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Research paper

Development of an infusion method for encapsulating ascorbyl palmitate in V-type granular cold-water swelling starch

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ABSTRACT

Certain lipophilic components can be inserted very efficiently as guest molecule in the existing single helical amylose cavities in V_H-type crystalline granular cold-water swelling starch (GCWSS). In the present study, ascorbyl palmitate (AscP) was used as a model guest compound. The impacts of temperature (20 and 60 °C) and ethanol [48 and 68% (v/v)] and AscP [1.0, 2.5, 5.0, 10.0% (w/w)] concentrations on encapsulation performance were investigated. First, native maize and potato starches were converted into V_H-type GCWSS by aqueous ethanol [48% (v/v)] treatment at 95 °C. Exposing GCWSS to AscP induced the formation of inclusion complexes when a particular solvent (and temperature) environment was met. In 48% (v/v) ethanol, raising the treatment temperature to 60 °C did not significantly impact on the encapsulation performance. Maximum degrees of AscP encapsulation were 2.9 and 1.5% (w/w) for maize and potato starch, respectively, as determined by proton nuclear magnetic resonance measurements. As maize GCWSS contained more 'parent' V_H-type crystals, it was capable of entrapping more AscP than potato GCWSS.

1. Introduction

The amylose (AM) fraction of starch adopts a left-handed single helical conformation in the presence of a diverse range of compounds, of which alcohols (Buléon, Delage, Brisson, & Chanzy, 1990) and fatty acids (Godet, Buleon, Tran, & Colonna, 1993) are predominant examples. This single helix has a hydrophobic internal cavity (Immel & Lichtenthaler, 2000) which can accommodate the apolar (part of a) ligand molecule thereby generating AM-guest inclusion complexes. Such AM helices can be stacked parallel into hexagonal (Brisson, Chanzy, & Winter, 1991) or orthorhombic (Rappenecker & Zugenmaier, 1981) V-type crystal lattices, giving rise to V-type wide angle X-ray diffraction (WAXD) patterns. It is of note that the presence of the ligand molecule in the helix cavity is not essential for maintaining V-type AM crystals, since V-type WAXD patterns have been reported even after removing the incorporated alcohol (Dries, Gomand, Goderis & Delcour, 2014; Whittam et al., 1989).

Based on the ligand used (Helbert & Chanzy, 1994), a number of V-type AM subtypes have been described. These differ in helical dimensions as well as in intra- or interhelical location of the ligand (Putseys, Lamberts & Delcour, 2010). The best described AM inclusion complex is the V_{6I}- or V_H-subtype (Biliaderis & Galloway, 1989; Brisson et al., 1991; Godet, Bizot & Buleon, 1995; Le Bail, Bizot, Pontoire & Buleon, 1995; Rappenecker & Zugenmaier, 1981). It can be obtained at high ethanol concentrations but is usually induced by linear aliphatic chains of fatty acids, emulsifiers or alcohols (Buléon, Veronese, & Putaux, 2007). Based on their thermal properties, AM inclusion complexes are classified as either type I or type II: the former dissociate at temperatures below or at 100 °C while the latter melt at higher temperature (Biliaderis & Galloway, 1989). As opposed to type II complexes which have clear crystalline WAXD reflections, type I complexes have been considered to display low, if any, crystallinity (Biliaderis & Seneviratne, 1990). However, a recent study by Goderis, Putseys, Gommes, Bosmans

Abbreviations: AM, amylose; AscP, ascorbyl palmitate; DP, degree of polymerization; DSC, differential scanning calorimetry; 2θ, diffraction angle; DMSO, dimethyl sulfoxide; dm, dry matter; GCWSS, granular cold-water swelling starch; ΔH_{IC}, melting enthalpy of inclusion complexes; ^{1}H NMR, proton nuclear magnetic resonance; λ, wavelength; WAXD, wide angle X-ray diffraction.

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and Delcour (2014) evidenced that type I complexes also consist of lamellar crystallites, but that the crystals are smaller or less perfect than those of type II complexes. They also showed that the melting temperatures are predominantly related to the crystal size along the helical axis.

AM-guest inclusion complexes find applications in various food-related systems. First of all, they can influence the digestibility of starch-containing foods (Putseys, Derde et al., 2010). Further, starch-lipid interactions are of major technological importance in *e.g.* bakery products (Riisom, Krog, & Eriksen, 1984). There is also considerable interest in the use of starch (or AM) inclusion complexes as potential carriers of flavor or bioactive compounds which are sensitive to *e.g.* high temperature or oxidation (Fathi, Martin, & McClements, 2014; Marinopoulou, Papastergiadis, Raphaelides, & Kontominas, 2016). In this context, studies have been performed for conjugated linoleic acid (Lalush, Bar, Zakaria, Eichler, & Shimoni, 2005; Yang, Gu & Zhang, 2009), genistein (Cohen, Schwartz, Peri, & Shimoni, 2011) and poly-unsaturated fatty acids (Zabar, Lesmes, Katz, Shimoni, & Bianco-Peled, 2009, 2010). Starch is an interesting encapsulation matrix because of its bioavailability and biodegradability and low cost. Furthermore, their esterification to fatty acids can extend the encapsulation potential of AM to hydrophilic or bulky compounds such as ascorbic acid and phytosterols (Ma, Floros, & Ziegler, 2011).

Preparation methods for AM-inclusion complexes can generally be divided in three distinct groups (Obiro, Ray, & Emmambux, 2012; Putseys, Lamberts et al., 2010). In the classical preparation of 'pure' AM inclusion complexes, previously extracted AM is dissolved in dimethyl sulfoxide (DMSO) or alkaline medium, ligand is added, the mixture is incubated at 60 or 90 °C to produce the aforementioned type I and type II complexes, respectively, and then cooled to precipitate them (Gelders, Vanderstukken, Goesaert, & Delcour, 2004; Lalush et al., 2005; Lesmes, Cohen, Shener, & Shimoni, 2009; Ma et al., 2011). In a second approach, a starch dispersion is heated under shear in presence of a ligand. This then leads to its *in situ* complexation by solubilized starch (Fanta, Shogren & Salch, 1999; Garcia & Franco, 2015; Lesmes, Barchechath, & Shimoni, 2008). Thirdly, an enzymatic method utilizes purified potato phosphorylase for *de novo* synthesis of AM in the presence of a ligand (Gelders, Goesaert, & Delcour, 2005; Kadokawa, Kaneko, Nagase, Takahashi, & Tagaya, 2002; Kadokawa, Nakaya, Kaneko, & Tagaya, 2003).

The above production methods entail several drawbacks, including exposure of the guest molecule to high temperatures (approaches 1 and 2) and harsh chemicals (approaches 1 and occasionally 2), complexation/crystallization times which vary from hours to days (approaches 2 and 3) and low cost-efficiency (approaches 1 and 3) (Chang, He, Fu, Huang, & Jane, 2014; Kong & Ziegler, 2014).

In this context, Kong and Ziegler (2014) explored the complexation of ascorbyl palmitate (AscP) by 'empty' V_H-type AM helices. The 'infusion' of AscP in the V_H-type helices itself was fast and indeed occurred at ambient temperature. Nonetheless, in our opinion, their methodology still suffers from several drawbacks. Two techniques were used to prepare 'empty' V_H-type helices. In the first method, starch or AM was dissolved in DMSO at 100 °C, stirred for 1 h, mixed with ethanol at 25 °C, centrifuged and dried (*i.e.* approach 1, *cf. supra*). In the second method, starch or AM was solubilized at 150 °C in a high pressure reactor, cooled to 90 °C, mixed with ethanol, centrifuged and dried (*i.e.* approach 2, *cf. supra*). First of all, when the air-dried end product contains residual DMSO, it is unfit for food applications, as recognized by the authors (Kong & Ziegler, 2014). Secondly, V_H-type starch and V_H-type AM were annealed to increase the V_H-type crystallinity, which, in turn, increased the encapsulation of AscP. The need to anneal as well to use pure AM both increase the cost of this technique. Regretfully, the amount of the guest compound effectively incorporated was not reported. Also, the work by Kong and Ziegler (2014) does not allow addressing the crystal structure of the complexes, since samples analyzed after precipitation of the (hot) starch/AM suspensions with ethanol themselves can give rise to V_H-type WAXD reflections (Dries et al., 2014; Whittam et al., 1989).

Previous work by our group (Dries et al., 2014) reported on the conversion of native maize starch into V_H-type crystalline granular cold-water swelling starch (GCWSS) by aqueous ethanol treatment. At well-chosen treatment temperatures and ethanol concentrations, the native double helical order of crystalline amylopectin is lost and the alcohol induces AM single helix formation with V_H-type crystallinity. However, in the isolated air-dried end product the alcohol is most likely (i) not located inside the single helix cavities (Dries et al., 2014; Rajagopalan & Seib, 1992) or (ii) mobile and freely exchangeable with water (Brisson et al., 1991) or possibly other ligands. The degree to which newly formed V_H-type crystals are present depends on the AM degree of polymerization (DP) (Dries, Gomand, Delcour, & Goderis, 2016): the V_H-type crystallinity in the final product decreases with increasing DP of the AM fraction, likely as a result of increasingly disturbing molecular entanglements.

The present study explores the use of V_H-type GCWSS as encapsulation matrix with AscP as model guest compound. V_H-type GCWSS are prepared from different botanical sources (maize and potato starch) to study the impact of different degrees of V_H-type crystallinity on the encapsulation performance. Historically, fatty acid esters of ascorbic acid have been developed to transfer the antioxidant capacity of vitamin C to lipophilic environments. Also, this derivative and its parent compound have the same biological activity (Sapper, Cameron, & Mantsch, 1981). The influence of temperature and ethanol and AscP concentrations on encapsulation efficiency is investigated by differential scanning calorimetry (DSC) and WAXD experiments. Finally, the level of AscP incorporated in the GCWSS matrix is quantified using proton nuclear magnetic resonance (^{1}H NMR). We here report on the outcome of this work.

2. Experimental section

2.1. Materials

Maize and potato starches were provided by Cargill (Vilvoorde, Belgium). Moisture contents equaled 12.0 and 19.1% respectively and were determined by the AACC approved method 44-15.02 (AACC, 1999). The AM peak DPs were determined by high performance size exclusion chromatography, and equaled 1710 and 3520 for maize and potato starch respectively (Dries et al., 2016). All reagents, solvents and chemicals were of analytical grade and obtained from Sigma-Aldrich (Bornem, Belgium). The ethanol used in this work is denatured with up to 5% diethyl ether.

2.2. Procedure for preparing granular cold-water swelling maize starch

Maize and potato starches were converted into V_H-type GCWSS by aqueous ethanol treatment (Dries et al., 2016, 2014). Native starches [20.0 g dry matter (dm)] were dispersed in 180 g 48% (v/v) ethanol in a pressure resistant Schott bottle. After 30 min at 95 °C under continuous shaking in a water bath, dispersions were cooled for 60 min at room temperature and then Büchner filtered. The starch pellets were washed with ethanol, air-dried and sieved (mesh size: 150 μm).

2.3. Inclusion complex formation

GCWSS (0.8 g dm) was accurately weighed in a test tube with screw cap and mixed with 3.2 or 4.8 g ethanol containing 8.0, 40.0,