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Structural and thermal transitions during the conversion from native to granular cold-water swelling maize starch

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ABSTRACT

Native maize starch was gradually converted into granular cold-water swelling starch (GCWSS) by aqueous ethanol treatments at elevated temperatures. At a treatment temperature of 95 °C, decreasing ethanol concentrations from 68 to 48% (v/v) led to decreased post-treatment gelatinization enthalpies in excess water, reflecting remaining original A-type crystals. Concomitantly to native A-type crystal melting, V_H-type crystals appeared. At an ethanol concentration of 48%, a granular cold-water swelling maize starch was successfully produced. All crystals in its intact granules were of the V_H-type and appeared birefringent when studied in ethanol under polarized light. Removal of all residual solvent by high temperature drying did not influence swelling power, proving that a high temperature drying step is not necessary to induce cold-water swelling capacity. Based on *in situ* calorimetric measurements, the thermal requirements to produce GCWSS from different ethanol:water mixtures were elucidated. This work is the first to demonstrate that the amylose fraction contributes almost exclusively to V_H-type crystal formation in GCWSS.

1. Introduction

Native starch is laid down in plant storage organs as water insoluble, partly crystalline granules which essentially consist of two glucose polymers: quasi linear amylose (AM) and highly branched amylopectin (AP) (Buléon, Colonna, Planchot, & Ball, 1998). Regions of AP double helical formation are embedded into crystalline lamellae which alternate with amorphous layers containing AP branching points (Jenkins, Cameron, & Donald, 1993; Oostergetel & Vanbruggen, 1989). It is generally accepted that AM is located in the amorphous regions and that it does not participate in formation of crystals in native maize starch (Saibene & Seetharaman, 2010). The specific radial arrangement of starch crystallites gives rise to a Maltese cross pattern when the granules are visualized by optical microscopy in the polarization mode (French, 1984).

Differences in packing arrangements of AP double helices in native starch crystallites lead to characteristic A-, B- or C-type wide angle X-ray diffraction (WAXD) patterns (Imberty, Chanzy, Perez, Buleon, & Tran, 1988; Imberty & Perez, 1988). A fourth pattern, the V-type, is the result of complexes of AM single helices with suitable ligands such as iodine, fatty acids and alcohols (Zobel, 1988). V_H-type crystals are obtained in the case of saturated fatty acids and linear alcohols. Upon drying, an anhydrous V_A-type diffraction pattern is obtained, which has the same general shape as the former but with reflections shifted toward larger Bragg angles (Le Bail, Bizot, Pontoire, & Buleon, 1995). Although suitable ligands are necessary for forming AM single helical structures, their occurrence inside the helix cavity is not necessary for obtaining a V-type diffraction pattern (Le Bail et al., 1995; Whittam et al., 1989). As opposed to native A-, B- or C-starch crystals, V-type crystals can be soluble in water at room temperature (French & Murphy, 1977).

Abbreviations: AP, amylopectin; AM, amylose; AML, amylose-lipid inclusion complex; CHL, carbohydrate leaching; $T_{C(V)}$, conclusion temperature of gelatinization (V-type crystal melting); DSC, differential scanning calorimetry; 2θ, diffraction angle; dm, dry matter; $\Delta H_{(V)}$, enthalpy of gelatinization (V-type crystal melting); $ETS_{(waxy)x\%/y^{\circ}C}$, ethanol treated (waxy) maize starch treated with x% (v/v) ethanol at a temperature of y °C; GCWSS, granular cold-water swelling starch; ΔH_{AML}, amylose–lipid inclusion complex melting enthalpy; $T_{O(V)}$, onset temperature of gelatinization (V-type crystal melting); $T_{P(V)}$, peak temperature of gelatinization (V-type crystal melting); RT, room temperature; $\Delta T_{(V)}$, temperature range of gelatinization (V-type crystal melting); TGA, thermal gravimetric analysis; λ, wavelength; WAXD, wide angle X-ray diffraction.

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At room temperature, native starch granules remain virtually intact and settle out from aqueous solutions. Starches with enhanced cold-water swelling capacity can be used in puddings, pie fillings, gravies, soups and sauces as thickening agents (Eastman, 1987). Such starches are traditionally prepared by drum drying gelatinized starch slurries (Colonna, Doublier, Melcion, Demonredon, & Mercier, 1984; Doublier, Colonna, & Mercier, 1986), but have inferior thickening properties due to their no longer being granular (Anastasiades, Thanou, Loulis, Stapatoris, & Karapantsios, 2002). To overcome this limitation, some effort has been made to develop granular cold-water swelling starches (GCWSS). At industrial scales, native starch granules are often gelatinized in hot steam and nozzle-spray dried (Pitchon, O'Rourke, & Joseph, 1981). According to Rajagopalan and Seib (1992b), this method yields amorphous GCWSS. Other technologies – the ones of interest to the present paper – Statistical analyses were performed with Statismake use of alcohols and produce GCWSS with increased levels of V-type crystallinity. These include (i) aqueous alcohol treatment at high temperature and elevated (Eastman, 1987; Eastman & Moore, 1984) or atmospheric pressure (Zhang, Dhital, Haque, & Gidley, 2012) (method I), (ii) polyhydric alcohol (*e.g.* propan-1,2-diol) treatment at high temperature and atmospheric pressure (Rajagopalan & Seib, 1992a,b) (method II) and (iii) alcoholic-alkaline treatment (Chen & Jane, 1994a,b; Jane & Seib, 1991) (method III).

Jane, Craig, Seib, and Hoseney (1986a,b) proposed a mechanism explaining the structural transitions during formation of GCWSS when prepared by method I in closed vessels at autogenic pressure. Rapidly after native crystal melting, the alcohol induces single helical formation and V-type crystallinity with the alcohol being located within the single helix cavities and possibly the interstices. This mechanism is supported by the observation that the endothermic heat of gelatinization in aqueous alcohol is lower than in pure water, supposedly since it is partially annihilated by the exothermic heat of V_H-type crystal formation. Alcohol removal from the helix cavity by drying produces semi-stable V-type crystals and confers cold-water swelling capacity upon the starch (Jane et al., 1986a). The integrity of the granules is thought to be preserved due to entanglement of AM with AP. This idea stems from the observation that the granular integrity could not be preserved in attempts to produce GCWSS of waxy starch, which is free of AM. However, AP is believed to contribute to formation of V-type crystals since in WAXD experiments (Jane et al., 1986b) the intensity of the V-type diffraction pattern from regular GCWSS accounts for more than the AM fraction alone. To our opinion, this mechanism requires considerable extra research.

First of all, the thermal requirements to produce GCWSS by method I have never been fully unraveled. For instance, the work by Zhang et al. (2012) does not allow making clear statements on the role of different alcohol:water ratios at a treatment temperature of 95 °C because, in their method, the actual temperature drifted during the protocol, solvent evaporation occurred and hence the starch concentration progressively increased. Also, calorimetric measurements by Jane et al. (1986a) only included a single *n*-propanol:water solution and melting of created V-type crystals was not reported.

Secondly, the involvement of AP in V-type crystal formation, as proposed by Jane et al. (1986a), has never been confirmed. Chen and Jane (1994b) found no V-type crystallinity in GCWSS from waxy maize starch produced via method III. The granules remained amorphous. Zhang et al. (2012) used method I at ambient pressure. All GCWSS displayed V-type crystallinity except for partially converted waxy maize starches. The idea was coined that AM is needed for nucleation of V-type crystallinity and that AP can contribute once triggered by AM.

Finally, whether or not removal of alcohol is strictly needed to impart cold-water swelling properties remains undecided since – to the best of our knowledge – no solubility or swelling experiments were ever conducted on V-type crystalline GCWSS that did not pass a drying step in which the alcohol was removed.

The present work wants to contribute to the understanding of the GCWSS production process. It focuses on method I. Therefore, the first part of the current paper reports on a study in which the water:alcohol ratio and the treatment temperature – in a predefined temperature range up to 95 °C – are systematically varied. The properties of the ensuing products are fully characterized. A second part discusses the importance of removing the alcohol from the V-type crystals for inducing cold-water swelling capacity. Alternative routes to produce GCWSS from the unsuccessful mixtures tested at 95 °C are proposed in a following part. This part provides clear answers on the temperature requirements for producing GCWSS by method I at a given water:alcohol ratio. Besides regular maize starch, waxy maize starch is included in this study to allow for a final discussion on the contribution of AP in the formation of V-type crystals.

2. Experimental

2.1. Materials

Normal and waxy maize starch were obtained from Cargill (Vilvoorde, Belgium). All reagents, solvents and chemicals were of at least analytical grade and obtained from Sigma-Aldrich (Bornem, Belgium). The ethanol used in this work is 5% diethyl ether-denaturated ethanol and will be further referred to as ethanol. This means more specifically that *e.g.* a stock solution of 48% (v/v) ethanol consists of 49.5% deionized water, 48% ethanol and 2.5% diethyl ether.

2.2. Procedure for preparing granular cold-water swelling starch on gram scale

GCWSS was produced by aqueous ethanol treatments at elevated temperature. The ethanol concentration ranged from 48 to 68% (v/v) and the treatment temperatures were 80, 85, 90, or 95 °C. Regular maize starch [20.0 g dry matter (dm) basis] (*cf.* Section 2.5) was suspended in a water:ethanol mixture [1/9 (w/w) starch dm/solvent] with varying ethanol concentration in a pressure resistant Schott bottle (250 ml) equipped with a leak proof screw cap. The bottles were hand shaken to disperse the starch and then continuously shaken in a water bath. After 30 min at the desired temperature, the suspensions were kept for 60 min at room temperature (RT), 200 ml ethanol was added and bottle contents were suspended. The starch suspensions were Büchner filtered and washed several times with ethanol. The resulting starch pellet was finely chopped with a spatula, spread over a paper filter sheet, air-dried overnight at RT, sieved (mesh size: 150 μm) and stored in air-tight plastic bottles. Sample codes are of the format $ETS_{x\%/y\,°C}$ where ETS stands for ethanol treated starch, *x*% stands for the volume percentage of ethanol in the used water:ethanol mixture and *y* °C for the treatment temperature. The subscript 'waxy' is used when waxy instead of regular maize starch was used. An alternative treatment for overnight air-drying included oven-drying for 60 min at 115 °C ($ETS_{x\%/y\,°C\text{-}115\,°C}$).

2.3. Differential scanning calorimetry

2.3.1. Gelatinization and amylose–lipid inclusion complex melting in excess water

Gelatinization and amylose–lipid inclusion complex (AML) melting of native starch and ETS in excess water were studied with