Encapsulation of Gallic acid in solid lipid core surrounded with maltodextrin shell

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Abstract. Multiple phase capsules had been prepared in a single spray drying process. The main goal of the present study was to investigate whether the conversion of a portion of the modified starch (wall material used in spray drying) to resistant starch (RS) would offer added protection of encapsulated material. To achieve this, dry gallic acid (GA; a model water soluble phenol compound used in the present study) was initially dispersed in palm oil and stabilized with Polyglycerol Polyricinoleate (PGPR 4175) as an emulsifier. This dispersion was homogenized with a modified starch (MS, dextrose equivalent of 15) solution, that was previously treated with high pressure and increased temperature to achieve starch retrogradation, and then spray dried. It was possible to produce only small amounts of RS from modified starch, varying from 0.1 to 0.2% of total carbohydrate content. GA content in the lipid phase of the capsule was determined by lipid droplet size in the O/W emulsion (the feeding solution), as smaller droplets results in the significantly bigger surface area, and more intensive GA diffusion from O to W phase. Maltodextrin shell wall was able to prevent leaking of the melted palm oil form the capsule core to the surface during seating tests, preventing agglomeration of capsules. This could be very important for the storage/transportation of capsules in the uncontrolled temperature conditions.

Key words: gallic acid, spray drying, encapsulation, resistant starch.

INTRODUCTION

Protection of sensitive bioactive compounds is an important aspect of modern food industry in order to provide high nutritional value added food products. Alternatively, there are many compounds that cannot be incorporated into food systems in their regular form due to specific taste, biochemical activity, and physical properties. In this situation, encapsulation steps in as a possible solution. It is a process of entrapping a specific component ('active compound' or core material) within a protective matrix ('encapsulant', wall or matrix material) (Garti & McClements, 2012).

Present work is focused on encapsulation of a water soluble phenol compound - gallic acid (GA). Phenolics are an extremely heterogeneous class of secondary plant metabolites. They protect plant against biotic (caused by herbivores, insects, and pathogens) and abiotic (caused by free radical) stresses (Schieber & Saldana, 2009). In human diet, phenolics are the most common antioxidants (Friedman, 1997; Lima et al.,

2014). Their preservation and application in food production can offer added nutritional value for human nutrition, and provide antioxidative protection for the food product itself.

In food industry, an efficient encapsulation system for protection of biologically active compound must be formulated using only food grade compounds, which were manufactured with solvent-free production methods (McClements et al., 2007; Acosta, 2009). This system should have minimum interaction with the encapsulated compound, provide high physicochemical stability (McClements et al., 2007; Donsi et al., 2011), and shield active compound from interaction with another food ingredients and environment factors such as temperature, pH, oxygen, and light (McClements et al., 2007). Additionally, this system should maximize the uptake of encapsulated compounds upon consumption (Acosta, 2009; Dordevic et al., 2015) and ensure controlled release in response to a specific stimulus in the environment (McClements et al., 2007). From technical point of view, it should be scalable to industrial production (Desai & Park, 2005; Donsi et al., 2010a; Donsi et al., 2010b).

There are many different encapsulation techniques, and spray drying is a most often used in food industry. It is cost-effective, flexible (drying parameters are easily controllable), and can be operated continuously (Desai & Park, 2005; Fang & Bhandari, 2010; Anandharamakrishnan & Padma Ishwarya, 2015). In short, core and wall materials are homogenised, fed into a spray dryer, and atomized with a nozzle or spinning wheel. Water is evaporated by the hot air stream that contacts the atomized material. During the drying process, droplets shrink and form round capsules, which are than collected (Gibbs et al., 1999). Most common wall materials for spray drying encapsulation are gum arabic, maltodextrin and modified starch (MS) (Munin & Edwards-Levy, 2011). For encapsulation of phenolic compounds, maltodextrins are frequently chosen as wall material. They can wary in dextrose equivalents (DE, a measurement of the amount of reducing sugars in the product), depending on the final product application (Ersus & Yurdagel, 2007; Krishnaiah et al., 2012; Kaderides et al., 2015; Pasrija et al., 2015; Saikia et al., 2015). Most phenolics possess bad sensory properties and maltodextrins had been successfully applied in spray drying processes to stabilize phenolics and mask their unpleasant bitter taste (Sansone et al., 2011). In addition, maltodextrin is able to provide good thermal protection, and was able to preserve the integrity of the anthocyanins during their encapsulation (Ersus & Yurdagel, 2007; Robert et al., 2010). Unfortunately, maltodextrin doesn't possess good enough emulsifying properties for lipophilic material encapsulation. As a result, it should be modified by adjusting a hydrophobic part to its molecule, forming a material called modified starches (MS). MS is a good choice for hydrophilic material encapsulation in the hydrophilic matric, and it will be used in present study for oil-in-water emulsion formation.

Despite good overall encapsulation properties, capsules and shells made from maltodextrin and MS are not stable against enzymatic digestion. It was shown that stability to enzymatic digestion of coatings (prepared form high amylose corn starch) can be improved by addition of resistant starch (RS) (Dimantov et al., 2004b). RS is a physiologically important indigestible starch fraction in human diet. It is usually present in relatively low amounts in food products. RS is enzyme resistant and is not digestible in the small intestine, but can be fermented by microorganisms in the large intestine (Eerlingen et al., 1993). Incorporation of 20% RS in the wall material, made of high amylose corn starch, is suitable for achieving targeted release of encapsulated active

compound in the colon (Dimantov et al., 2004a). Increased concentrations of RS considerably improve the stability of the coatings to enzymatic digestion, although resulting in the crack on the capsule surface (Dimantov et al., 2004b).

Alternatively, to ensure capsule stability in the hydrophilic media and against non-lipid digestible enzymes, active compounds can be encapsulated in the solid hydrogenated lipids (Mukherjee, 2009; Eltayeb et al., 2013; Wolfe et al., 2015). Resulted capsule particles possess a great water barrier, but their thermal stability is highly dependent on the melting point of the chosen lipid phase. For additional protection, hydrophilic (modified starch) and hydrophobic (solid lipids) systems can be combined to produce multiple layered capsules. In this case, solid lipid core usually is surrounded by MS shell by using fluidized bed technology (Arshadey, 1999). In this process, solid particles are moved in the air in fluidized bed reactor and simultaneously sprayed with a liquid coating material, which is solidifying due to the temperature and humidity control system. It is a two-step process consistent of preparation of solid core and coating it with shell material.

In present study, multiple phase capsules (consistent of solid lipid core and modified starch shell) will be prepared in a single spray drying process for water soluble phenolic compound encapsulation. The aim of the present study is to investigate whether the conversion of a portion of the modified starch (wall material, used in spray drying) to resistant starch (RS) would offer added protection of encapsulated material (water soluble phenolics).

MATERIALS AND METHODS

Chemicals and Reagents
Modified starch 'Capsul®' was provided by Ingredion, Inc. (Westchester, USA); Calcium Chloride dihydrate, Gallic acid, Glacial Acetic acid, Potassium Hydroxide, Sodium Azide, Sodium Carbonate, Maleic acid, and Sodium Hydroxide were purchased from Sigma-Aldrich (St. Louis, USA); Ethanol (200 proof, anhydrous 99.5%) was purchased from Pharmco-Aaper (Brookfield ,USA); Folin-Ciocalteu phenol reagent purchased from VWR International (Radnor, USA); Palm Oil kernels were purchased form Bulk Apothecary (Aurora, USA); Polyglycerol Polyricinoleate (PGPR 4175) was provided by Palsgaard, Inc. (Morris Plains, USA).

Preparation of the wall material
To produce resistant starch (RS), Eerlingen et al. (1993) method was used. MS was dispersed in distilled water in ratio 1:2, and autoclaved at 120 °C for 1 h. in AMSCO, American Sterilizer (Erie, USA). When temperature and pressure dropped to the safe limit, samples were immediately transferred to baths at 22 ± 2, 68 ± 2 and 100 ± 2 °C for 24 h. Control sample, without autoclave treatment, was incubated under magnetic stirring at 80 °C for 30 min to ensure full MS gelatinization. Prepared solutions were used for further oil-in-water (O/W) emulsion preparation, forming W phase (shell wall material).

Resistant starch content determination

RS content was determined by using Megazyme RS analyse kit K-RSTAR 10/15, AOAC method 2002.02, AACC method 32-40.01 (Mccleary et al., 2002; AACC 32-40.01).

Sample preparation

Capsule core had been made as a suspension of GA in the melted lipids, forming a O phase for the further O/W emulsion preparation. To achieve this, palm oil kernels were melted (with melting point at ≈50 °C) at 50 °C and GA was added in proportion 4:1, and 0.1% of PGPR (w/w) was added as stabiliser. PGPR is broadly used in chocolate production water-in-oil emulsifier, and had been chosen for the present research as it is food grade (E 476), not carcinogenic, 98% digestible in rats, and is utilized in the body as a source of energy superior to starch (Wilsona et al., 1998). Mixture was homogenized by magnetic stirring at 600 rpm for 5 min. Obtained dispersion was added to the prepared wall material solution at a proportion 1:2, and homogenized by high shear mixer for 30 sec, obtaining O/W emulsion. Mixture was immediately fed to Buchi Mini Spray Dryer B-290 (New Castle, USA). Drying parameters were set as followed: inlet and outlet temperatures − 170 and 75 °C, respectively; sample feed rate − 15 mL min^{-1}; spray gas flow − 667 L h^{-1}. Feed solution had been kept on the hot plate at 60 °C under constant intensive stirring to prevent oil solidification. Collected samples were stored in double plastic bags at -20 °C. Whole experiment was repeated three times.

Gallic acid extraction from different capsule parts

All samples were divided in three parts. First part was used to determine total GA content (TGA): 0.5 g of sample was mixed with 5 ml of 70% ethanol and magnetically stirred for 30 min at 50 °C, and filtered through a paper filter Nr.3. Second part was used for the surface GA content determination (SGA): 0.5 g of sample material was washed with 5 mL ethanol and filtered through the paper filter. Third part was used for GA content determination in the wall material: 0.5 g of sample was mixed with 5 mL of 70% ethanol and magnetically stirred for 30 min at room temperature to dilute wall material, and filtered through the paper filter.

All filtrates were collected and used for the GA content determination in different parts of produced capsules.

GA content determination

For the GA content determination in the filtrates, Ragazzi & Veronese (1973) Folic-Ciocalteu method with slight modifications. Briefly, 200 µL of the sample were mixed with 1 mL of distilled water and 100 µL of Folin-Ciocalteu phenol reagent (preciously diluted with distilled water 1:1, v/v). After 5 min, 2 mL of the 10% sodium carbonate solution was added. Acquired mixture was allowed to stand at room temperature for 60 min. The absorbance was measured at 725 nm by laboratory spectrophotometer UV-1800 (Shimadzu, Japan).

Encapsulation efficiency

Encapsulation efficiency (EE) was calculated by the following equation:

$$EE = 100 \times \left(1 - \frac{SGA}{TGA}\right) \qquad (1)$$

Heat stability and optical microscopy

Heat stability was analysed visually. 0.5 g of each sample were placed in the oven on the filter paper for 30 min at 100 °C. Sample optical microscopy was prepared by using BX40 (Olympus, United States) microscope.

Particle size distribution

Particle size distribution was analysed using laser diffraction particle size analyser LA 960 (HORIBA, Japan).

Moisture content determination

Moisture content was determined using HTF 2000 Moisture analyser (DSC, United States). Data was used for GA content recalculations on dry weight.

Statistical analysis

One-way ANOVA ($P \leq 0.05$) and Tukey's test were applied for the statistical analysis of the distribution of GA in the different capsule fractions.

RESULTS AND DISCUSSION

In present study, three phase encapsulation system (solid lipid core, containing water soluble phenolic compound, surrounded with modified starch shell wall) had been developed in a single spray drying process.

Based on the fact that RS fractions can be obtained by hydrothermal treatment and retrogradation of starches (Herman & Remon, 1989; Sievert & Pomeranz, 1989; Eerlingen et al., 1993), wall material previously was autoclaved at 121 °C in excess water with further incubation at 22 °C, 68 °C, and 100 °C (Eerlingen et al., 1993). Unfortunately, it was possible to produce only small amounts of RS in the chosen MS material: 0.12% in samples incubated at 22 °C and 68 °C, and 0.19% in samples incubated at 100 °C, against 0.10% for control sample. Achieved concentrations are not enough to ensure enzymatic resistance of the shell, as RS is not a chemically reactive substance in present conditions and will not influence physical or chemical properties of the capsule shell at present concentrations. It can be seen that increase in the incubation temperature directly influence RS formation, and incubation at 100 °C results almost in double amounts of RS in comparison to incubation at 22 and 68 °C. This fact matches previously reported data by Eerlingen et al. (1993). No correlation had been detected between RS concentration in the wall material and GA content in the lipid core of produced capsules (Fig. 1). It was expected that (at the sufficient concentrations) higher increase in RS content could influence GA diffusion from the lipid core into the coating material, or from the coating to the surface (as both GA and MS are water soluble, GA is evenly distributed inside the coating matrix, and GA content on the surface is dependent on the volume-to-surface ratios of the coating itself). At the same time, too high RS concentrations can cause cracking in the MS coating due to reduced intermolecular interactions, caused by the nature of RS (Dimantov et al., 2004b). This cracking results in lower integrity of the shell and could be a reason for further additional GA losses, due to the more intensive water evaporation during the spray drying process. Alternatively, high RS content could result in bigger amount of free water in the W phase

of the O/W solution that could increase GA diffusion from the lipid core phase or capsule surface into the wall material phase.
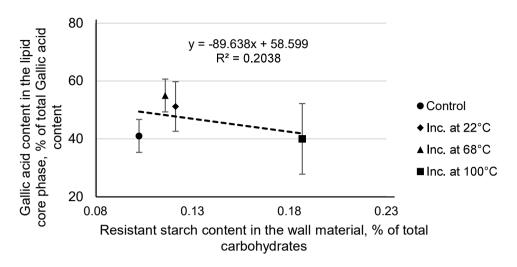

Figure 1. Gallic acid content in the produced capsules depending on the resistant starch concentration. Where, Inc. – incubation.

In the produced capsules, GA was approximately evenly distributed between core and shell fractions, with little remains on the capsule surface (Fig. 2). It is a result of GA diffusion during O/W emulsion preparation, when O phase was mixed with W right before mixture feeding into the spray dryer. It is possible that increase in PGPR concentration or addition of another emulsifier could cause better system stabilization and decrease diffusion and increase GA content in the lipid phase. In this case, bigger portion of lipid phase would be concentrated on the O/W phase surface, blocking GA migration by stronger hydrophilic polarity.
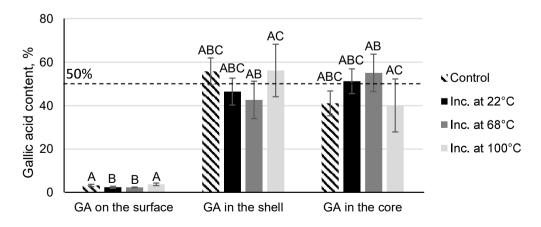

Figure 2. Distribution of gallic acid in different capsule fractions. The data is presented as a mean ($n = 9$); similar uppercase letters indicate no significant difference among samples of the same fraction ($P \leq 0.05$). Where, GA – gallic acid; Inc. – incubation.

Holser (2013) showed that ferulic acid, another phenolic compound with antioxidative properties, encapsulated in lipid matrix capsules was stable during 3 months storage at ambient conditions. In another study, lipid nanoparticles placed in water were able to stabilize (-)-epigallocatechin-3-gallate during 4 weeks period while (-)-epigallocatechin-3-gallate solubilized in water exhibited 100% degradation within 4 hours period (Barras et al., 2009). Solid lipid fraction, used in present study, had a melting point approximately of ≈50 °C. This allows to conclude that GA in produced capsules is well protected from environmental factors. It is not only encapsulated in the hydrophobic core, but also surrounded by additional MS shell that should protect melted lipids from leakage and capsule agglomeration, in case of capsule storage at temperature that exceeds 50 °C.

Fig. 2 shows that big part of total encapsulated GA had been diffused into the water phase during sample preparation period and was fixed in the MS matrix. In present study used commercial MS is known for its great encapsulation properties and ability to mask undesirable odours and flavours of encapsulated substance, including phenolics (Spinelli et al., 2016). This means that GA in the shell can be considered as shielded, till capsule will come in contact with aqueous phase that will dilute shell wall material or cause GA diffusion from MS phase into the surrounding aqueous phase.

Based on discussed factors, it can be assumed that produced capsules could be added to different types of food products (ground meat or fish, or dough) in order to release phenolics from the shell wall to the surrounding media. Released phenolics could serve as antioxidants for the food product itself. If there will be no temperature rises combined with intensive mixing that would break integrity of lipid core (as in sausage production), lipid phase phenolics will remain fixed in the lipid phase and protected till will come into the human digestive system. Wada & Fang (1992) had shown that phenolics are able to inhibit polyunsaturated fatty acid oxidation in frozen-crushed bonito meat. In whole and ground meat products, phenolics were effective in retarding rancid odour and flavour, and colour changes (Shah et al., 2014). Better retention of colour and protection of lipids against peroxidation due to the addition of phenols had been observed also in irradiated meats (Kanatt et al., 2005). Similar results were acquired for minced horse mackerel (Sabeena Farvin et al., 2012). In case of human nutrition, phenolics are known to have multiple positive effects on the health by alleviating oxidative stress (Singh & Rajini, 2004; Singh & Rajini, 2008).

Only small percentage of total GA had been exposed on the capsule surface: 2.4 ± 0.5% for samples incubated at 22 °C, 2.3 ± 0.2% for samples incubated at 68 °C, 3.8 ± 0.6% for samples incubated at 100 °C, against 3.3 ± 0.5% for control sample. This amounts can be considered as permanent loses, bringing the total encapsulation efficiency to 97.1 ± 0.4%. In present study, particles with mean size form 23.1 ± 0.5 to 30.7 ± 2.1 µm were produced (Table 1), resulting in fine white powder that should not be visible and sensible in case of adding it to the ground meat/fish products or dough.

Table 1. Particle size and distribution of microcapsules incubated at different temperatures

Parameter	Control	22 °C	68 °C	100 °C
Median, µm	18.7 ± 1.4	21.4 ± 0.8	22.3 ± 1.0	20.2 ± 1.6
Mean, µm	23.1 ± 0.5	27.7 ± 1.9	30.7 ± 2.1	26.5 ± 3.3
Variance, µm^2	306.9 ± 168.8	615.51 ± 184.6	947.9 ± 105.6	597.5 ± 250.9
Mode, µm	18.6 ± 2.5	21.2 ± 0.0	21.3 ± 0.1	19.5 ± 1.6

Fig. 2 shows GA distributions between different capsule fractions (core, wall, and surface). Statistical analysis showed that GA amounts in the lipid core phases are dependent on the particle mean size (Fig. 3, Table 1). This can be explained by the fact that in present experiment produced particle size is dependent on the lipid droplet size in the O/W emulsion. Bigger lipid droplet can accommodate more GA than small ones. With increase of lipid core size, core-to-shell ration also increases. As a result, the smaller is the shell in proportion to the core, the less GA in proportion to the core GA it can contain.
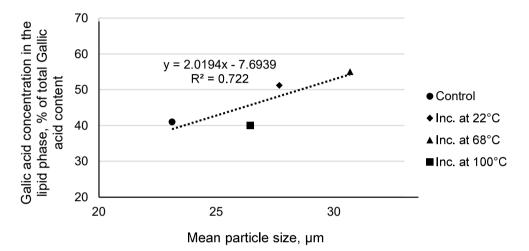

Figure 3. Gallic acid content in the lipid phase of produced capsules depending on the mean particle size ($n = 9$). Where, Inc. – incubation.

Capsules had been heated at 100 °C for 30 min to test integrity of the shell, and visually no melted lipid leakage or capsule agglomeration had been detected. In combination with previously discussed aspects, it can be concluded that produced capsules can be considered as stable and can be stored at ambient conditions. As an example, in case of uncontrolled temperature increase, capsule shell will maintain its integrity and particles will not stick together lowering powdered product quality, as it can happen during capsule transportation in the summer time without specialized cooling equipment. As starch is not a reactive material, capsules does not require specific storage conditions and package material, except protection from the excess moisture to prevent dilution of the shell and GA diffusion/dissolution. This minimises storage expenses and overall potential produced capsule price.

CONCLUSIONS

In present study, three phase encapsulation system (solid lipid core, containing water soluble phenolic compound, surrounded with modified starch shell wall) had been developed in a single spray drying process for GA encapsulation. Produced RS amounts in the maltodextrin were too small to impact encapsulation process. Present capsule structure can be considered as stable for the long term storage at ambient conditions. Real storage study should be conducted to determine optimal storage conditions and time

limits. Due to diffusion processes during capsule formation, GA was evenly distributed between core and shell wall materials. Depending on the capsule application, this fact can be considered as negative (if GA content in the shell wall is considered as loses) or as positive (assuming that shell wall GA can be released in the surrounding media in order to provide antioxidative and antiradical protection for the mentioned media). Produced capsules have a great potential for application in food production, as GA can be replaced with any another water or oil soluble biologically active compound to produce stable encapsulation system for protection of the active compound and masking its possible undesirable sensory properties. In case of hydrophilic compound encapsulation, it is assumed that chosen compound will be evenly distributed between capsule phases and, after adding capsules to the moisture rich food system, will partially participate in the antioxidative protection of the chosen food system. Remaining active compound could remain protected till it will reach digestive system. Present work makes a basis for future studies on natural plant phenolic compound encapsulation and application in food industry.

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