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DSC studies of starch in cereal and cereal products

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Abstract

Heat flux calorimetry was used to study the thermal behaviour of different cereals and their products. The endothermal reactions of the samples occurred when measurements were made with sufficient water and sealed cells. According to the interpretation of the calorimetric curves, these reactions correspond to the change (disintegration or association) of the originally ordered secondary structure of the starch, or to the reassociation of the gelatinised starch into a new molecular order. The data derived from DSC explain the functional properties of starch in complicated food systems, even without the necessity of first extracting the starch. The results indicate the feasibility of DSC in the evaluation of the character and intensity of structural modifications of cereal starch caused by different types of treatment in the food industry.

INTRODUCTION

The major constituent of a cereal kernel is starch which occurs as granules in the endosperm. Cereal starches contain two polysaccharide components that contribute to its molecular structure: amylose, a linear chain molecule, and amylopectin, a non-linear highly branched molecule, both consisting of glucose residues. As a result of its hydrogen bonds between neighbouring polymer chains, starch forms a secondary molecular order. Within the starch granule, there are water-accessible amorphous zones and crystalline regions in which the bonds between the chains are too strong to allow permeation by water, see Fig. 1. Because of its unstable condition, the secondary structure of this natural biopolymer undergoes alterations during post-harvest treatment of the cereal and during food processing. Even weak reactions induced by water, temperature ($< 50\,^\circ$C) and time can alter the structure and functional properties of cereal starch: the amorphous sequences of the starch can be partially changed into a more stable quasi-crystalline condition, see Figs. 1 and 2. This annealing effect leads to modifications in the thermal behaviour of starch which can be examined by DSC [1–3].

Food producers pay particular attention to major structural alterations that are induced by mechanical forces or heating during processing and lead

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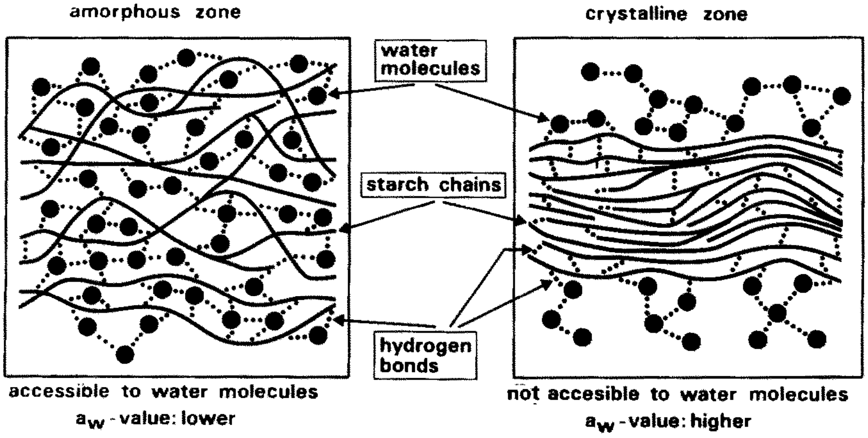


Fig. 1. Schematic model of starch structure.

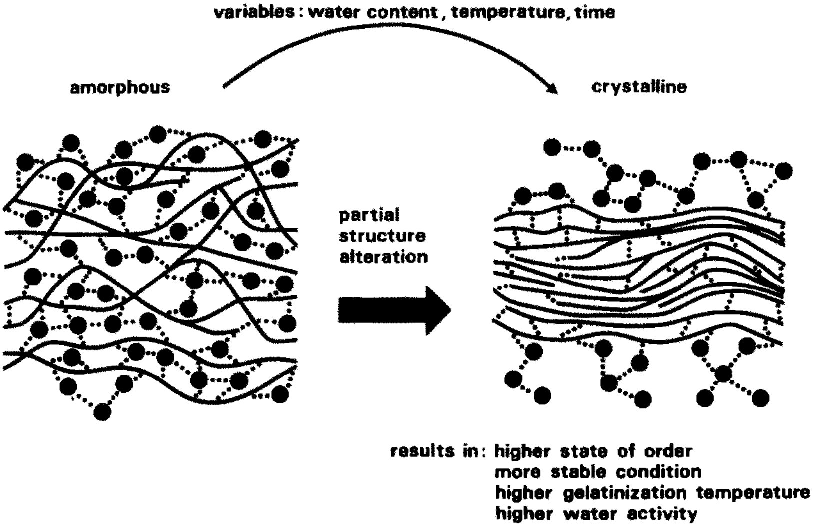


Fig. 2. Annealing effects of starch induced by water, temperature and time.

to a change in the functional behaviour of starch. Therefore, the melting or disintegration of cereal starch and amylose–lipid complexes and retrogradation effects were studied in the present paper. These conformational changes occur during the grinding of cereals or during extrusion, drying, steaming, baking, toasting, kilning or cooking processes.

EXPERIMENTAL AND RESULTS

The principles and methods of DSC thermal analysis are described elsewhere [4,5]. A Netzsch heat flux DSC 444 was used in the present study

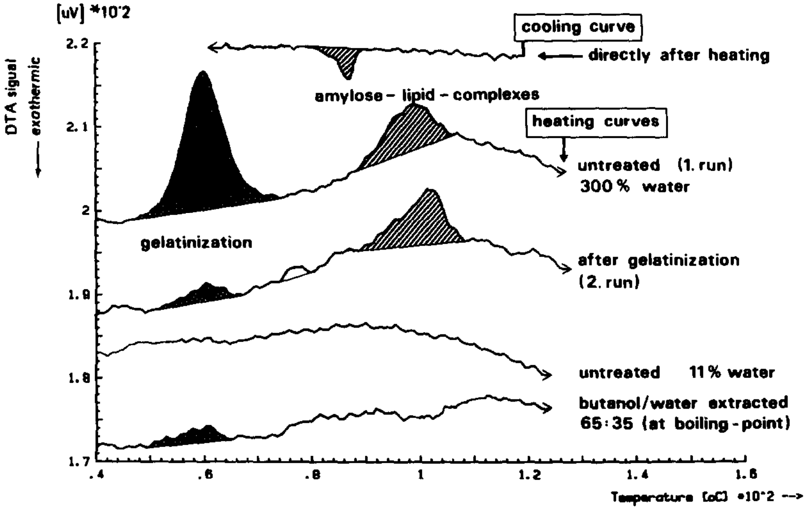


Fig. 3. Thermoanalytical characterisation of oat starch by DSC. Thermograms show disintegration (starch with an excess of water). Reintegration of the amylose–lipid complex is shown on the cooling curve. No phase transition is detectable with a water content of 11%.

[2,3]. All scans were performed at heating or cooling rates of 3° C min^{-1} with Al_2O_3 as a reference. The measurements were made using sealed stainless steel crucibles, mainly with a sample to water ratio of 1 : 4 (excess of water). The temperature range of interest was between 40 and 130° C. In addition, DSC was used to produce thermal events to study the thermal behaviour of natural untreated samples or to evaluate the character and intensity of a pre-induced treatment. Samples of wheat, oat, wheat flour, wheat starch and wheat breadcrumb were chosen.

There were two endothermal disintegrations of untreated cereal starch: the first, in excess water and above 50° C, is an irreversible disruption of the secondary molecular order within the starch granule; and the second, above 90° C, is a reversible disintegration of the amylose–lipid complexes, see Fig. 3. The transition temperatures of both thermal events depend on the availability of water. As moisture levels of flour or starch are reduced, the starch transition temperatures rise to increasingly higher values. The shift is much greater for the amylose complexes than for gelatinisation, see Figs. 4 and 5. Observations on the water-dependent thermal stability of starch are of general interest, especially because most food systems exist in limited water conditions. As soon as the water level drops below about 30%, the temperature of gelatinisation increases steeply, see Fig. 4. In further experiments, no endothermal transitions were seen when the water content was below 22.5% (see Fig. 6). In this case, no notable thermal event occurs in the expected range of 50–90° C.

Because of the limited water content present during cereal processing, a high degree of starch gelatinisation will not appear in breakfast cereals or

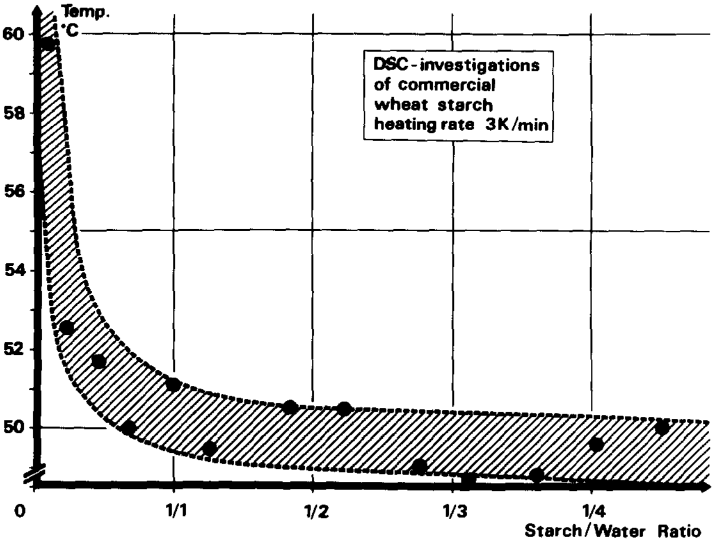


Fig. 4. Phase transition temperatures (onset of gelatinisation) of isolated wheat starch.

most bakery products. However, the processing conditions, including water availability, pressure, temperature and mechanical forces, differ greatly both between processes in general and within a process in particular. Therefore, starch may be modified to forms with very different functional and nutritional properties [6,7]. If the extracted starch dries under high temperature conditions, an alteration of the thermal behaviour follows. After heat treatment, wheat starch in excess water displays pre-cooking effects, seen in

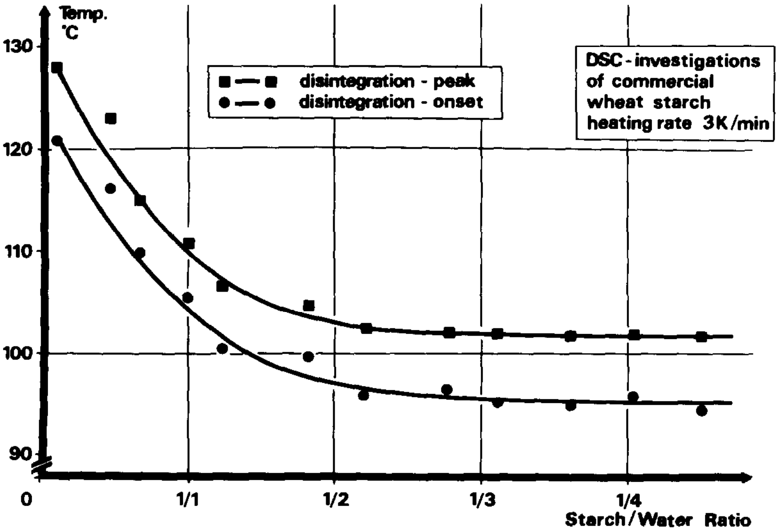


Fig. 5. Melting temperatures of amylose–lipid complexes of isolated wheat starch.

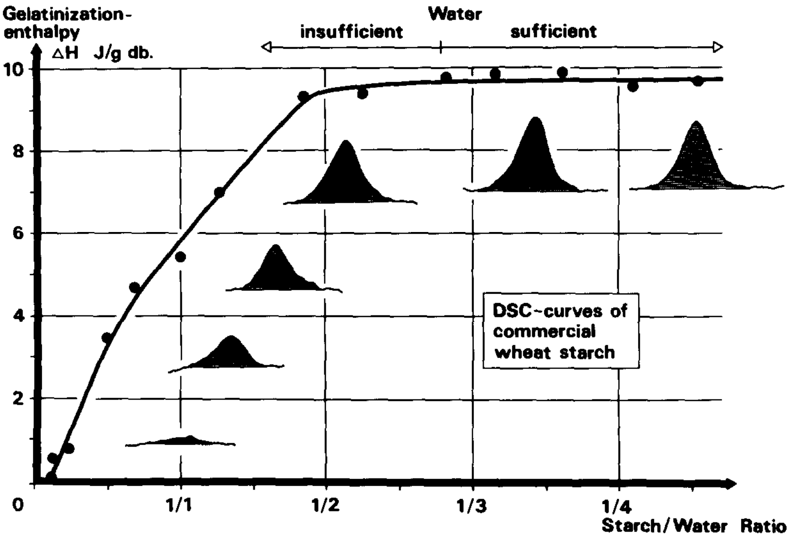


Fig. 6. Degree of gelatinisation of isolated wheat starch plotted against water availability.

the DSC thermograms of Fig. 7. Depending on the heat treatment, both the ranges of gelatinisation and the remaining gelatinisation enthalpy shift to decreasingly lower values. An analogous situation exists in oat starch during the production of oat flakes, see Fig. 8.

When cereal is milled to produce flour, some of the starch granules are damaged by mechanical action. The disruption of the crystalline regions of the starch suffered during the grinding process, leads to a higher accessibility

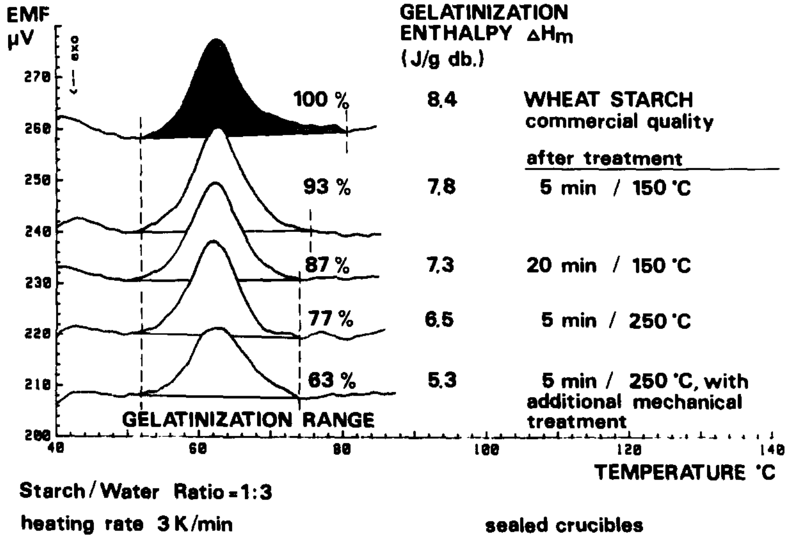
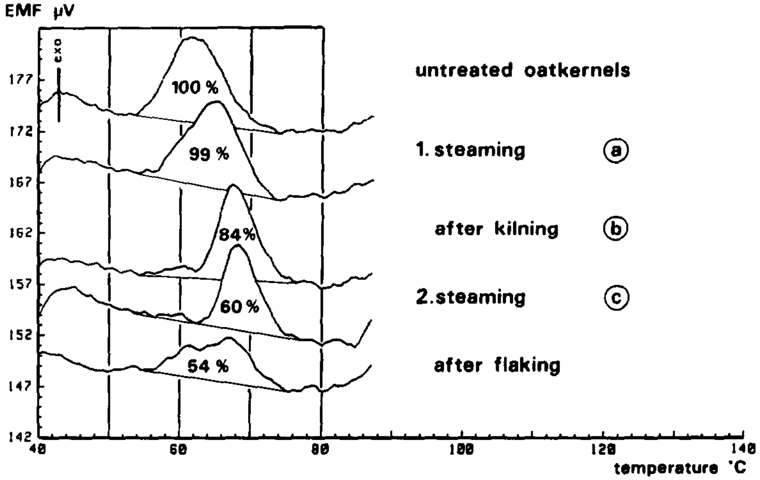


Fig. 7. DSC thermograms of untreated and heat-treated isolated wheat starch.



a · constant 15 min / 100 °C
b : altogether 90 min, (60 min at 100 °C)
c : after reaching 100 °C, 15 min affecting time

material/water - ratio = 1 : 3
heating rate 3 K/min
steeping 3 h/25 °C

Fig. 8. DSC thermograms of raw and processed oat samples. Peak area indicates the remaining gelatinisation level during the production of oat flakes.

of water to the starch molecules. Therefore, the gelatinisation onset of starch falls to lower values, whereas the gelatinisation peak temperature slightly increases, see Fig. 9. The diminished energy required for the melting of the remaining crystalline zones indicates an irreversible conformational change

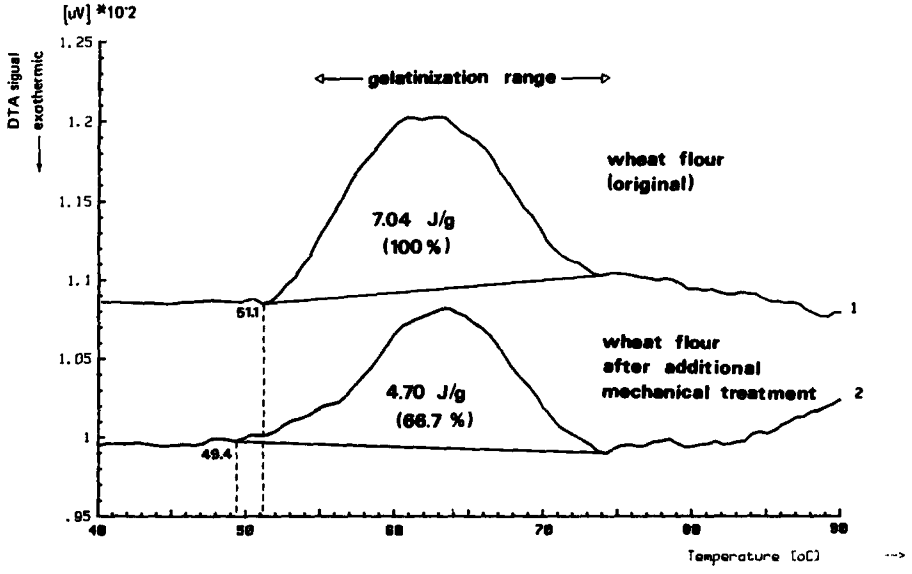


Fig. 9. DSC thermograms of untreated and ball-milled wheat flour (ash type 550).

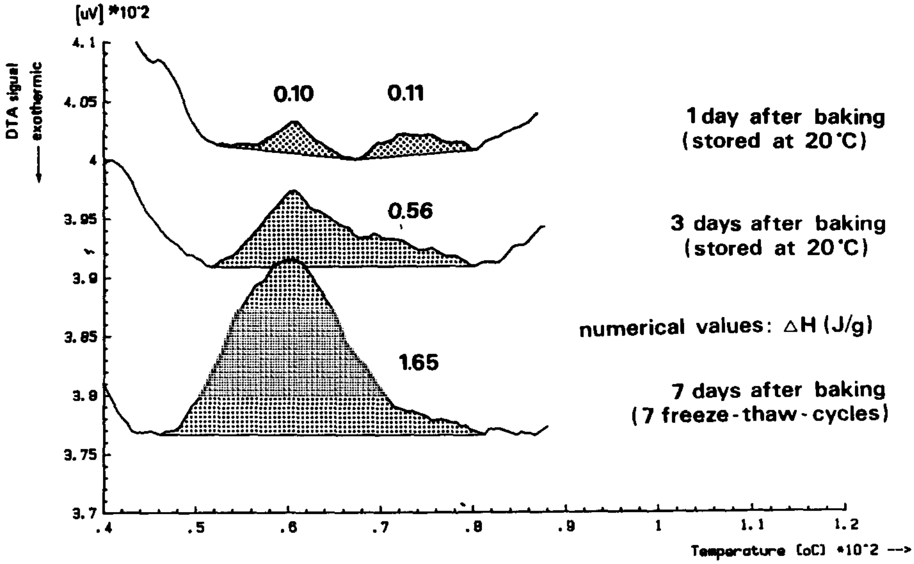


Fig. 10. DSC thermograms of sweet (sucrose) yeasted breadcrumb after storage at 20 °C for 1, 3 and 7 days.

of the starch, induced by mechanical forces during grinding. The area below the peak is directly proportional to the level of starch damage.

As time passes after gelatinisation, the starch hardens by reassociation of the molecules comprising the gelatinised starch. This is called "retrogradation of starch". Retrogradation is an exothermal change from a swollen, gel-like state to a more crystalline state; it occurs even in food systems where the starch is not in solution, which includes most starch-based food. The undesirable staling of bread during its storage is caused in part by this retrogradation of starch. It has long been known that bread can be refreshened by heating (e.g. toasted bread). In this case an endothermic transition would be observed when retrograded bread crumbs are heated. As retrogradation progresses during storage time, the area of these endothermal peaks increases (Fig. 10).

CONCLUSIONS

The information obtained from these DSC investigations should be useful to the cereal processing industry for quality control and equipment design. As can be seen from this brief review, DSC analysis can be applied to a wide range of physiocochemical changes which occur during cereal treatment. DSC measuring measurements can lead to an enhanced knowledge of both the functional and nutritional qualities of cereal starch.

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