LWT - Food Science and Technology 64 (2015) 381–389

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Encapsulation of roasted coffee oil in biocompatible nanoparticles

Eliza Brito Freiberger [a], Karine Cristine Kaufmann [b], Evandro Bona [a], Pedro Henrique Hermes de Araújo [c], Claudia Sayer [c], Fernanda Vitória Leimann [a], Odinei Hess Gonçalves [a, *]

[a] Federal University of Technology – Paraná (UTFPR), Post-Graduation Program of Food Technology (PPGTA), Caixa Postal 271, Via Rosalina dos Santos, CEP 87301-899 Campo Mourão, PR, Brazil
[b] Federal University of Technology – Parana (UTFPR), Food Department (DALIM), Caixa Postal 271, Via Rosalina dos Santos, CEP 87301-899, Brazil
[c] Federal University of Santa Catarina (UFSC), Department of Chemical and Food Engineering (EQA), Caixa Postal 476, Campus Reitor João David Ferreira Lima, CEP 88040-970, Brazil

ARTICLE INFO

Article history:
Received 2 December 2014
Received in revised form
19 May 2015
Accepted 26 May 2015
Available online 5 June 2015

Keywords:
Biodegradable nanocapsules
Flavor encapsulation
Full factorial design
Sequential simplex optimization
Miniemulsification-solvent evaporation

ABSTRACT

Nanoencapsulation is a promising approach to protect the volatile compounds in natural lipid mixtures like roasted coffee oil. In this work, Nanocapsules were obtained by the miniemulsification-solvent evaporation technique using poly(L-lactic acid) (PLLA) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) as encapsulant polymers. The aromatic profile of both *in natura* and encapsulated oil was determined by Gas Head-Space Solid Phase Membrane Extraction/Chromatography coupled to Mass Spectroscopy. The total amount of effectively encapsulated oil was evaluated using a combination of full factorial experimental design and the simplex optimization algorithm and the following independent factors were evaluated: encapsulant polymer, dispersion mechanism, polymer:oil mass ratio and surfactant. The total oil content (oil recovery) was significantly influenced ($p < 0.05$) by two-way and three-way interactions confirming that a complex dependence between the factors took place. If PLLA was the encapsulant polymer, then sonication yielded the highest oil recovery. For PHBV as encapsulant, high shear homogenization (Ultraturrax) led to the highest oil recovery. In both cases, polymer:oil ratio and surfactant must be adjusted accordingly. FTIR spectra and HS-SPME/GCMS suggested that the major aroma constituents of coffee oil were successfully encapsulated demonstrating that miniemulsification-solvent evaporation was appropriate to encapsulate roasted coffee oil.

1. Introduction

The oily fraction of roasted coffee is composed mainly by free and esterified fatty acids, diterpenes, sterols and volatiles compounds (Clarke & Vitzthum, 2001; Farah & Donangelo, 2006; Fisk, Kettle, Hofmeister, Virdie, & Kenny, 2012; Franca, Mendonça, & Oliveira, 2005; Sunarharum, Williams, & Smyth, 2014; Toci & Farah, 2014). Functional properties of coffee and its by-products were extensively revised (Lin, Toto, & Were, 2015; Summa, de la Calle, Brohee, Stadler, & Anklam, 2007) as roasted coffee oil is extensively used by the food industry. In addition, there has been some effort to use coffee oil to improve the sensorial properties of instant coffee preparations since aroma is the major factor in purchase decision (Bhumiratana, Adhikari, & Chambers, 2011). Aroma of instant coffee differs from ground and roasted coffee due to the aggressive conditions used during the extraction and drying stages (Paquin, 2009). The actual amount of the volatile compounds presented in coffee oil must be precisely know because coffee aroma is a complex result of the interaction between a number of molecules. Gas Head-Space Solid Phase Membrane Extraction/Chromatography–Mass Spectroscopy (HS-SPME/GC–MS) is considered the most suitable method to quantify the most important volatile compounds in coffee (Viegas & Bassoli, 2007).

Some approaches were designed to improve the aroma of instant coffee such as adding steam distilled coffee volatiles right after packaging (Clinton, Plains, & Pitchon, 1962); extracting the oil from roasted coffee and adding the oil back in a later stage (Klein, Raben, & Herrera, 1968); and cryogenically collecting coffee aroma and adding such condensate to an instant coffee product or a precursor thereof (Clinton, Kraut, & Pitchon, 1966; Lemonnier, 1954; Patel, 1974). Although they have achieved a relative success, in all cases the volatile compounds were not effectively

* Corresponding author. Tel.: +55 44 91451328.
E-mail address: odinei@utfpr.edu.br (O.H. Gonçalves).

http://dx.doi.org/10.1016/j.lwt.2015.05.039
0023-6438/

protected against evaporation. Therefore, roasted coffee oil encapsulation could be a promising alternative to stabilize the flavoring compounds or even to promote their controlled release (Weiss, Takhistov, & McClements, 2006).

The microencapsulation of green or roasted coffee oil was carried out by spray dryer atomization (Carvalho, Silva, & Hubinger, 2014; Chmiel, Liu, Furrer, & Rushmore, 2000; Frascareli, Silva, Tonon, & Hubinger, 2012; Liu, Nickerson, & Anderson, 1986; Silva, Vieira, & Hubinger, 2014; Yu et al., 2012) and extrusion (Garwood, Mandralis, & Westfall, 1999; Panesar, 2004). However, both processes need high temperatures (90–190 °C) decreasing the volatile content of the final microcapsules. Coacervation/crosslinking technique (Gaonkar, Nicholson, & Tufts, 1998) was also proposed to roasted coffee oil microencapsulation but the crosslink agent used glutaraldehyde, which is considered toxic. It is expected that flavor nanoencapsulation provides better results than microsized capsules, because nanocapsules can promote a faster release from the encapsulated material and present higher degradability, due to its high surface area (Leimann, Cardozo, Sayer, & Araújo, 2013; Sanguansri & Augustin, 2006).

The different techniques available to the nanoencapsulation of aromas and other food ingredients were described in the literature (Madene, Jacquot, Scher, & Desobry, 2006; Nedovic, Kalusevic, Manojlovic, Levic, & Bugarski, 2011; Tramón, 2014) and, in the case of encapsulated food ingredients, all substances must be biocompatible. Biopolymers like poly(L-lactic acid) (PLLA) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) are of interest because they can be easily shaped as nanoparticles (Weiss et al., 2006). Also, PLA resins are approved by the US Food and Drug Administration (FDA) and European regulatory authorities for all food applications, some surgical applications and as drug releasing systems (Lasprilla, Martinez, Lunelli, Jardini, & Filho, 2012). A promising approach of encapsulation is the miniemulsification-solvent evaporation (Leimann, Cardozo, et al., 2013; Loxley & Vincent, 1998; Staff et al., 2013; Urban, Musyanovych, & Landfester, 2009; Zhao, Fickert, Landfester, & Crespy, 2012) since it generally allows an efficient entrapment and the solvent can be readily removed from the final nanoparticles powder. Final particles size was found to be defined by the initial droplets distribution (Musyanovych, Schmitz-Wienke, Mailänder, Walther, & Landfester, 2008; Zhao et al., 2012). Many operational parameters affect the nanoparticle properties such as homogenizer operating conditions, surfactant type and concentration, encapsulant material and particles composition (Asua, 2002; Boschetto et al., 2013; Fernandes, Marques, Borges, & Botrel, 2014; Staff et al., 2013; Zhao, Meng, Liu, & Li, 2014). The interaction between these variables must be well known in order to correctly design the most suitable encapsulation procedure.

It is often important to know what combination of polymer/dispersion system favors the encapsulation process. The correct choice of conditions could be difficult to make if complex interactions between the experimental parameters took place and in this case an optimization algorithm could be used. The sequential simplex algorithm is a widely used evolutionary direct search method for solving constrained optimization problems. A simplex is a geometric figure in n dimensions that is the convex hull of $(n + 1)$ vertices and the algorithm iteratively generates a sequence of simplexes to approximate an optimal point (Bona, Borsato, Sérgio dos Santos Ferreira, & Paula Herrera, 2000; Gao & Han, 2010).

In this work roasted coffee oil was nanoencapsulated by the miniemulsification-solvent evaporation technique. The volatile compounds profile in the nanocapsules were determined by HS-SPME/GC–MS and compared to *in natura* roasted coffee oil. Full factorial experimental design and sequential simplex optimization were applied to investigate the oil recovery.

2. Material and methods

2.1. Material

Lactide (Purac) and tin octanoate (Sigma–Aldrich, 99%) were used in the poly(L-lactic acid) synthesis. Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV, 8.2 HV mol, Mw 255,660 g mol^{-1}) was kindly supplied by PHB Industrial S.A. Sodium borohydride ($NaBH_4$), dichloromethane, chloroform, hexane, and methanol (Nuclear, P.A.), lecithin (Alfa Aesar) and Tween80 (Oxiteno) were used in the PHBV molecular weight reduction and in the nanoparticles preparation. Roasted coffee oil was kindly supplied by CIA Iguacú de Café Solúvel.

2.2. Polymer preparation and characterization

2.2.1. PHBV purification and molecular weight reduction

To purify PHBV, a PHBV-chloroform solution (5 g/100 g) was prepared by heating the solution under magnetic stirring. The solution was filtered under vacuum and precipitated in hexane. Finally, the precipitated PHBV was dried at 60 °C in a circulation oven until no mass variation could be detected.

PHBV molecular weight was reduced using the $NaBH_4$ route (Baran, Özer, & Hasirci, 2002). PHBV (15 g) was dissolved in chloroform (400 mL) and $NaBH_4$ (130 mg) was dissolved in methanol (44 mL). Then the solutions were mixed and continuously stirred for 6 h at room temperature. After that, the solution was precipitated in cold methanol, filtered under vacuum and dried at 60 °C in a circulation oven until no mass variation could be detected.

2.2.2. PLLA synthesis and purification

Poly(L-lactic acid) (PLLA) was synthesized from L-lactide (Purac) by ring opening polymerization (Bendix, 1998) using tin octanoate (Sigma–Aldrich, 99%) as catalyst. L-Lactide and catalyst (10,000 $mol_{L\text{-}lactide}$ mol_{cat}^{-1}) were added to a stainless steel reactor, and gaseous nitrogen was used to remove oxygen from the reaction medium. Vacuum was applied (−53,000 Pa) and the reactor was maintained in an oil bath at 120 °C during 24 h. Non-reacted L-lactide was removed by dissolution of the resulting material in chloroform and precipitation in cold methanol. The obtained polymer was stored under vacuum at −10 °C.

2.2.3. Molecular weight averages (M_w and M_n) of PLLA and PHBV

Gel permeation chromatography (GPC) was used to determine the number average molecular weight and polydispersion index (Mn and PDI) of PHBV and PLLA using polystyrene standards. In the case of PHBV, the apparatus was described elsewhere (Urban et al., 2009). In the case of PLLA, the following apparatus was used: GPC (LC-20A, Shimadzu) with a refraction index detector RID-10A, automatic injector SIL-20A, oven CTO-20A and three columns (0.8 × 30 cm, GPC-801, GPC-804 and GPC-807). The samples were dissolved in tetrahydrofuran (THF, Sigma–Aldrich) at 7.5 mg mL^{-1}, filtered through a 0.45 μm Nylon filter and then analyzed at 35 °C.

2.3. Nanocapsules preparation

Nanocapsules were prepared by the miniemulsion/solvent evaporation technique (Leimann, Biz, et al., 2013; Staff et al., 2013). Experimental conditions as well as materials used were selected based on previous works (Leimann, Biz, et al., 2013; Leimann, Cardozo, et al., 2013; Valério, Araújo, & Sayer, 2013). The organic phase was composed by polymer, coffee oil, lecithin and dichloromethane and the water phase was composed by distilled water and Tween80. In all formulations, the organic phase concentration was kept constant at 0.35 $g_{organic\ phase}/g_{total}$. The amount of capsules