OIL THERMO-OXIDATIVE STABILITY AND SURFACE OIL DETERMINATION OF BIOPOLYMER MICROCAPSULES

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Abstract

Cod liver oil was encapsulated with gum arabic, mesquite gum and maltodextrin or their blends by spray drying. Microcapsules at pH 4 showed lower surface oil content, achieving the highest oil retention with 100% gum arabic. The thermo-oxidative stability of the oil contained in the microcapsules with different wall materials was evaluated by dynamic differential scanning calorimetry. The values of the activation energy varied from 70.27 to 295.99 kJ mol^{-1}. In general terms the microcapsules made at pH 4 had better thermo-oxidative stability, with the exception of the microcapsules made with 100 % mesquite gum and 100% maltodextrin at pH 8, which exhibited activation energies of 295.99 and 228.80 kJ mol^{-1}, respectively.

Keywords: cod liver oil, surface oil, thermal oxidation, biopolymers, microencapsulation.

Resumen

Se microencapsuló por secado por aspersión, aceite de hígado de bacalao, teniendo como agentes encapsulantes la goma arábiga, goma de mezquite, maltodextrina, solos y en mezclas. Se determinó el aceite superficial de los microencapsulados y los menores porcentajes correspondieron a los tratamientos a pH 4, siendo las microcápsulas de goma arábiga las que mejor retuvieron el aceite. La estabilidad térmica oxidativa del aceite contenidos en las microcápsulas de los diferentes tipos de pared, fue evaluada por calorimetría diferencial de barrido en régimen dinámico. Los valores aproximados de la energía de activación variaron de 70.27 a 295.99 kJ mol^{-1}. En general las microcápsulas elaboradas a pH 4 resultaron en una mejor estabilidad oxidativa, a excepción de las microcápsulas elaboradas con goma de mezquite y maltodextrina al 100% a pH 8, que tuvieron respectivamente energías de activación 295.99 y de 228.80 kJ mol^{-1}.

Palabras clave: aceite de hígado de bacalao, aceite superficial, oxidación térmica, biopolímeros, microencapsulación.

1. Introduction

Microencapsulated artificial diets for use in shrimp larvae cultures must not only comply with specific nutrition requirements but must also possess certain specific desirable characteristics such as shape, particle size, lixiviation rates, etc. so that the ingredients contained in the diet are stable, maintain their nutritive value and are available to the organisms consuming them.

Polyunsaturated fatty acids are essential ingredients of shrimp larvae diets, and are highly susceptible to oxidation due to several environmental factors. Thus the selection of the microcapsules wall material is of the utmost importance, as it constitutes the main critical point for providing stability and cost efficiency to the system, and must be compatible with the microencapsulating technique followed.

Pedroza-Islas *et al.* (1999, 2000) encapsulated, by the spray-drying technique, shrimp larvae artificial diets using maltodextrin DE 10, mesquite gum and gum arabic as wall materials on their own and in blends. Wall composition affected significantly particle size, morphology,

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microstructure, dissolution and floatability kinetics of the microcapsules. A methodology was proposed by which the best potential microcapsules, from a physical point of view, could be selected by determining those that exhibited the longer characteristic dissolution and floatability time constants, without having to realize cumbersome and time-consuming bioassays with all the experimental diets.

The objective of this work was to encapsulate a lipid phase consisting of a cod liver oil-sunflower oil-lecithin blend with the biopolymer wall material treatments reported by Pedroza-Islas *et al.* (1999, 2000), and to evaluate their encapsulation efficiency and the thermo-oxidative stability provided to the system.

2. Materials and methods

2.1. Materials

The wall materials used were: gum arabic (*Acacia senegal*) (GA) "Spray-gum" from Colloids Naturels (Marseilles, France), mesquite gum (*Prosopis juliflora*) (MG) collected from the Mexican State of San Luis Potosi, Mexico; and maltodextrin DE 10 (MD) (Arancia, S.A. de C.V., Mexico) (Pedroza-Islas *et al.*, 1999).

Cod liver oil (Drogueria Cosmopolita, S.A. de C.V., Mexico) and a commercial blend of sunflower and canola oil (trademark 123, Industrial Jabonera La Corona, S.A. de C.V., Estado de Mexico, Mexico) and soybean lecithin (Alcolec 495, American Lecithin Co., Danbury, CT) composed the oil phase to be encapsulated.

Monosodium phosphate acid, sodium acetate, acetic acid and sodium chloride (Sigma de Mexico, S.A. de C.V., Toluca, Mexico) were employed as buffer solutions (Pedroza-Islas *et al*., 1999). All the water used in these experiments was double distilled.

2.2. Experimental design

The three biopolymers GA, MD and MG were mixed following a Simplex Centroid experimental design (Hare, 1974), as shown in Table 1.

2.3. Microcapsules formation

A lipid phase consisting of cod liver oil-sunflower oil-soybean lecithin blend in a 0.4:0.4:0.2 ratio was incorporated into the ten biopolymers aqueous solutions (Table 1) at pH 4.0 (E-pH4) and pH 8.0 (E-pH8), and at wall material-feedstuff 3:1.

Table 1. Experimental design for using biopolymer blends as microcapsule wall material.

Treatment	Biopolymer		
Code Number	Gum Arabic	Mesquite Gum	Maltodextrin
GA100	100	0	0
MG100	0	100	0
MD100	0	0	100
GA50-MG50	50	50	0
GA50-MD50	50	0	50
MG50-MD50	0	50	50
GA33-MG33-MD33	33.33	33.33	33.33
GA66-MG17-MD17	66	17	17
GA17-MG66-MD17	17	66	17
GA17-MG17-MD66	17	17	66

In each and every case the total solids content of the dispersions was 25% (w/w) before spray drying. The aqueous dispersions were dried in a Mobile Minor Niro-Atomiser (Copenhagen, Denmark) spray dryer, equipped with a rotary centrifugal atomiser. The dispersions were fed to the spray dryer at a rate of 20 mL/min, a 2 bar air pressure, and an inlet temperature of 170±5 °C (Pedroza-Islas *et al*., 1999).

2.4. Surface oil

Surface oil (SO) in the spray-dried powder was determined gravimetrically (Beristain and Vernon-Carter, 1995). Five grams of microcapsules were placed an extraction thimble, covered with glass wool and extracted with hexane for 4 h. Solvent was evaporated with a nitrogen stream and a water bath at 30 °C, and the microcapsules brought to complete dryness in a vacuum oven at 60 °C until a constant weight was achieved. The surface oil was determined by weighing the residue.

2.5. Dynamic thermo-oxidative behavior of microcapsules

The thermal oxidative stability of the encapsulated lipid phase was determined using a non-isothermal differential scanning calorimetry (DSC) technique (Litwinienko *et al*., 1995), employing a TA Instruments mod. 3510 Differential Scanning Calorimeter (New Castle, DE). The measurements were performed in triplicate on 1 to 2 g samples using a dynamic temperature scan with heating rates of 2.5, 5, 7.5 and 10 °C min^{-1}, from 150 to 400 °C, and airflow of 25 mL min^{-1}. The sample pans were open to the atmosphere to allow sample contact with the airflow.

The maximum temperature value of the oxidation exotherm at the four heating rates studied was obtained and the parameters of the Arrhenius equation were computed (ASTM, 1984):

$$k = Z\, e^{-E/RT} \tag{1}$$

where k is the rate constant, Z the pre-exponential factor, E the activation energy, R the gas constant and T the absolute temperature. The sample temperature is increased at linear heating rate (β). The recorded values of maximum heat flow temperatures (T_{MP}) for different values β can be described as:

$$\log \beta = a T_{MP}^{-1} + b \tag{2}$$

where a and b are coefficients.

The approximate values for activation energy and the Arrhenius pre-exponential factor are calculated as follows (Litwinienko *et al*., 1995):

$$E' = -2.19R \frac{d \log \beta}{d T_{MP}^{-1}} \tag{3}$$

$$Z = \frac{\beta E e^{\frac{E}{RT}}}{R T_{MP}^{2}} \tag{4}$$

where β and T_{MP} are taken from the middle of the range.

2.6. Statistical analyses

Results were subjected to one-way analysis of variance (ANOVA). Duncan's multiple range test was applied to determine significance of differences between means.

3. Results and discussion

3.1. Surface oil

The superficial oil content for the different microcapsules treatments is shown in Table 2. An statistical analysis indicates that there is a significative difference in the surface oil content due to the second order

interactions between pH and biopolymer concentration, pH and biopolymer blend, and by biopolymer blend and concentration ($p<0.05$). Duncan's multiple range test indicated that the GA100 microcapsules were different from MD100, GA50-MD50, GM50-MD50, GA33-GM33-MD33, GA17-GM66-MD17 and GA17-GM17-MD66 microcapsules.

Table 2. Superficial oil content of microcapsules.

TREATMENT	SURFACE OIL (%)	
	E-pH4	E-pH8
GA100	0.189	0.384
MG100	0.400	0.575
MD100	0.879	0.646
GA50-MG50	0.221	0.502
GA50-MD50	0.489	0.885
MG50-MD50	0.581	0.820
GA33-MG33-MD33	0.409	0.602
GA66-MG17-MD17	0.326	0.761
GA17-MG66-MD17	0.426	0.760
GA17-MG17-MD66	0.519	0.780

The ability of the biopolymers blends to encapsulate the cod liver oil depends among other factors, of having an adequate biopolymer concentration. The type of wall material also plays an important role. In this case, treatments GA100 and GA50-GM50 resulted best. The efficiency of gum arabic as encapsulating agent has been investigated by other authors, mainly with essential oils (Westing *et al*., 1989; Trubiano and Lacourse, 1989; Reineccius *et al*., 1995), and has been reported as having a lower encapsulating ability than modified starches. On the other hand, it has been reported that it is an excellent encapsulating agent of high molecular weight fatty acids (Imagi *et al*., 1990), which is in agreement with the results found in this work, as it resulted the best agent for encapsulating high molecular weight and polyunsaturated fatty acids (PUFA).

Imagi *et al*. (1990) reported that as the molecular weight of the wall material is higher, lower is the superficial oil content of the microcapsules. In this work this was found to be also true as, in general terms, the microcapsules made with pure maltodextrin (MW~ 80,000) (MD100) or in which maltodextrin was in high proportion in the biopolymer blend, larger was the superficial oil content of the microcapsules, whereas microcapsules made with pure gum arabic (MW>1,000,000) (Islam *et al*., 1997) or mesquite gum (MW>2,000,000) (Vernon-Carter *et al*., 2000) or blends in which both gums predominate showed lower surface oil content.

3.2. Thermo-oxidative stability

Fig. 1 shows a representative heat flow-temperature plot for different β values of the cod liver oil encapsulated with GA100. The thermograms obtained for the other pure biopolymers and biopolymer blends (not shown here) showed a similar behavior. Table 3 shows the values of the parameters obtained from the DSC curves for the cod liver oil microencapsulated with the biopolymer blends at pH 4, whereas Table 4 shows those obtained at pH 8. In general terms the treatments at pH 4 exhibited more consistent Ea values ranging from 112.98 to167.35 $kJ.mol^{-1}$, with treatment GA-MD and GA-MG having the highest Ea values. However, some microcapsules at pH 8, in particular MG100 and MD 100, yielded Ea values of 295.99 and 228.80 $kJ.mol^{-1}$, respectively.

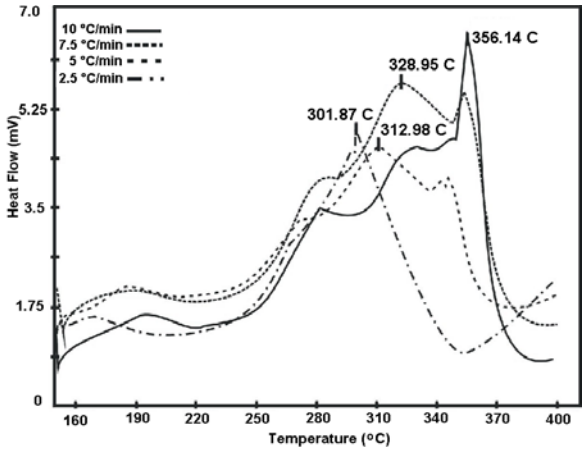

Fig. 1. DSC curve of cod liver oil observed in dynamic method for different β.

Thus, the wall materials that yielded higher Ea values are those providing the cod liver oil with a greater resistance against thermo-oxidative degradation. In this work all the microcapsule wall materials used yielded exotherm peak temperatures above 200 °C. It has been reported that the maximum peak temperature reached with hydrophilic wall materials such as egg albumen, caseinates, gelatin and carboximethylcellulose was 185.14 °C measured by DSC, and that the maximum stability provided to PUFA was 6 weeks (Taguchi *et al*., 1992; Lin *et al*., 1995). Our results suggest that the use of biopolymer blends used in this study can provide an extended shelf-life to PUFA, as our peak temperatures, and thus Ea´s, were higher than those reported in the literature, and also pinpoint to an increased possibility of their use in high temperature processes, in which the encapsulated materials retain their functional properties.

Conclusions

The use of biopolymers on their own or in blends have an effect on microcapsule functional properties. Surface oil of microcapsules was lower when wall materials were used at pH 4, but the best protection against thermo oxidation was provided by when biopolymers were employed at pH 8. Thus, a compromise must be arrived to in which one must decide in having low surface oil but poor oxidative stability, or good oxidative stability but high surface oil. In general terms, the best treatments compromising between these two extremes were: GA100 at pH 4, GA50-MG50 at pH 4, GA17-MG66-MD17 at pH 4, and MG100 at pH 8.

Acknowledgements

The authors thank the Consejo Nacional de Ciencia y Tecnología (CONACyT) for partially financing this project through grants G-33565-B and 38193-B.

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Table 3. Data obtained from DSC curves for ASTM method of microcapsules at pH 4.

Treatment	β (°C.min^{-1})	T_{MP} (K)	Ea (kJ.mol^{-1})	Z (min^{-1})	k (min^{-1})
GA100	2.5	574.87	125.99	$3.67\text{x}10^{10}$	$3.13\text{x}10^{-12}$
	5.0	586.09			
	7.5	595.82			
	10	604.64			
MG100	2.5	576.15	112.98	1.799	$2.89\text{x}10^{-11}$
	5.0	591.71			
	7.5	599.75			
	10	608.54			
MD100	2.5	577.69	117.08	$5.72\text{x}10^{9}$	$1.77\text{x}10^{-11}$
	5.0	585.14			
	7.5	594.09			
	10	608.15			
GA50-MG50	2.5	585.83	160.52	$4.73\text{x}10^{13}$	$3.61\text{x}10^{-15}$
	5.0	588.81			
	7.5	598.83			
	10	607.00			
GA50-MD50	2.5	578.00	167.35	$2.66\text{x}10^{14}$	$1.29\text{x}10^{-15}$
	5.0	584.07			
	7.5	591.75			
	10	601.12			
MG50-MD50	2.5	575.35	121.86	$1.33\text{x}10^{10}$	$5.98\text{x}10^{-12}$
	5.0	588.99			
	7.5	599.76			
	10	605.33			
GA33-MG33-MD33	2.5	577.69	122.81	$1.71\text{x}10^{10}$	$5.23\text{x}10^{-12}$
	5.0	587.95			
	7.5	597.30			
	10	610.50			
GA66-MG17-MD17	2.5	575.25	127.94	$5.08\text{x}10^{10}$	$1.97\text{x}10^{-12}$
	5.0	587.92			
	7.5	596.25			
	10	604.97			
GA17-MG66-MD17	2.5	579.69	153.01	$9.5\text{x}10^{12}$	$1.5\text{x}10^{-14}$
	5.0	589.19			
	7.5	597.23			
	10	604.25			
GA17-MG17-MD66	2.5	577.69	129.89	$7.26\text{x}10^{10}$	$1.28\text{x}10^{-12}$
	5.0	589.13			
	7.5	598.55			
	10	606.75			

Table 4 . Data obtained from DSC curves for ASTM method of microcapsules at pH 8.

Treatment	β (°C.min^{-1})	T_{MP} (K)	Ea (KJ.mol^{-1})	Z (min^{-1})	k (min^{-1})
GA100	2.5	568.76	70.27	1.74×10^{5}	8.5×10^{-8}
	5.0	591.45			
	7.5	610.37			
	10	618.95			
MG100	2.5	587.01	295.99	1.07×10^{26}	1.52×10^{-26}
	5.0	590.64			
	7.5	596.84			
	10	612.77			
MD100	2.5	584.70	228.80	7.50×10^{19}	6.26×10^{-21}
	5.0	590.15			
	7.5	593.93			
	10	602.15			
GA50-MG50	2.5	571.88	120.63	1.17×10^{10}	8.67×10^{-12}
	5.0	585.67			
	7.5	595.07			
	10	602.58			
GA50-MD50	2.5	573.43	95.53	5.83×10^{7}	1.00×10^{-9}
	5.0	587.22			
	7.5	595.07			
	10	612.84			
MG50-MD50	2.5	575.35	134.98	2.60×10^{11}	5.89×10^{-13}
	5.0	585.16			
	7.5	597.30			
	10	601.12			
GA33-MG33-MD33	2.5	573.10	98.78	1.06×10^{8}	5.28×10^{-10}
	5.0	586.62			
	7.5	592.10			
	10	610.50			
GA66-MG17-MD17	2.5	570.67	71.74	3.23×10^{5}	6.00×10^{-8}
	5.0	584.41			
	7.5	596.43			
	10	619.95			
GA17-MG66-MD17	2.5	573.26	126.68	4.17×10^{10}	2.68×10^{-12}
	5.0	586.46			
	7.5	596.28			
	10	602.29			
GA17-MG17-MD66	2.5	572.20	128.37	6.70×10^{10}	2.18×10^{-12}
	5.0	584.11			
	7.5	594.13			
	10	601.00			