Proceedings of the Nutrition Society (2023), **82 (OCE1)**, E9 doi:10.1017/S0029665123000174

Winter Conference 2022/23, 24–25 January 2023, Architecture of food: processing, structure and health

Delay in gelatinisation of hybrid starch microgels

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Starch is a homopolymer of linear amylose chains and extensively branched amylopectin. A fraction of starch termed resistant starch (RS) functions as dietary fibre. Metabolites released during colonic fermentation of RS are known to influence systemic metabolism and reduce the risk of cardiovascular and metabolic diseases [(1)]. Resistant properties of starch can be attributed to structural elements such as granule morphology, amylose to amylopectin ratio, degree of branching, and supra-molecular architecture of starch assemblies, which influence enzymatic hydrolysis through steric hindrance mechanisms and the reduction of mass transfer [(2)]. One of the key approaches for increasing starch resistance is via retrogradation, the process when starch chains re-align following gelatinisation.

In this work, we hypothesise that starch retrogradation can be modified by designing hybrid starch microgels in which the density of helical complexes is amplified by the presence of amylose chains with low degree of polymerisation (low-DP).

To develop hybrid starches, we have isolated low-DP amylose from parent amylopectin of either waxy (ca. 98% AP) or native corn starch (ca. 70% AP) and incorporated these back into the amylopectin- rich granules of waxy corn starch. The isolation of the low-DP amylose chains is performed using isoamylase hydrolysis of amylopectin followed by sequential temperature fractionation based on solubility in water. The incorporation of the low-DP amylose chains into the parent granule was monitored using turbidity analysis, complemented by microscopy evaluation utilising fluorescently labelled low-DP amyloses. Structural properties of starch microgels were assessed using rheological analysis including the time-temperature superimposition principle coupled to the Arrhenius model and differential scanning calorimetry.

Fabrication of the composite starch hydrogels was performed by gelatinising waxy corn starch in the aqueous solution of low-DP amylose. Successful hybrid gels were formed in the systems with 1:1 waxy corn starch:low-DP amylose ratio. The presence of the low-DP amylose in solution resulted in the delayed onset of gelatinisation by 4.2 ± 0.43°C ($n = 5$) for the hybrids. Further evidence of inhibited gelatinisation was obtained by time-resolved polarised-light microscopy. Image analysis revealed that at 70°C the number of starch granules with detectable birefringence (commonly referred to as 'Maltese-cross') increased from 1.9 ± 0.1% for unhybridised waxy corn starch to 23.4 ± 1.2% in the hybridised materials ($p < 0.05$, Tukey post-hoc test), which constitutes a 10-fold increase in the number of starch granules with inhibited gelatinisation. These findings provide possible mechanism for the observed changes in gelatinisation temperature.

Taking advantage of inhibited gelatinisation and its onset, future work will focus on assessment of digestibility of retrograded hybrid starch microgels and their structural evolution on storage. Thus, this work offers novel avenues for improved management of starch hydrolysis during digestion.

Acknowledgments

Thoithoi Tongbram is a Commonwealth Scholar, funded by the UK government.

References

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