Application of electrostatic extrusion – flavour encapsulation and controlled release

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Introduction

Food manufacturers usually concern how to preserve aromatic additives, since aroma compounds are not only delicate and volatile, but also very expensive. Encapsulation provides an effective method of protection of flavour compounds from evaporation, degradation, and migration from a food (Madene et al., 2006). Namely, creating of a suitable microenvironment around flavours can reduce the volatility and/or mobility of the flavour constituents and provide a better retention during baking.

Flavour encapsulation can be accomplished by a variety of methods. The two major industrial processes are spray-drying and extrusion (Madene et al., 2006). A novel promising technique for control production of uniform beads is extrusion based on the use of electrostatic forces to disrupt a liquid filament at the capillary/needle tip and form a charged stream of small droplets (Bugarski et al., 2005). The size of produced polymer spheres is a complex function of several operating parameters, the system properties and the properties of the polymer solution which is being extruded (Bugarski et al., 2005). In previous experiments, excessive investigations were conducted to determine the specific influence of each parameter on beads diameter and encapsulation efficiency (Bugarski et al., 1994; Bugarski et al, 2004), which helped us to optimize conditions for obtaining uniform particles of desirable size. Producing particles of optimal size is important for achieving optimal release kinetics, since the flavour loss from alginate beads is mass transfer controlled, and consequently, size dependent.

In this paper we applied electrostatic extrusion technique to immobilize an aromatic compound in calcium alginate gel beads. Ethyl vanilline (3-Ethoxy-4-hydroxybenzaldehyde) was used as an aroma agent (in further text vanilline). Vanilline is important food additive as flavour enhancer. This compound is widely used to contribute to the fragrance to commercial foods such as candies, cookies, chocolate and beverages. Although it enhances the scent and consume of food, vanilline must be carefully added. Large amounts of the flavour cause headaches, nausea and vomiting (Ni et al., 2005). In order to determine the smallest amount of the aroma which will give an optimal result, encapsulated aroma behavior under heating conditions that mimic usual food processing was investigated by TGA-DSC measurements.

Material and methods

Investigated polymer was low viscosity sodium alginate Protanal LF 20/40 was purchased from FMC Biopolymer. Ethyl vanilline was supplied from Borregaard Synthesis (Sarpsborg, Norway) as

food grade quality (purity >99,9%) and was used without further purification. Calcium chloride dihydrate and potassium sulphate were purchased from SIGMA.

^{1}H NMR spectroscopy

The mole ratio of mannuronate (M) to guluronate (G) residues (M/G) and the mole fraction of GG, MM and GM diad sequences F_{GG}, F_{MM} and F_{GM} were determined by ^{1}H NMR according to Grasdalen (Grasdalen et al, 1979). The alginate sample was partly degraded by vary mild hydrolisis with acid in order to diminish the viscosity of solution. Hydrolized alginate sample was dissolved in D_2O at neutral pD. ^{1}H NMR spectra were run at 400 MHz on a Bruker AC 250 E NMR spectrometer.

Thermal analysis

Thermal behaviour of the particles has been investigated using TA Instruments model SDT Q-600 simultaneous DSC-TGA. The samples (mass app. 20 mg) were heated in a standard alumina sample pan. All experiments were carried out under air with a flow rate of 0.1 dm^3/min. A 10 °C/min run was used.

Preparation of samples

Polymer-vanilline dispersion was prepared by dissolving Na-alginate powder (2 % w/w) in distilled water containing ethyl vanilline (10 % w/w). Spherical droplets were formed by extrusion of the polymer-vanilline dispersion through a blunt stainless still needle using a syringe pump (Razel, Scientific Instruments, Stamford, CT) and a 10 ml plastic syringe. Electrode geometry with the positively charged needle and a grounded hardening solution was applied. Hardening solution was $CaCl_2$ at a concentration of 1.5%. The potential difference was controlled by a high voltage dc unit (Model 30R, Bertan Associates, Inc., New York) and was kept constant at 4.5 kV. Distance between the needle tip (22 gauge) and the hardening solution was 2.5 cm, while the flow rate of polymer solution was 25.2 ml/h. A sample of 30 microbeads was taken from each experiment and diameters of microbeads were measured with an accuracy of 10 μm using a microscope (Carlzeiss Jena). The average microbead diameter and standard deviations were then calculated from the measured data.
Prior to DSC measurements, alginate particles containing vanilline were first filtered under low vacuum and than stored under 97 % relative humidity of saturated potassium sulphate for two hours. It was established that after two hours under conditions of high humidity, loss in weight of alginate microbeads due to drying process, becomes negligible. It was found that this step improves reproducibility of DSC measurements.

Results and discussion

Chemical characterization results of alginate obtained by H-NMR spectroscopy revealed that alginate used in this study had high content (67 %) of guluronic residues and was rich in GG diad blocks (F_{GG} = 55%). Mole fractions of MM and GM diad sequences F_{MM} and F_{GM} were 21 and 12 %, respectively. The H-NMR spectra showed no significant peaks originating from proteins or other impurities. The chemical composition of investigated polymer revealed that it belongs to the group of alginates with very high guluronic content which classify it among high-quality immobilisation matrixes due to desirable immobilisation properties, such as presence of open pore structures and mechanical strengthens. Gels made of alginates with a high G-block content are stronger, more stable and better retain incorporating compounds as compared to low G-block content alginate gels.

The microbeads incorporating vanilline and produced by electrostatic droplet generator applying voltage of 4,5 kV were 450±20 μm in diameter, appeared as regular spheres and very uniform in size. Compared with empty alginate microbeads produced under same conditions, they are slightly larger. It was previously established that incorporating material (cells or other active compounds) can cause increase in particles size (Manojlovic et al, 2006) due to strong impact of ethyl vanilline molecules on two-phase fluid dynamics in the capillary and mechanism of droplet formation, which needs extensive additional examination to be fully understood.

Thermal analysis

Figure 1 shows the TG and DTG curves of the vanilline encapsulated beads in the 20-400 °C range. It can be seen that there are two well resolved weight losses. The first weight loss occurs in the 50-150 °C range with the maximum at approx. 112 °C on the DTG curve. According to prior measurements of vanilline-free beads, this loss can be attributed to the dehydration of the polymer network. This event is also accompanied by an endotherm in the DSC curve (Figure 2). The TG curve exhibits a plateau up to 220 °C indicating that ethyl vanilline stays entrapped inside the polymer matrix. The second weight loss occurs in the 220-325 °C range and it corresponds to the vanilline release. There are three DTG maxima in this temperature range and the main one is centered at 247 °C. The facts that the release of vanilline occurs over a relatively wide range of temperatures and that it proceeds in several steps strongly support the conclusion that ethyl vanilline is mostly encapsulated inside the polymer matrix (not only physically adsorbed at the surface of the bead) and that the encapsulation enables a slow release of this flavor agent. As an example, a cooking process is usually finished by 230 °C at which temperature most of vanilline stays *intacta*.

The analysis showed that all vanilla has been completely released from the capsules during the heating process which can be undesirable effect when high retention during processing is required. This is a result of several factors influencing release of aroma compound from alginate gel beads: small size of capsules (450 microns), high moisture content (88%), and absence of oil solvent that eventually increases the viscosity of surrounding media and increases mass transfer resistance. Retention of flavourings encapsulated in alginate beads increases with an increase of the particle size due a lower particle surface area and the longer distance from the center of the beads to the surface (Bouwmeesters and De Roos, 1998). It has been determined that retention is increasing with a decrease of the moisture content of the beads. The higher the moisture content in the beads, the higher is the amount of steam developed. The steam works as a carrier that transfers flavour compounds to the surrounding air, thus disturbing the phase equlibria and increasing the driving force for mass transport (Bouwmeesters and De Roos, 1998).

Conclusions

Electrostatic extrusion appeared to be convenient technique for immobilisation of vanilla into alginate particles. Apparently, DSC-TGA is a suitable method for investigation of vanilla release from alginate beads and preliminary studies showed that decomposition process under elevating temperatures consists of two consecutive distinctive steps: polymer dehydration and vanilla evaporation. Vanilla release began at temperature about 150ºC and was most rapid at 247ºC. In order to determine conditions for desirable aroma release, further extensive examinations are required, from the aspect of optimizing alginate concentration, vanilla content, microbeads size, heating conditions and other parameters.

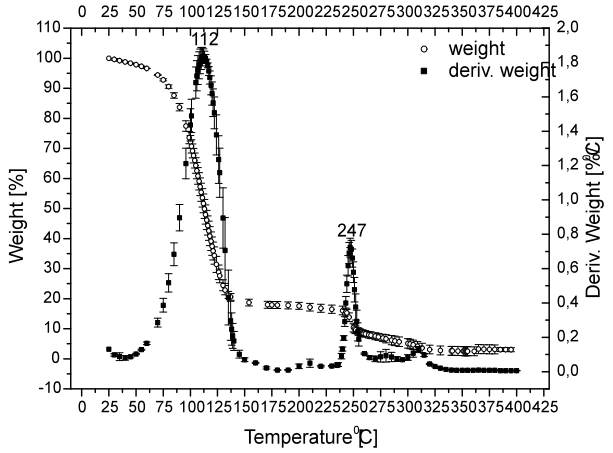

Figure 1. TGA and DTA curves of 2% alginate beads entrapping 10% ethyl vanilline (data present average of n = 4).

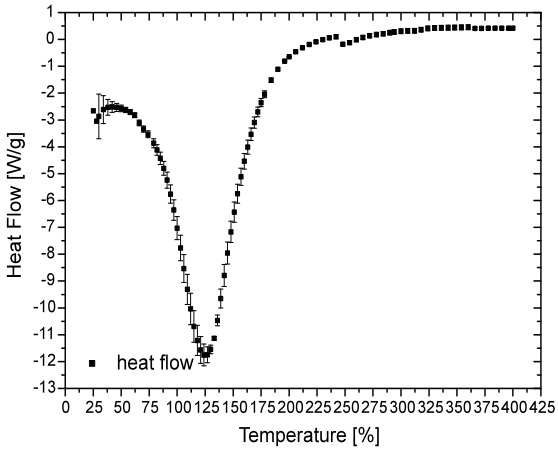

Figure 2. DSC curve of 2% alginate beads entrapping 10% ethyl vanilline (data present average of n = 4).

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