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Study of simple microparticles formation of limonene in modified starch using PGSS – Particles from gas-saturated suspensions

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ABSTRACT

Supercritical CO_2 was studied for impregnation or encapsulation of essential oils in modified starches via Particle from Gas Saturated Solutions or Suspensions (PGSS). Modified starches were choose as function of its low cost. The advantage of this method over conventional encapsulation that use modified starch via spray drier refers to the low temperatures used and absence of water in the process. Modified starch presents hydrophobic elements and this molecules present amphiphilic character. Usually it is employed in the encapsulation of essences as wall material with excellent volatiles retention due to its polar and nonpolar interface. Considering its hydrophobic characteristics, interactions between the modified starch and supercritical CO_2 occurred, resulting in two different structural interactions of the limonene and modified starch in the PGSS (50 °C and 60 °C at 100 bar and 120 bar). When hydrous ethanol was used in the suspension, impregnation occurred and, when anhydrous ethanol was used, encapsulation occurred. Analysis of particle morphology via scanning electron and confocal microscopy, thermo-oxidative characterization by differential scanning calorimetry and determination of microencapsulated limonene via gas chromatography coupled to mass spectrometry indicated limonene microencapsulation and impregnation occurred despite the highly solubility of limonene in supercritical CO_2. The retention of limonene by Purity Gum Ultra® was 86% when encapsulated and, 53% when impregnated, similar values to those obtained in conventional microencapsulation methods via a spray drier or via PGSS-drying.

1. Introduction

Microencapsulation technology permits the protection of components such as pigments, flavours, acidulants and microorganisms. It is defined as a trapping of solid, liquid or gaseous materials, sealed in capsules that release their contents in controlled amounts under specific conditions [1]. Principal methodologies used in microcapsule formation are spray drying, spray cooling, spray chilling, microencapsulation by extrusion, fluidized bed drying and coacervation. Microencapsulation using supercritical fluid has also recently been studied, showing promising results. Supercritical fluids have been used to encapsulate heat-sensitive materials in processes similar to spray drying. The greatest advantage of this process could be the absence of water; therefore, the component to be encapsulated need not be dispersed in an aqueous solution, so low temperatures can be employed in the process. Thus, it is a suitable process for encapsulation of sensitive materials such as enzymes, aromas and volatile compounds [2].

Two processes have been used specifically for particle formation or encapsulation, RESS (Rapid Expansion of Supercritical Solutions) and PGSS (Particles from Gas-Saturated Solutions or Suspensions). In RESS CO_2 is pumped through a reaction vessel with a solution containing the encapsulating agent and the compound to be encapsulated. Expansion of this solution is triggered by a nozzle, which enables the substrate to precipitate in a vessel at low pressure (precipitation unit) causing an extremely rapid nucleation in the form of small particles or fibres and films when the spray is directed onto a surface. The morphology of the capsules formed depends on the material structure and the process parameters (temperature – T, pressure – P, distance and angle of the atomizer with respect to the surface contact, size of the precipitation unit, etc.) [3]. In PGSS (Particles from Gas-Saturated Solutions or Suspensions) a supercritical fluid is dissolved into a solution or dispersion of the substrate in a liquid solvent or liquefied mixture, followed by rapid depressurization through a nozzle which causes the formation of solid or liquid particles in accordance with the constituent used [3,4].

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Depending on the mixture (solution, dispersion) and substrate, fine solid particles or liquid droplets are formed in PGSS [5]. In this process the encapsulant or core material is not necessarily soluble in a supercritical fluid. However, the supercritical fluid should be soluble in the liquid phase, which makes the process suitable for polymers, which generally absorb a large amount of CO_2. The PGSS process can also be used for suspensions of active substrates in an encapsulating agent for the formation of microparticles containing compounds such as drugs, for example [6].

PGSS has been studied for micronizing food products as soy lecithin, mono and diglycerides, citric acid, chocolate and cocoa butter, for example [7]. And, some research groups have studied the formulation of essential oil in biopolymer via PGSS as menthol as mentioned by Weidner [7], linalool and lavandin essential oil in modified starch [8].

Modified starches are used in food technology as thickeners, stabilizers, emulsifiers, gelling agents, and microencapsulating agents (wall materials), among other functions. As an encapsulating agent, it protects the volatile components from high temperatures. When a mixture is dissolved for final preparation of the product, the aromas entrapped in the microcapsules are released [9,10].

In this research, limonene dispersions in modified starch were studied in contact with supercritical CO_2 using the PGSS process for different conditions of P and T. Two modified starches, HI-CAP 100 and Purity Gum Ultra®, were used as wall material.

HI-CAP is a chemically modified starch obtained from waxy maize. It is suitable for flavour, pigment, medicine and spice encapsulation. It has excellent resistance to oxidation. HI CAP-100 is recommended as a substitute for other encapsulating agents in food formulations such as Arabic gum and gelatin. HI-CAP 100 has been used to encapsulate cardamom oleoresin encapsulation [11,12], cumin oleoresin [13] and essential oil from peppermint [14].

Purity Gum Ultra® is an innovative modified starch developed by Ingredion™, which has an emulsifying power higher than that of conventional starches. It presents special properties and has been most commonly used for the production of beverages, offering four times the emulsifying power in comparison with traditional emulsifiers, drastically reducing processing costs. This modified starch was tested in this research since its efficient emulsifying properties could have a more pronounced hydrophobic behaviour than other modified starches.

2. Materials and methods

2.1. Materials

Wall capsule materials were modified starches (HI-CAP 100 and Purity Gum Ultra®) from Ingredion™ BR. Soy lecithin (Acros Organics, New Jersey, USA) was used as surfactant. Tixosil 38A® supplied by Solvay Rhodia Group BR was used as an anti-caking agent. The encapsulated material used was (R) – (+) – limonene 97% (Sigma–Aldrich, EUA).

Both HI-CAP 100 and Purity Gum Ultra® are chemically modified starches produced by esterification reactions between hydroxyl groups of these molecules with octenyl succinate anhydride (OSA) [14]. Due to this modification, the hydrophobicity of the octenyl succinate is introduced while the starch's hydrophilicity is maintained. In other words, the normally hydrophilic starch gains octenyl groups as hydrophobic elements, resulting in an amphiphilic character for the starch molecules. Due to these alterations the modified starches can be used as encapsulants with excellent volatile retention. Ingredion™, formerly Corn Products, is a corporation that retains most of the patents to obtain OSA starches made mainly from waxy maize [15]. The difference between HI-CAP 100 and Purity Gum Ultra® is the degree of hydrophobicity, which is greater for Purity Gum Ultra®.

Silica Tixosil 38A® (Rhodia Solvay Group) is a new generation of innovative silica consisting of spherical cluster shaped microbeads. This product opened new opportunities for the dietary supplements market since it is used to promote high flow in premix steps, avoiding dust formation or agglomeration. Tixosil 38A® is compatible with all therapeutic agents and active ingredients and can be used both in colours and as a transparent gel. Applications include agrochemical formulation, biocides, dietary supplements, polymer processing, food processing, spray drying and toothpaste production. Specifically in this study, Tixosil 38A® was used to prevent particle agglomeration in the PGSS depressurization system.

2.2. Dispersion preparation

The dispersion composition was prepared based on Bertolini (1999) [16], whose result was used as a comparison parameter (conventional vs. PGSS). This dispersion was composed of solids with 10 g of modified starch HI-CAP 100 or Purity Gum Ultra®, 0.003 g of Tixosil 38A®, 1 g of limonene and 0.5 g of soy lecithin, and 25 g of EtOH anhydrous EtOH (99.9%) and hydrous (92.8%, 85% and 80%) as solvent. The prepared dispersion was agitated at 5000 rpm (Ultra Turrax®, IKA-T25, Hamburg, GE) for 3 min before being placed on the reactor in contact with 100 g of supercritical CO_2.

2.3. Encapsulation

Encapsulation via PGSS consists of three basic steps. First, the dispersion is prepared, followed by contact with supercritical CO_2 in an autoclave; depressurization and expansion of the mixture then occurs in the particle formation chamber.

In this process, conditions of P and T in the reaction chamber were studied in order to provide physical and chemical changes in the mixture to maximize uniform and stable particle formation. A SFC/RESS (Thar Instruments Co./Waters, Pittsburgh, USA) (Fig. 1) was used in this work. Pure modified starch and its dispersions with supercritical CO_2 were tested under four different conditions (50 °C, 100 and 120 bar, 60 °C, 100 and 120 bar) at 1250 rpm during 45 min in the autoclave following by depressurization (1 min). These conditions of P and T, the process and depressurization times were defined based on the work of other authors [4,8,16–18].

The equipment employed has spray nozzles in the depressurization chamber with internal sapphire rings with diameters of 2, 4 and 6 μm. These different diameters can be varied according to the desired particle size. In this study, we used the sapphire ring with a diameter of 6 μm.

2.4. Physical particle analysis

The particles of HI-CAP 100 and Purity Gum Ultra® were analyzed before and after they were submitted to the PGSS process, aiming to identify morphological changes. After the encapsulation process using modified starches as wall material and limonene as the core, the microparticles were also analyzed in order to determine whether the limonene had been impregnated or encapsulated in the modified starch.

Optical microscopy assisted in checking the dispersion morphology in the preparation of the mixture of ethanol with the wall material, the limonene, and surfactant. For this step an optical microscope (Bel View 6.2.3.0, Milan, IT) with a digital camera (1.3 mega pixels) coupled was used. Samples of the dispersions were fixed on slides employing silicone oil as dispersant.

The particles were also analyzed by scanning electron microscopy (SEM) (Hitachi TM 3000, JP) to observe the particle