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Waxy starch as a perspective raw material (a review)

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ABSTRACT

Modern techniques in plant breeding as well as the fact that the technologies of starch isolation and modification have become more sophisticated and efficient – have enabled development of new food and non-food uses of waxy starches. This paper concerns the physical processing of these starches (via gelatinization, gelation, extrusion, annealing, and heat moisture treatment) and with their chemical and biochemical modification (e.g. acetylation or debranching of amylopectin). New food applications of waxy starches comprise e.g. emulsions, films and coatings; they are also focused on influencing digestibility and bread softening. There are also non-food uses such as fillers and reinforcing agents in polymer composites. Some of these uses are linked with nanoparticles prepared from waxy starches by various ways.

Contents

1. Introduction

Waxy starch consist almost exclusively of amylopectin, highly branched and high molecular weight macromolecule composed of α-(1 → 4)-D-glucopyranose chains linked by α-(1 → 6)-linkages. E.g. Chakraborty et al. (2004) found amylose content in starches from seven waxy genotypes originating from two wheat classes, tetraploid durum and hexaploid hard red spring (HRS) in the range from 2.3% to 2.6% in waxy durum lines, compared to 29.2% in normal durum control, and 2.1%–2.4% in waxy HRS, compared with

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26.0% in normal HRS control.

The branches in amylopectin form double helices which are arranged in a clustered structure -crystalline regions (Bresolin et al., 2006; Zeeman, Kossmann, & Smith, 2010). The crystalline organisation of the starch granule is unique for the source of starch (Jane et al., 1999). Cereal starches display a progressive transformation of the crystal pattern from A-type to B-type with increased amylose content, as reported in maize (Cheetham & Tao, 1998). Zhou et al. (2015) found that waxy starches of sweet potato show a slightly higher proportion of DP > 25 chains and thus a lower crystalline level than that of wild type; meanwhile, the high-amylose starches contain a large amount of long chains and show a sharp decrease in crystallinity level. It is believed that long chains are negative factors for crystallite formation because long chains can permeate them (Jane, Wong, & McPherson, 1997).

The internal organisation of the chains within the building blocks of starch granules is connected with the shape and size of the granules. They may be identified by many instrumental methods such as optical or electron microscopy (SEM) linked with an image analysis system, laser diffraction or sedimentation measuring (Šárka & Bubník, 2009). Zhou, Zhang, Chen, Zhang, and Wang (2014) used SEM and found that waxy wheat starch (isolated from wheat coming from breeding programmes at School of Food Engineering and Biotechnology, Tianjin University of Science & Technology, China) contained a smaller proportion of (smaller) B-type granules, a larger average granule diameter, and a higher degree of crystallinity than normal wheat starch.

Previously, scientific texts only cited applications of waxy *maize* starch, some examples of the suppliers are also given in the text of this paper. More recently the production as well as the uses of other waxy starches in industry have increased, e. g. the Lyckeby Company (Sweden) produces barley waxy starch or Avebe Company (Netherland) offers the potato waxy starch Eliane™ for food products (bakery, dairy, noodles etc.). It is common to apply waxy rice and waxy rice flour in the kitchen e.g. in China, Korea, Thailand etc. Compared with waxy maize, waxy wheat is relatively very new and of great interest.

2. Gelatinization and gelation of waxy starch

Molar size and branch-chain length of amylopectin affect the gelatinization behaviour of waxy starches. The swollen granules solubilise faster when compared with normal starch because higher amylose contents inhibit the extensive granule swelling (Schirmer, Höchstötter, Jekle, Arendt, & Becker, 2013). Waxy-starches develop higher paste viscosities but they are highly susceptible to mechanical breakdown. Waxy starch provides a viscoelastic gel that is more liquid-like at high frequencies, as found by Kong, Kasapis, and Bao (2015) for the waxy rice mutant GM077 containing 2.6% amylose in starch. Weakening of gel texture means also lower gel hardness. Waxy starch gels have great clarity, high breakdown value, and low retrogradation tendencies.

According to Zhang, Zhang, Xua, and Zhou (2013) waxy wheat starch (isolated in laboratory from flours donated by Chulong Flour, Taizhou, China) had a high gelatinization temperature, but on the other hand Zhou et al. (2015) found that waxy starch from sweet potato had practically the same value of pasting temperature when compared with normal starch, but the amylose content had a positive correlation with setback value ($r = 0.87$) and with cold paste viscosity ($r = 0.74$) and a negative correlation with breakdown value ($r = -0.98$). Schirmer et al. (2013) found by DSC analysis that all waxy starches (maize, barley, potato) showed a higher enthalpy of gelatinization (ΔH) but had practically the same value of gelatinization temperature (T_o) when compared with normal starch.

Waxy rice starch (WRS) has a gelatinization peak temperature Tp of 67.6 °C, followed by maize starch (MS; 68.0 °C) and waxy maize starch (WMS; 69.7 °C), and native rice starch (RiS) has a very high Tp (75.7 °C). WRS and WMS show a higher peak viscosity and a larger breakdown than their regular counterparts, which is due to their higher swelling power. Setback is high for MS and RiS, while waxy starches show hardly any setback. This is due to the formation of an amylose network in the former case (Waterschoot, Gomand, Willebrords, Fierens, & Delcour, 2014).

3. Affecting digestibility

The digestibility of waxy starch in food/feed compared with normal starch may depend on animal species. Although Pfeffer, Beckmann-Toussaint, Henrichfreise, and Jansen (1991) and Bergot (1993) observed better growth and utilisation in rainbow trout (*Oncorhynchus mykiss*) fed diets with waxy maize starch, Enes, Panserat, Kaushik, and Oliva-Teles (2006) found no differences in growth performance and feed utilisation in European sea bass (*Dicentrarchus labrax*) fed diets with waxy and normal starch. However, Sá, Pousao-Ferreira, and Oliva-Teles (2008) found that normal starch diets had higher energy digestibility and lipogenic enzyme activities compared with waxy starch diets in white sea bream (*Diplodus sargus*).

As to human nutrition, starch in food may be generally divided to rapidly digestible (RDS), slowly digestible (SDS) or resistant starch (RS). The RS passes into the colon, where it is metabolised into secondary products (short chain fatty acids) by colonic microflora and behaves in a way similar to dietary fibre (Šárka et al., 2015). The digestibility of waxy starch is influenced by the interplay of various factors including granule size, granule porosity, amylopectin chain length distribution, and degree of crystallinity (Singh, Dartois, & Kaur, 2010). Cooking increases digestibility for all starch substrates, but with different effects depending on the starch cultivars. Zhou et al. (2014) found this phenomenon for waxy wheat starch as well. Similar action may be done by cooking extrusion but this process can be also used for slowing down the digestibility – see chap. 4.1.

Xie, Hu, Jin, Xu, & Chen et al. (2014) found that the maximum SDS yield (40.41%) and the lowest proportion of RS (25.66%) were obtained from waxy potato starch (National Starch Specialties Shanghai Ltd., China) subjected to two cycles of retrogradation treatment with a time interval of 48 h.

The crystallization of starchy gels into resistant starch (type RS3) is a result of retrogadation, i.e. re-association of amylose chains in the form of loosely arranged double helices resisting the diffusion and binding of hydrolytic enzymes (Eerlingen, Crombez, & Delcour, 1993). The absence of amylose molecules therefore defends the retrogradation; the way how to increase RS3 content coming from waxy starches would require previous debranching of the molecule – see chap. 4.3.

The other possibility to decrease starch digestibility may be the creation of starch-lipid complexes (resistant starch RS5), however amyloso-lipid complexes have a preference. With the development of new waxy starches and their increasing application to foods, a good understanding of the interactions between amylopectin and lipids and their effect on starch functionality has become progressively more of interest for food processing and nutrition. However, these interactions need to be investigated further (Wang & Les Copeland, 2013).

The absence of long-chain amylose and greater abundance of amylopectin favoured modification as found by Kittisuban, Lee, Suphantharika, Bruce, and Hamaker (2014) who tested seven types of starch (waxy maize, normal maize, waxy rice, normal rice, waxy potato, normal potato, and tapioca) to produce slowly