for preparing water-soluble microcapsules for the food industry [15]. When are used for controlled release in food applications, these proteins show good results with regard to emulsification, gelification, and the formation of films, with good encapsulating properties for volatile-compound and non-volatile compound nuclei and excellent protection from oxidation [15–18]. Interactions between proteins and volatile compounds are generated by the bonding ability of whey proteins due to the carbohydrate and lipid content. Beta-lactoglobulin, alpha-lactalbumin, and

* Corresponding author at: Cra 30 Calle 45 Ciudad Universitaria, Agronomy Department, Post Harvest Laboratory, National University of Colombia, Universidad Nacional de Colombia, Bogota, Colombia. Tel.: +57 3165100x19205; fax: +57 19206.
E-mail address: aoherreraa@unal.edu.co (A. Herrera).

0032-5910/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.powtec.2013.11.005

Table 1
Ratio of matrices with gum Arabic (GA), cassava starch (Y), whey protein concentrate (WPC), and limonene (L), as adopted from García et al., relation whey protein cassava starch 17:83* [30].

Encapsulating material	Matrix/limonene ratio	Entry temperature (°C)	Exit temperature (°C)	Drying yield (%)
GAL	100:3	170 °C +/−2	52 °C +/−2	20
WPCL	100:3	170 °C +/−2	83 °C +/−2	55
WPCYL	50:50:3	170 °C +/−2	70 °C +/−2	55
WPCYL	17:83:3*	170 °C +/−2	80 °C +/−2	57
GAYL	50:50:3	170 °C +/−2	70 °C +/−2	35
GAYL	17:83:3*	170 °C +/−2	80 °C +/−2	50

casein present adequate characteristics for protecting foods or active compounds when previously denatured to free disulfur groups and for promoting stable three-dimensional networks [19–21].

The performance of encapsulating matrices and changes in the encapsulant surface under different storage conditions may be evaluated using scanning electron microscopy (SEM) [17,22,23]. The evaluation of microcapsules takes into account the volatile compound content and time-dependent stability in addition to the structural changes of the matrices, all of which may be studied using gas chromatography (GC) [24] and X-ray diffraction [25]. These techniques allow the study of the interaction of matrices with encapsulated material and the study of the effect of storage conditions on the stability of the encapsulating matrix-nucleus system.

The objective of this work was to use X-ray diffraction, scanning electron microscopy, and gas chromatography to characterize the encapsulating matrix for an unstable essential oil, limonene, using individual matrices, gum Arabic, whey protein concentrate and mixtures of gum Arabic–cassava starch, whey protein concentrate–cassava starch.

2. Materials and methods

2.1. Experimental procedure

The encapsulating matrix mixtures were prepared from different concentrations of cassava starch (PROYUCAL, Colombia), whey protein concentrate (Saputo Cheese Inc., USA), and gum Arabic (as a control, CE Roeper GmbH, Germany) and the encapsulated material, limonene (MCI Miritz Citrus, Germany). The gum Arabic–cassava starch mixtures and whey protein concentrate–cassava starch were evaluated in proportions of 50:50 and 17:83 for each mixture.

Spray drying of the encapsulating matrices was performed in triplicate for each of the mixtures. Based on a completely random design, the differences among the means were determined using the Tukey's test ($p < 0.05$) for the encapsulated limonene contents using the SAS® 9.2 statistical software suite (SAS Institute Inc., USA).

2.2. Microcapsule spray drying

The gum Arabic (GA), whey protein concentrate (WPC), and mixtures of gum Arabic (GA)–cassava starch (Y) and whey protein concentrate (WPC)–cassava starch (Y) were prepared at 30% with distilled water. Limonene (L) was added to 3%, relative to the total content of solids [4,26,27]. The emulsions were prepared in a mixer (RHJ-10, Wuxi Machinery Development, China) until completely homogeneous. Drying was performed using a spray dryer (model 190, Büchi, Switzerland), fed by a peristaltic pump under 30% feeding conditions and an atomizing pressure of 4.5 bar. The entering and exit temperatures are shown in Table 1 for each of the matrices studied, their mixtures, and the ratio of encapsulating matrix. Unmixed gum Arabic was used as a control.

The output yield from the drying process was calculated using the following formula:

$$\%Performance = \frac{grams\ of\ dry\ powder\ in\ the\ collector}{grams\ of\ encapsulating\ matrix\ in\ the\ oil\ mixture + grams\ oil} \times 100.$$

2.3. Storage conditions

Samples of each of the dry powders obtained from spray drying were stored at −20 °C in metalized bags (adapting the method of Turchiuli et al. [27] and Imagi et al. [28]). For the accelerated stability study, the samples were stored under controlled temperature and humidity conditions (40 °C and 75% relative humidity [RH]) over an initial period (t_1) and two storage times named time 2 (t_2,11 days) and time 3 (t_3, 22 days). The samples were removed from the stability chamber for characterization at each of the times indicated [3,29].

2.4. Scanning electron microscopy

The morphology of the dry powder was observed using a scanning electron microscope (FEI QUANTA 200, USA) with electron gun tungsten filament, in the low vacuum operating mode (2×10^{-2} torr) with auxiliary nitrogen gas (N_2) and a wide field detector; to study morphology detector ETD (Everhart-Thorney detector), secondary electrons and to study composition SSD detector backscattered electron. The dry powders were mounted and fixed using two-sized carbon tape (9,17,22,23, 29) without metallic covering.

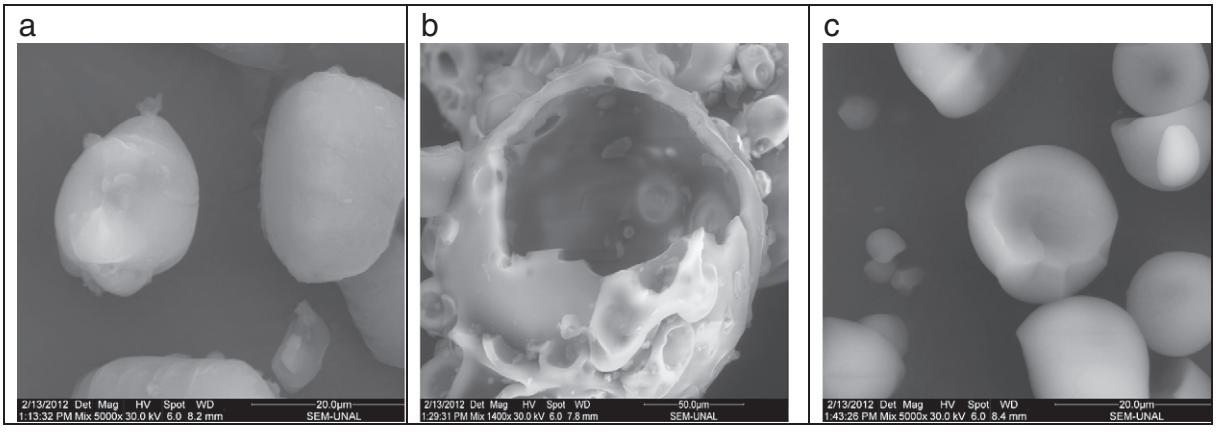

Fig. 1. Encapsulating matrices without mixing, before the spray-drying process. a. Gum Arabic. b. Whey protein concentrate. c. Cassava starch.