

## MOLECULAR REARRANGEMENT OF STARCH DURING ENZYME DIGESTION AS INFERRED BY SCATTERING TECHNIQUES

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### INTRODUCTION

Resistant starch (RS) is defined as the fraction of starch that escapes digestion in the small intestine, serving as a fermentation substrate for the beneficial colonic bacteria. Understanding the structure that makes these fractions resistant to digestion is of outstanding importance as it assists in the design of food products with increasing RS content. Several studies have been focussed on the description of the RS fractions from several starch varieties, but little attention has been paid to the digestion process itself, which from the present work, seems to play a key role in the understanding of what is RS.

### MATERIALS AND METHODS

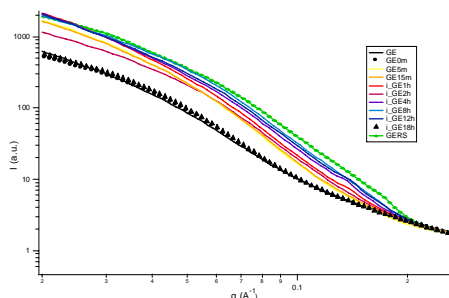
High-amylose starch samples extruded in a capillary rheometer, and provided by the CSIRO Food Futures Flagship, have been characterized at different stages of in vitro enzyme digestion using scanning electron microscopy (SEM), small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD). Control samples kept for 18 hours in the digestion solution without  $\alpha$ -amylase were used for comparison purposes.

### MICROSTRUCTURE AS A FUNCTION OF DIGESTION

From Figure 1 it can be observed that just after extrusion (0 min), big amorphous agglomerates of starch are formed. Keeping the processed starch in the digestion medium during 18 hours without the enzyme (c), does not alter the appearance of the starch particles. On the other hand, just after 5 minutes of digestion a great reduction in particle size is observed. Moreover, the surface of the particles becomes smoother as digestion goes on.

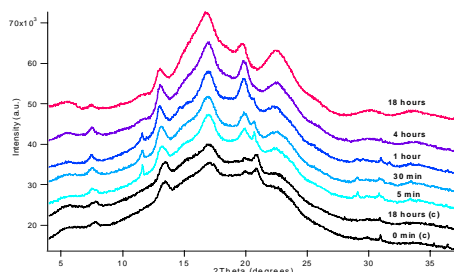
### MOLECULAR REARRANGEMENT OF EXTRUDED STARCH DURING DIGESTION

Figure 2 shows the SAXS patterns of extruded starch as a function of digestion. The increase in the intensity of the curves is related with an increase in the molecular order of the samples during the enzymatic process.

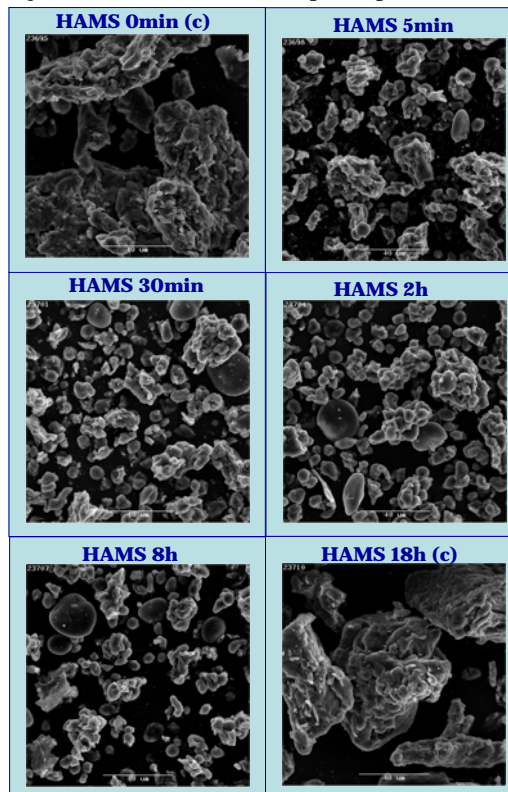


**FIGURE 2.** SAXS patterns of extruded HAMS as a function of digestion (patterns in black are the control samples)

An increase in the diffraction peaks was also observed during digestion (see Figure 3) which is explained by an increase in the crystallinity taking place in parallel to enzymatic hydrolysis. This seems to point out that as digestion goes on, the shorter chains generated are more mobile and, therefore, able to reorganize in crystallites.



**FIGURE 3.** XRD patterns of extruded HAMS at various times of digestion (patterns in black are the control samples)



**FIGURE 1.** SEM micrographs of extruded high-amylose maize starch (HAMS) as a function of digestion. HAMS 0min and 18h (c) are control samples kept in the digestion medium without enzyme

### CONCLUSIONS

The changes found suggest that RSIII-type resistant starch does not refer to a specific structure present in native starches, but it is in fact formed during the in vitro enzyme digestion process through the rearrangement of the highly mobile hydrolysed amylose chain fragments into crystals.

\*This work is part of the project "Molecular basis for processing functionality of resistant starch" within the Food Futures Flagship.