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Review

New processing and applications of waxy starch (a review)

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A R T I C L E I N F O

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A B S T R A C T

Waxy starches consist almost exclusively of amylopectin and don't contain amylose molecules. Despite extensive knowledge - and certain applications - of waxy *maize* starch in former times, the production and use of other high amylopectin starches is now increasing. This review deals with the physical processing of these starches (via gelatinization, gelation, extrusion, annealing, and heat moisture treatment) and with chemical and biochemical modification (e.g. acetylation, debranching of amylopectin, hydrolysis). Great attention is paid to the digestibility of the products and the formation of nanoparticles. Both usual and new food and non-food uses of rice, maize, wheat, barley and potato waxy starches are referred to.

Contents

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Nomenclature

Abbreviations

CDex	cluster dextrin
CLWMS	cross-linked waxy maize starch
CPB	cardiopulmonary bypass circuit
DBS	debranched starch
HA	high-amylose maize starch
HMT	heat-moisture treatment
MW	molecular weight
NpAS	*Neisseria polysaccharea* amylosucrase
OSA	octenylsuccinic anhydride
OSA-starch	*n*-octenyl succinate starch
PE	polyethylene
PAAm	polyacrylamide
PS	potato starch
RA	regular maize starch
RDS	rapidly digestible starch
RS	resistant starch
RS3	type of resistant starch (retrograded amylose)
RVA	Rapid ViscoAnalyzer
SCA	short-chain amylose
SDS	slowly digestible starch
SNC	starch nanocrystals
St-g-SA	starch-graft-sodium acrylate copolymer
St-g-PAAm	starch-graft polyacrylamide copolymer
TPS	thermoplastic starch
WF	wheat flour
WMmdx	waxy maize maltodextrin gels
WMS	waxy maize starch
WRF	waxy rice flour
WWF	waxy wheat flour

1. Introduction

Starch is the main storage carbohydrate in plant organisms. Normal starch in granular form is generally composed of two types of molecules, amylose and amylopectin. Amylose is a linear (1,4)-α-D-glucan, although there is now some evidence of a few 1,6 branches in some amyloses. Amylopectin is a branched structure containing both (1,4)-α-D linkages between D-glucose residues and (1,6)-α-D branch points. Waxy starches consist almost exclusively of amylopectin, a high molecular weight molecule (Murray and Phisarnchananan, 2014).

The branches in amylopectin are arranged in a clustered structure that allows adjacent chains to form double helices (Bresolin et al., 2006; Zeeman et al., 2010). The packing of these helices results in crystalline regions of the starch. The crystalline organisation of the starch granule is linked to the amylopectin branch chain distribution profile, which is typical for the source of starch (Jane et al., 1999).

Starch is isolated by a technology which comprises many processing machines, e.g. mills, mixers, decanter and filtration centrifuges, hydrocyclones and cyclones, vacuum filters, fluid dryers, and sieves. Also some new methods (annealing, heat moisture treatment, nanofiltration) of starch processing have been tested. Shape and size of the starch granules, in which form starch naturally occurs, is therefore very important for starch processing and differs for waxy starch. E.g. waxy *wheat* starch has a more spherical disc-like morphology compared to normal wheat starch (Zhou et al., 2014) and a larger average granule diameter, and a higher degree of crystallinity than normal wheat starch.

Foods may be enriched by flour or native and/or modified starches, where they thicken, decrease the price of a product, form gels (see chap. 2) and stabilize the food product. Stabilisation prevents syneresis, meaning that, compared with native starches, starch is suitable for use e.g. in yoghurt, chilled sauce, mayonnaise, dressing, cooking margarine, ketchup, fruit preparation, fruit pie and filling, relishes, pickles and baby food. Starches also absorb much of the available free water and provide desirable structure and texture in many foods (Daniel et al., 2002; Šárka and Bubník, 2009). Recent applications of starch in food comprise special nutrients such as fat-replacers (Burdock, 1997) or resistant starch (see chap. 3) as well.

Although waxy starch manufacturing is a mature technology, new developments of processes and applications occur.

2. Gelatinization and gelation

For thickening foods, sizing and coating papers, textile sizing, use in drilling muds, adhesive formulations, and many other applications, starch gelatinization is required. The related phenomenon - formation of solid gel, gelation - occurs upon the cooling of gelatinized starch.

Gelatinization of starch is the phase transition of starch granules from an ordered to a disordered state during heating with excess water (Šubarić et al., 2011). Starch granules conversely absorb water and swell when their aqueous dispersion is heated. This penetration of water, combined with the increased separation of the starch chains, increases randomness and decreases crystallinity in the granule. During gelatinization, granules swell extensively (Smrčková et al., 2013). For waxy starches — which are essentially free of amylose - amylopectin molecules remain initially inside the granules during swelling; however, upon prolonged heating, the majority of the granules break up, and the system is converted to a macromolecular amylopectin solution (Schirmer et al., 2013). On the other hand the swollen granules are highly susceptible to mechanical breakdown and solubilise faster.

Swelling ability contributes to important characteristics of starchy food products. Gelatinization of native starches usually occurs over a small temperature range. Table 1 shows the differences of the gelatinization temperature between various waxy and normal starches. Molar size and branch-chain length of amylopectin affect the gelatinization behaviour of waxy starches and the rheological properties of their pastes and gels (Kalichevsky et al., 1990; Chung et al., 2008).

Gelation can be characterized as the process by which dispersed starch molecules in an aqueous medium begin to re-associate and form three-dimensional network structures. For starch gels, non-covalent chain interactions are generally believed to involve intermolecular double helix formation stabilized by hydrogen bonding (BeMiller and Whistler, 2009). Amylopectin (although a good thickening agent having high viscosity) forms very weak gels at relatively high concentrations that break down on shear (Murray and Phisarnchananan, 2014). Weakening of gel texture means lower gel hardness (Lo and Ramsden, 2000). Additionally, waxy starch provides a viscoelastic gel that is more liquid-like at high frequencies, as found by Kong et al. (2015) for the waxy rice mutant GM077 containing 2.6% amylose in starch. Waxy starch is generally described as having great clarity, high breakdown value, and low