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Effect of microencapsulation on the reactivity of ascorbic acid, sodium chloride and vanillin during heating

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ABSTRACT

Food composition undergoes significant changes due to chemical reactions occurring during heating. This study aimed to restrict the reactions of ascorbic acid, vanillin and sodium chloride by means of microencapsulation. Carnauba wax, maltodextrin, Arabic gum and β-cyclodextrin were used as coating materials in different core/coating ratios. Model systems composed of ascorbic acid–ferric chloride, sodium chloride–glucose, and vanillin–asparagine prepared using free and encapsulated compounds were heated under certain conditions to determine the effects of encapsulation on the formations of furan, hydroxymethylfurfural and acrylamide, respectively. According to the results, Arabic gum and maltodextrin coatings of ascorbic acid significantly decreased furan formation up to 57% at 120 °C ($p < 0.05$) while carnauba wax coating of sodium chloride decreased hydroxymethylfurfural formation up to 18% at 200 °C. Despite vanillin could be coated successfully with β-cyclodextrin, encapsulation increased acrylamide formation from asparagine during heating at 150 °C.

1. Introduction

Food additives such as flavors, antioxidants, minerals are mostly sensitive to heat, oxygen and light. They are highly reactive and can interact with other food components easily. The most common technology to stabilize and restrict the reactivity of sensitive compounds is encapsulation. Microencapsulation is a process, which encloses the active molecule within a layer of coating/wall and therefore, it provides a physical barrier between the core compound and the other components of the product. By this time, microencapsulation has been used for different purposes in food industry such as, improving handling properties of core material, to control release of the core material, to reduce the core reactivity with environmental factors, and also to mask the core taste (Shahidi and Han, 1993; Gharsallaoui et al., 2007).

Ascorbic acid is an important ingredient/additive and used for its vitamin and antioxidant properties in food industry (Comunian et al., 2014). Owing to its sensitivity to oxidation, ascorbic acid can be easily degraded during processing. It was found to be responsible for the formation of furan, a cooking carcinogen, in foods during heating (Fan, 2005; Mogol and Gökmen, 2013; Comunian et al., 2014). Furan is classified as a possible human carcinogen by the International Agency for Research on Cancer (IARC, 1995). Vanillin is widely used in food industry as a flavoring agent. However, it was reported that vanillin plays critical role in the conversion of asparagine to acrylamide during heating at elevated temperatures (Hamzalıoğlu and Gokmen, 2012). Acrylamide is an undesirable product of the Maillard reaction, formed by asparagine and reducing sugars during heating (Stadler et al., 2002). Acrylamide possesses genotoxic, neurotoxic and carcinogenic properties and is known as a probable human carcinogen (IARC, 1994). Sodium chloride is added to foods as a flavor enhancer, preservative, texture and color developer. On the other hand, it significantly accelerates the decomposition of mono- and disaccharides leading to the formation of hydroxymethylfurfural (HMF) in foods during thermal processing (Gökmen and Şenyuva, 2007). HMF is formed from direct dehydration of sugars or via the Maillard reaction during heating (Kroh, 1994). HMF has cytotoxic effects at high concentrations and can be regarded as one of the most important heat-induced contaminants occurring thermally processed foods (Capuano and Fogliano, 2011).

This study aimed to restrict the reactivity of ascorbic acid, vanillin and sodium chloride by microencapsulation using freeze–drying technique. There are lots of wall materials used in microencapsulation. Among these materials, carnauba wax (CW), maltodextrin DE 19 (MD), Arabic gum (AG) and β-cyclodextrin (β-Cd) were used as wall materials. Arabic gum is one of the most common wall materials due to its low viscosity, good emulsifying and film forming properties (Gupta et al., 2015). Maltodextrins

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exhibit low viscosity at high solid content and has good solubility. Maltodextrins are considered as good encapsulating materials because they offer protection against oxidation. Cyclodextrins have a hydrophobic cavity in their molecule structure and make very specific interaction with apolar guest molecules and form inclusion complexes. Carnuba wax used in food formulations as a formulation aid, anticaking agent and surface finishing agent in baked foods and mixes and it is the hardest natural wax. It is significantly less viscous then other waxes and thus it is easier to manipulate during capsule processing (Milanovic et al., 2010).

Thermal and physical characteristics of microencapsulated materials were evaluated by means of differential scanning calorimeter (DSC) and particle size analyses, respectively. Model systems composed of ascorbic acid–ferric chloride, sodium chloride–glucose, and vanillin–asparagine prepared using free and microencapsulated ingredients were heated under certain conditions to determine the effects of microencapsulation on furan, HMF and acrylamide formations, respectively.

2. Materials and methods

2.1. Chemicals and consumables

L-(+)-Ascorbic acid (min. >99.7%), furan (99.9%), L-asparagine (98%), sodium chloride and silica gel were obtained from Merck, and Fe(III)-chloride anhydrous was obtained from Riedel-de Haën (Seelze, Germany). Vanillin was purchased from Fisons Scientific Apparatus Ltd. (Leichestershire, England). Acetonitrile, water, and methanol were obtained from Merck (Darmstadt, Germany). Formic acid (98%) was purchased from J.T. Baker (Deventer, The Netherlands). Acrylamide, 5-hydroxymethylfurfural, glucose and AG were purchased from Sigma (St. Louis, MO, USA). β-Cd and MD (Glucidex with a dextrose equivalent of 19) were obtained from Roquette, (France) CW was obtained from Yılmaz Kimya (Turkey). Syringe filters (nylon, 0.45 μm), Oasis MCX (1 mL, 30 mg) solid-phase extraction cartridges, Atlantis T3 column (4.6 × 150 mm, 3 μm) and Atlantis dC18 column (4.6 × 250 mm, 5 μm) were supplied by Waters (Millford, MA, USA).

2.2. Preparation of the microcapsules of ascorbic acid, vanillin and sodium chloride

Emulsions of ascorbic acid, vanillin and sodium chloride were prepared according to the ratios given in Table 1. AG, MD and mixture of AG-MD (3:1, w/w) were used to encapsulate ascorbic acid. The coating materials were first dissolved in distilled water (25 °C) to a concentration of 25%. While mixing the solution, ascorbic acid was added at amounts to achieve final core:coating ratios (w/w) of 1:10 and 2:10. β-Cd was used to encapsulate vanillin. It was dissolved in distilled water (25 °C) to a concentration of 1%. While mixing the solution, vanillin was added at amounts to achieve final core:coating ratios (w/w) of 1:20 and 1:40. CW was used to encapsulate sodium chloride. The specified amount of CW was first melted in a water bath at 90 °C. Sodium chloride was dissolved in distilled water (25 °C) and added into melted CW at amounts to achieve final core:coating ratios (w/w) of 1:1 and 2:1.

All emulsions were prepared in two stages by using low and high-shear homogenizers. The mixtures prepared as explained above were first homogenized for 3 min at 2000 rpm (Heidolph, Silent M. Crusher). Then, the coarse emulsions were passed through a micro fluidizer (M110P, Micro fluidics, Newton, MA, USA) for 6 cycles at 30 ksi. Finally, the emulsions were freeze-dried to obtain the microcapsules in powder form.

Table 1
Composition of the emulsions used to prepare microencapsulated ingredients.

Emulsion	Core compound	Coating material	Coating (%)	Core:coating ratio (w/w)
AA-MD-1	Ascorbic acid	Maltodextrin	25	1:10
AA-MD-2	Ascorbic acid	Maltodextrin	25	2:10
AA-AG-1	Ascorbic acid	Arabic gum	25	1:10
AA-AG-2	Ascorbic acid	Arabic gum	25	2:10
AA-MD-AG-1	Ascorbic acid	Maltodextrin:Arabic gum (3:1)	25	1:10
AA-MD-AG-2	Ascorbic acid	Maltodextrin:Arabic gum (3:1)	25	2:10
Van-βCd-1	Vanillin	β-cyclodextrin	1	1:20
Van-βCd-2	Vanillin	β-cyclodextrin	1	1:40
NaCl-CW-1	Sodium chloride	Carnauba wax	5.5	1:1
NaCl-CW-2	Sodium chloride	Carnauba wax	12.5	1:1
NaCl-CW-3	Sodium chloride	Carnauba wax	5.5	2:1

2.3. Thermal characterization by DSC

Thermal characteristics of the microcapsules were determined using a TA Q20 model DSC apparatus (TA Instruments, New Castle, DE, USA). For comparison, free forms of ascorbic acid, vanillin and their coating materials were also analyzed. Appropriate amount of sample was weighed into an aluminum pan and hermetically sealed. The apparatus was calibrated with indium (melting point = 156.6 °C, ΔH = 28.5 J/g). The DSC runs were operated under nitrogen gas atmosphere (30 mL/min) using an empty pan as the reference. The pan into the apparatus was scanned over a temperature range of 25–270 °C at a heating rate of 5 °C/min.

2.4. Particle size distribution

Particle size distributions of the microcapsules were determined by using Malvern Mastersizer 2000SR particle size analyzer equipped with Hydro 2000S wet dispersion module with a stirred and ultrasonic probe. The speed of stirrer was fixed to 2000 rpm and 15 s. Ultrasound treatment was applied by means of inbuilt probe which can assist the dispersion of cohesive samples homogeneously at the beginning of measurement. Particle size distributions were given by the characteristic volume-based $D_{(0.1)}$, $D_{(0.5)}$ and $D_{(0.9)}$ values.

2.5. Determination of reactivity

Three different model systems were prepared to determine the reactivities of microencapsulated ascorbic acid, vanillin and sodium chloride during heating. The composition of the model systems, heating conditions and reaction products monitored are given in Table 2. The first model system was designed to determine the effect of ascorbic acid encapsulation on furan formation during heating in the presence of ferric chloride (Fe^{3+}) as an oxidizing agent. A total of 100 μL reaction mixtures were prepared containing 10 μmol ascorbic acid (control) or the capsules containing 10 μmol ascorbic acid, mixed with 1 μmol Fe^{3+} and 30 mg of silica gel in 20 mL headspace vials. After that the mixtures were covered with an additional 270 mg of silica gel. The vials were sealed with crimp cap immediately, and then heated in a temperature-controlled oven (Memmert UNE400, Germany) at 120 °C for 60 min. All reactions were performed in duplicate. The reaction mixtures were analyzed for furan using gas chromatography coupled to mass spectrometry.

A second model system was designed to determine the effect of sodium chloride encapsulation on HMF formation from sugars during heating. 100 μmoles of glucose mixed with the capsules containing 100 μmoles of sodium chloride was transferred to a 25 mL test tube (Pyrex, 25 mL) as their aqueous solutions. The

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