Structural changes during gelatinization and retrogradation of rice starch gels


Laboratory of Food Chemistry, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium

Laboratory of Macromolecular Structural Chemistry, K.U. Leuven, Celestijnenlaan 200 F, B-3001 Heverlee, Belgium

European Molecular Biology Laboratory, EMBL c/o Desy, Notkestrasse 85, D-22603, Hamburg, Germany

Rice starch granules (with diameters of ca. 5 µm), consist of two α-D glucose polymers: nearly linear amylose and highly branched amylopectin. Within starch granules, three different regions are distinguished, i.e. alternating amorphous (low electron density) and semi-crystalline growth rings (thickness 120-400 nm). The latter consist of crystalline (high electron density) and amorphous (low electron density) lamellae with a repeat distance of 9-11 nm [1]. Crystalline lamellae result from double helix formation of amylopectin side chain chains which aggregate to form crystals, whereas amorphous lamellae mainly contain amorphous amylopectin branch points [2].

When starch granules are heated in excess water above the gelatinization temperature, the supramolecular order (crystallinity) and 9-11 nm repeat are lost. Apart from this phenomenon, water absorption and thus swelling of the granule and amylose leaching occur during gelatinization. Upon cooling a starch gel is formed, which undergoes structural changes during staling. This so called retrogradation process involves crystallisation of amylose (after some hours) and amylopectin (after several days or weeks). The long range order differs, however, from that in native starches [3].

The present work intended to clarify the influence of amylose on both the gelatinization and retrogradation of rice starches. For this purpose, rice starches with varying amylose contents (AC 0-28%) and gelatinization characteristics (onset of gelatinization: 58.7-68.5 ºC; conclusion of gelatinization: 73.1-81.3 ºC), were used. The gelatinization of the starches was studied by subjecting aqueous starch suspensions (33% w/w) to differential scanning calorimetry and temperature resolved Small Angle X-ray Scattering (SAXS) measurements (heating rate 2°C/min). The retrogradation was investigated by SAXS (heating rate 2°C/min) of aged starch gels. The latter were obtained by heating starch suspensions (33% w/w) to either complete (95°C) or partial (70-79°C) gelatinization and subsequently the gels were stored at 5°C during 8 days.

At ambient temperature, native rice starches display slightly differing repeat distances (8.8-9.4 µm), which are not correlated with their amylose content. Upon heating, the different starches behave very differently. During a first stage of heating, the integrated Lorentz corrected intensity increases, with the larger increase observed for the starches with the higher amylose content (fig.1). Further heating lowers the integrated intensity, either before the onset of gelatinization (for the low amylose starches) or at the onset of gelatinization (for the high amylose starches). The increase of the overall scattered intensity during the initial heating stage is accompanied by a synchronous improvement of the definition of the 9 nm peak. This suggests that the electron density differences between the amorphous ring, crystalline lamellae and amorphous lamellae increases during heating. The fact that the three different regions become more clearly defined when high amylose starches are treated, combined with the hypothesis [4] that amylose disrupts the packing of amylopectin double helices, may imply that amylose leaches out of the semi-crystalline lamellae into the amorphous growth ring during heating (increased crystalline lamellae and amorphous growth ring electron density, decreased amorphous lamellae intensity).

Completely and partially gelatinized retrograded rice starch gels exhibit a shoulder-like peak superimposed on the amorphous background [3] at ambient temperature. Furthermore, for incompletely gelatinized rice starch gels, an additional small peak, ascribed to remaining lamellar structure (9 nm repeat), was observed. Upon heating above 30°C, the Lorentz corrected intensity immediately decreases (fig.2), in contrast to what is observed with native rice starch suspensions. However, for incompletely gelatinized starch gels, the intensity levels off between 65°C and 85°C, after which it further decreases. Most probably mainly amylose double helices and some co-crystallised amylose-amylopectin double helices are formed during staling, although without much supramolecular order. Upon heating, the obtained structure quickly melted. The fraction of remaining lamellar structure (average ratio of Lorentz corrected intensity peak integral between 65-85°C and 30°C) is larger for rice starches that have been
heated to temperatures closer to conclusion temperature (retrograded starches 2 and 4: 23.4% and 26% respectively compared to 6.3 % en 14.2 % for retrograded starches 1 and 3). The fraction of remaining lamellar structure is expected to be smaller. A possible explanation might be that, for rice starches that gelatinize at higher temperatures the lamellar structure is maintained to a larger extent due to the presence of more stable crystallites. The influence of amylose on retrogradation behavior of rice starches is not clear from the present measurements. Other important structural properties (e.g. different amylopectin side chain lengths for the different rice starches) are probably as important in determining structural changes during retrogradation.

Fig. 1. Integrated Lorentz corrected intensity ($I_\lambda s^2$) as a function of temperature for native rice starches (rescaled between 0-1); AC : amylose content.

Fig. 2. Integrated Lorentz corrected intensity ($I_\lambda s^2$) as a function of temperature for retrograded rice starches heated to 95°C and to 2.5-4.8% below conclusion of gelatinization (rescaled between 0-1). Codes 1-4 for the starches correspond to those in figure 1.

References