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DEMONSTRATION OF CHANGES IN STRUCTURE IN CEREAL STARCHES BY HEAT FLUX DSC*

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SUMMARY

The origin of gelatinization behaviour of cereal starch has changed by the affecting variables water content, heat and time. These alterations are due to overmolecular changes of the starch and are called annealing. The effects were detected with wholemeal of rye and wheat and wheat starch by DSC measurements. Annealing leads to a change in gelatinization enthalpy, contraction of the temperature range of gelatinization and an increase of phase transition temperature.

INTRODUCTION

Amorphous-semicrystalline biopolymers, such as native cereal starches, are not in a thermodynamically stable condition. Therefore, spontaneous overmolecular changes in structure appear when there is sufficient mobility of the system. In the range between glass transition and melting, amorphous sequences of the starch can partially turn into a more stable and quasi-crystalline condition favoured by the variables water content, temperature and time (refs. 1-2) . This results in an association of mobile and linear molecular chains because of cohesive forces; at the same time direct intermolecular hydrogen bonds emerge. Therefore, the portion of the hydroxyl groups for the water accumulation decreases (increasing water activity). With further mobility loss crystalline micells with higher order condition, higher thermal stability and less sorption ability for water can emerge (refs. 3-5) .

PRINCIPLE

The thermodynamic characteristics of starch change by the partial transformation of starch from disordered crystallites to more stable ones. As there are no real phase transitions it must be said to be a thermodynamic reaction of second order: no transition heat, increase in specific heat capacity (C_P). An increased order condition of starch structure can be demonstrated indirectly by Differential Scanning Calorimetry (DSC) on the basis of the following characteristics: increase of water mobility (freezable water, water activity), increase of glass transition temperature (T_g), increase of melting or gelatinization temperature (T_m), increase of gelatinization enthalpy (ΔH_m)and contraction of temperature range of gelatinization. The description of the changes in

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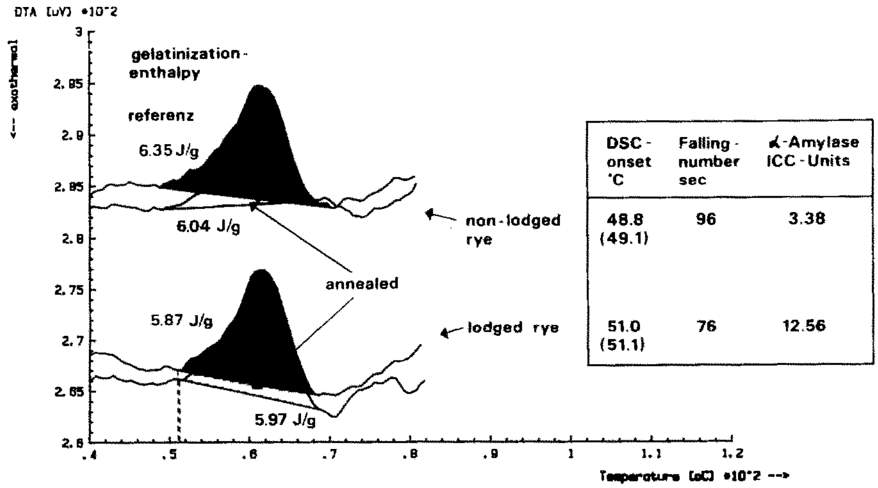
structure was made indirectly in the investigation by recording the behaviour of starch gelatinization.

EXPERIMENTAL

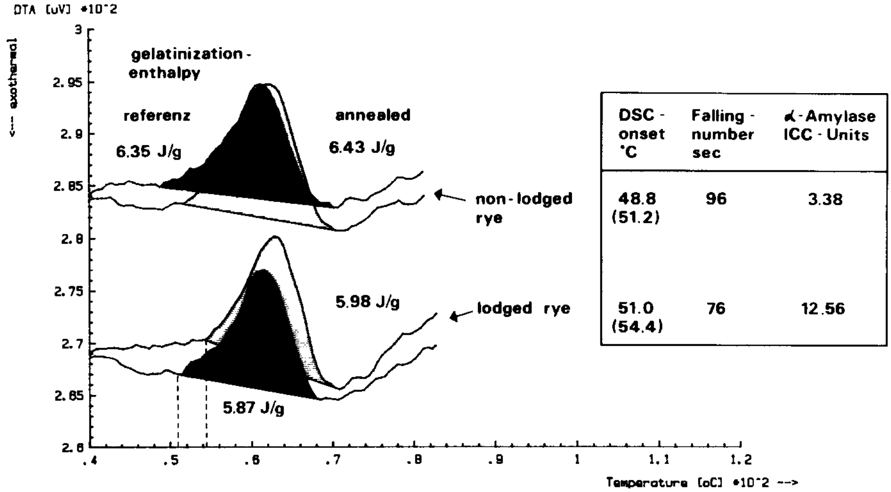
Gelatinization is a characteristic thermodynamic reaction of the first order in general appearing under water surplus at heating. As the overmolecular structures are disintegrated by losing hydrogen bonds the reaction takes an endothermic course. A three dimensional loosely bound network (gel condition) results from an amorphous-crystalline structure by phase transition. This network also behaves metastably (retrogradation of starch). Rye suspensions gelatinize in the temperature range of about 50 to 70 °C, wheat at 50 to 80 °C. A water content of more than 250 % on dry basis was determined for a complete gelatinization.

The investigations were made on a NETZSCH DSC 444 with wholemeal of rye and wheat (see Figs. 1-4) as well as with commercial starch (see Figs. 5 and 6) of different qualities (with and without thermal modification). The measurements were made in the temperature range of 40 ... 90 °C with a heating rate of 3 K/min in closed pressure-tight high-grade steel crucibles. The samples were treated under water surplus (relation between material and water 1 : 3). The measurements were duplicated for each material.



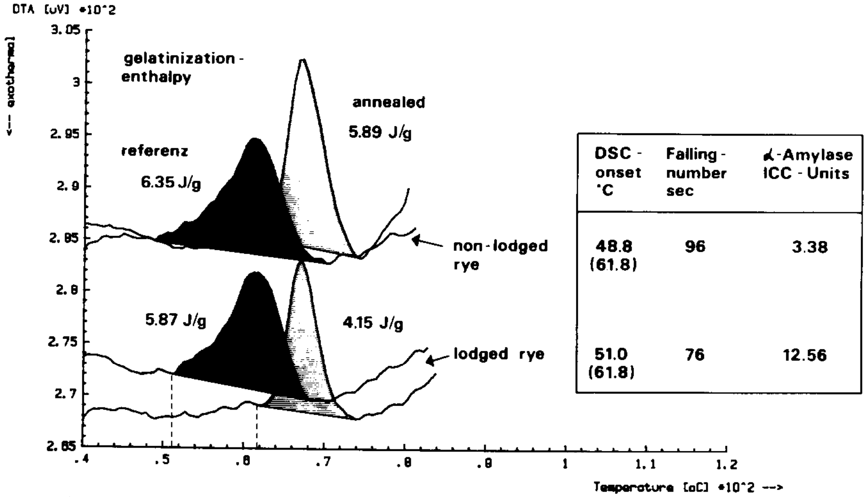
DSC-onset °C	Falling-number sec	α-Amylase ICC-Units
48.8 (49.1)	96	3.38
51.0 (51.1)	76	12.56

Fig. 1. Influence of Tempering (8 °C, 16 h, water activity 0,96) on the gelatinization of wholemeal rye (two different qualities) Dark area: comparative experiment without treatment



DSC - onset °C	Falling - number sec	α-Amylase ICC - Units
48.8 (51.2)	96	3.38
51.0 (54.4)	76	12.56

Fig. 2. Similar to Figure 1 (25 °C, 16 h, water activity 0,96)



DSC - onset °C	Falling - number sec	α-Amylase ICC - Units
48.8 (61.8)	96	3.38
51.0 (61.8)	76	12.56

Fig. 3. Similar to Figure 1 (45 °C, 16 h, water activity 0,96)

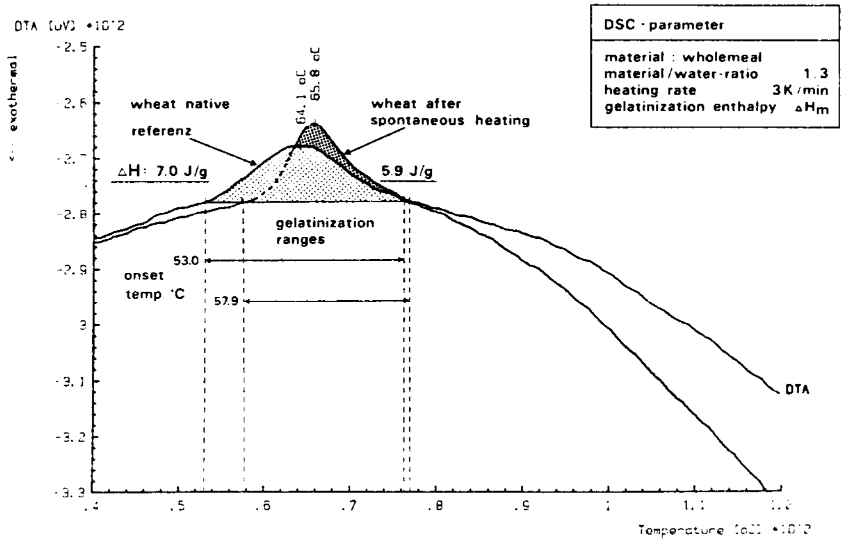


Fig 4. Changes of gelatinization of wholemeal wheat after self-heating (within 23 days to 67,2 °C, 21,5 % moisture content of grain, variety: Kanzler

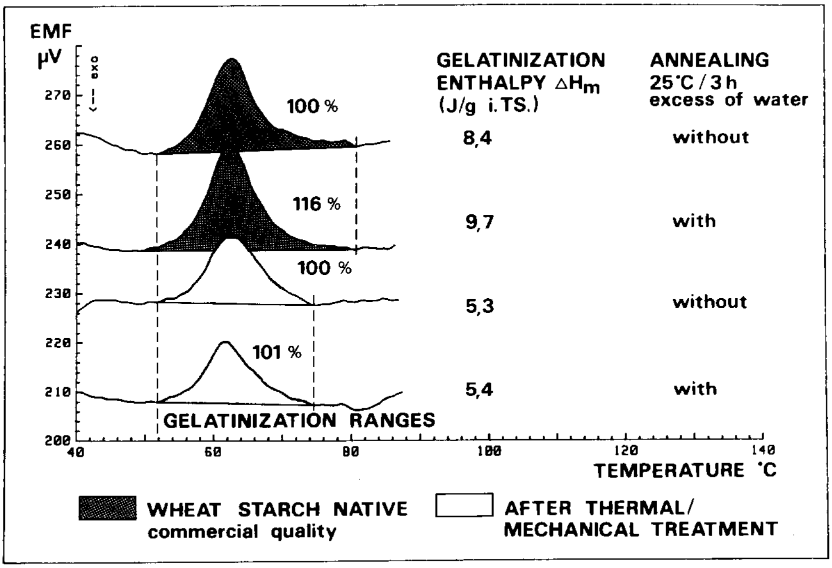


Fig. 5. Changes in gelatinization of wheat starch by primary treatment (25 °C, 3 h, water activity 0,96)

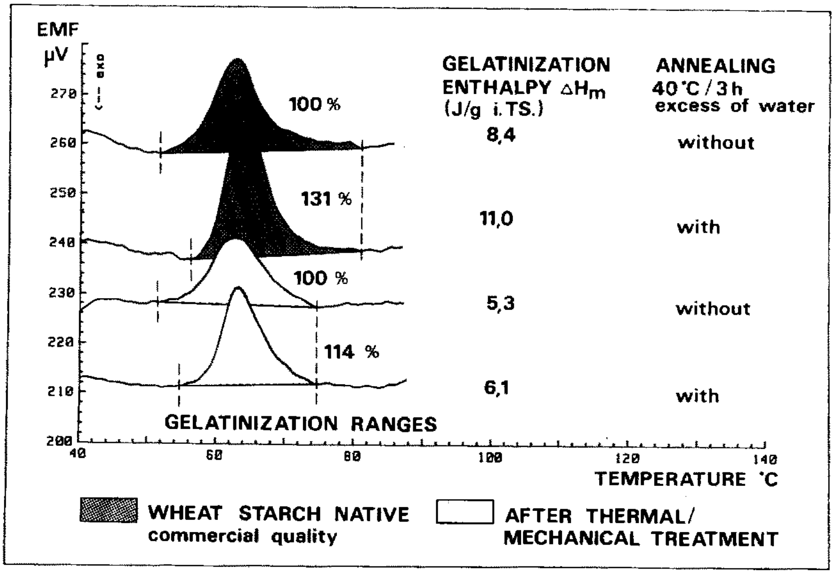


Fig. 6. Changes in gelatinization of wheat starch by primary treatment (40 °C, 3 h, water activity 0,96)

RESULTS

The experimental investigations show that the mentioned phenomena of changes in structure appear dependent on temperature and time, both under simulated conditions of a natural development in the field (see Figs. 1 - 3), and during the real development after harvest in the grain store under self-heating (see Fig. 4) and furthermore in commercial wheat starch which was tempered for 3 hours (see Figs. 5 and 6). In comparison to the initial samples, the DSC gelatinizations show the typical characteristics of the change in structure concerning starch (see Figs. 3, 4, and 6), especially under stronger heat influence. That is, there results a movement of the gelatinization temperature (T_m), and a narrower gelatinization range. The increase of the gelatinization enthalpy could only be determined where the time interval of the thermal annealing was low, on the basis of little-existing amylolytic enzymes. In the other cases a decomposition of starch polymers appeared under a higher temperature influence on the basis of the enzyme effect during treatment. This can be seen from the lowered gelatinization enthalpy (ΔH_m) in comparison to the reference sample (see Figs. 3 and 4).

CONCLUSIONS

From the application-technical view these results mean that the hydrothermal influence on native biopolymers must be given greater consideration because depending on the strength of the changes in structure, the gelatinization process requires different quantities of heat. The results concerning rye are extraordinarily relevant where the gelatinization temperature is an important criterion for quality. The quality of the starch can be favourably influenced by well-aimed manipulation as well as by suitable weather conditions in natural environment during maturation.

The figures given in this study are part of a poster, presented at the 8 th Ulm Calorimetry.

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