

Thermal Modifications of Starch During High-Temperature Drying of Pasta

C. Zweifel,¹ B. Conde-Petit,^{1,2} F. Escher¹

ABSTRACT

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Changes in starch at the molecular level during high-temperature (HT) drying of pasta were studied with differential scanning calorimetry (DSC). Pasta was manufactured from durum wheat semolina into the shape of spaghetti on a pilot-plant installation. The HT phase (100°C) was applied at relatively high (27 g/100 g, wb), intermediate (20 g/100 g), and low (15 g/100 g) product moisture, respectively. Spaghetti dried at 55°C served as reference samples. The changes in the thermal properties of starch during drying were dependent on the drying conditions. The gelatinization enthalpy of pasta dried at 55°C was reduced by 30% during drying, which indi-

cates a partial melting of the starch crystallites. With the beginning of the HT phase, the gelatinization enthalpy increased to final values that were close to or higher than those of freshly extruded pasta. In general, HT drying of pasta induced a broadening of the gelatinization range. Starch crystallinity remained unchanged during extrusion and drying at HT. Based on a state diagram of starch and on DSC measurements of pasta during drying, it is hypothesized that HT drying favors molecular rearrangements of starch polymers at the double helical level.

Drying is the most critical as well as the most difficult step in pasta production. Traditionally, pasta was dried at $\leq 50^\circ\text{C}$ for 20–30 hr, yielding a product moisture content of 12 g/100 g, wb. Such a process is usually referred to as conventional or low temperature drying (Mondelli and Milatović 1991). In the past 20 years, the drying temperatures have been continuously increased to $\leq 100^\circ\text{C}$. Two different approaches are being taken by pasta manufacturers to obtain the maximum benefit of high-temperature (HT) drying: HT is either applied at the initial phase of the drying process, or during the final drying phase after predrying at low temperatures (Pavan 1981). There is some indication that the latter method may be more effective in improving pasta cooking quality (Manser 1979, Dexter et al 1981, Resmini and Pagani 1983, Abecassis et al 1984, De Stefanis and Sgrulletta 1990). Literature data confirm that the water activity of pasta at the time of application of HT and the duration of the HT phase are particularly critical to pasta properties (Dexter et al 1981, Dexter et al 1984, Baroni 1988, Feillet 1988).

Overall quality of durum wheat pasta is influenced primarily by the properties of the protein and the starch fraction, and the transformation during extrusion, dehydration, and cooking (Aktan 1990). Different physicochemical techniques such as wide-angle X-ray diffraction and nuclear magnetic resonance may be applied to study the changes taking place at the molecular level on processing starch. However, the most commonly used technique for starch characterization is differential scanning calorimetry (DSC). This technique, which detects the heat flow as thermal events of polymeric materials occur, provides valuable insight into order-disorder phenomena of granular starches (Donovan 1979, Biliaderis et al 1980, Kugimiya et al 1980, Burt and Russell 1983).

While the influence of protein on the properties of pasta is well documented in the literature, less information is available on the influence of starch on pasta quality. Several authors have documented physicochemical transformations of the starch fraction of pasta, with emphasis on HT drying processes at $>100^\circ\text{C}$ (Dalbon et al 1985, Pagani et al 1986). The consequences of any starch transformation at HT drying processes for structure development and product quality is far from being clear. Cunin (1995) observed that the gelatinization temperature shifted to higher values when HT drying was applied. Furthermore, the gelatinization enthalpy values were reduced when drying was shifted from low temperature (40°C) to HT (90°C) conditions. Vansteelandt and Delcour (1998)

determined the effect of an industrial drying cycle on starch properties. The authors found that starch isolated from HT-dried pasta showed higher gelatinization temperature and viscosity and lower swelling power and solubility. It was suggested that HT drying of pasta results in less permeable and thus more rigid starch granules. Yue et al (1999) found that starch isolated from HT-dried pasta showed a narrower gelatinization range, but they did not detect changes in onset (T_o) and melting temperatures (T_p), nor in gelatinization enthalpy (ΔH). A comparison with starch in unprocessed semolina and wheat revealed that all starch extracted from pasta shifted to higher gelatinization temperatures with narrow gelatinization ranges but no changes in gelatinization enthalpies. The melting enthalpy of the amylose-lipid complexes was not affected by the drying cycles.

There is still a lack of information on the effect of HT drying on the properties of starch, as most investigations did not follow the changes of the physicochemical properties of starch at the different stages of drying. There are indications that the gelatinization behavior does not change steadily in the course of drying (Vansteelandt and Delcour 1998). To date, no investigation dealt with the effect of HT drying at high, intermediate, and low product moisture, respectively, on the structural changes of the starch fraction at the molecular level.

The aim of the present study was to study the changes in the starch fraction during HT drying of durum wheat spaghetti. The drying conditions were selected in such a way that the high temperature was applied at high (early HT phase), intermediate (intermediate HT phase), or low (late HT phase) product moisture content. The changes in the starch fraction were assessed by DSC and X-ray diffraction. Furthermore, the pasta processing steps are discussed based on a starch-water state diagram. The latter was constructed based on DSC measurements of semolina at various moisture levels.

MATERIALS AND METHODS

Durum Wheat Semolina

Commercial durum wheat semolina was delivered from Swiss-mill (Stadmuehle Zuerich, Zurich, Switzerland). According to the manufacturer, the durum wheat semolina consisted of a mixture of Canadian western amber durum (CWAD) and U.S. amber durum (USAD) in a proportion of 55:45. The moisture content of the semolina varied from 10.8 to 12.5 g/100 g, wb, protein content from 13.9 to 14.3 g/100 g, db, and ash content from 0.76 to 0.84 g/100 g, db. The particle size distribution was: 15% of 125–200 μm , 37–47% of 200–315 μm , 25–35% of 315–400 μm and 18% of 400–500 μm .

Pasta Processing and Drying

For the production of standard pasta, 3.0 kg of semolina were weighed into a mixer (UM 12, Stephan Ltd., Hameln, Germany).

¹ Institute of Food Science, Swiss Federal Institute of Technology (ETH), CH-8092 Zurich, Switzerland.

² Corresponding author. Phone: +41 1 632 37 31, Fax: +41 1 632 11 23, E-mail: beatrice.conde@ilw.agrl.ethz.ch

Tap water (total water hardness: 1.5 mmol/L, pH 8.1) at 35°C sufficient to obtain a moisture content of 31.0 g/100 g, wb, was slowly added in two equal portions. After each addition of water, mixing was done at 1,400 rpm for 30 sec. The sample was allowed to rest for 10 min and again mixed at the same conditions. The dough was mixed in a vacuum mixer of a pasta extruder for 12 min (single screw, length-to-diameter ratio 35:5, capacity 20-70 kg/hr) (Buehler Ltd., Uzwil, Switzerland) until a second batch of dough of equal size to the first one was ready for extrusion. The dough (≈ 8 kg) was extruded at $40 \pm 2^\circ\text{C}$, extrusion pressure of 120 ± 8 bar, low mixing pressure of 0.2 bar, and with a mass flow of 30 kg/hr. The pasta was formed into the shape of spaghetti through a Teflon-coated die (1.85 ± 0.01 mm, diam) (Osterwalder Ltd., St. Gallen, Switzerland). The total residence time at ambient conditions ($25 \pm 2^\circ\text{C}$, 65-75% rh) until a rack was ready for drying was <10 min.

The spaghetti strands were dried in a laboratory dryer (10 kg fresh pasta) (Afreim Ltd., Lyon, France) using four different temperature-time profiles as shown in Fig. 1A-D. The relative humidity was the same for all drying profiles. The humidity was kept constant at 80% rh until cooling started and was then lowered to 60% rh. The main difference concerned the time at which 100°C (HT) was applied. An early HT phase reduced the moisture content of the product from 27 to 13 g/100 g, an intermediate HT phase reduced the moisture content of the product from 20 to 13 g/100 g, and a late HT phase reduced the moisture content of the product 15 to 13 g/100 g. Pasta dried at 55°C served as a reference.

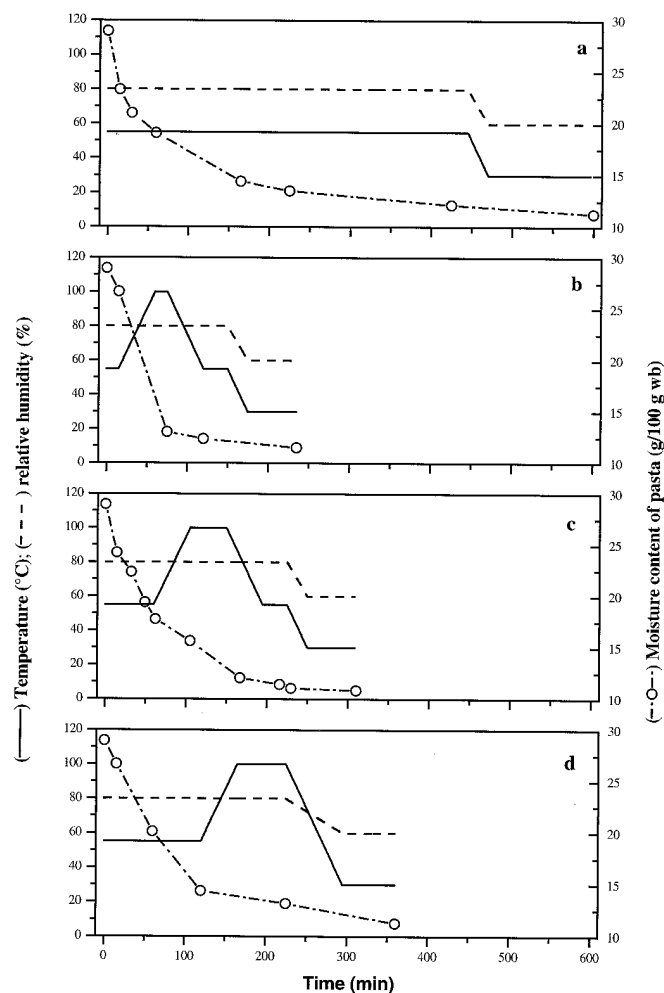


Fig. 1. Temperature-humidity profiles and drying curves during pasta drying: reference profile at 55°C (a); drying profiles with a HT phase at 100°C: early HT phase 100°C (b); intermediate HT phase 100°C (c); and late HT phase 100°C (d).

The heating and cooling rates were 1°C/min. The air flow (≈ 5 m/sec) was vertical to the spaghetti to ensure uniform drying. Depending on the drying temperature, the total process time was 4–10 hr.

DSC

Pasta samples were taken out of the drier at regular intervals, immediately milled to pass through a 0.5-mm mesh screen on a centrifugal mill (Typ ZW1, Retsch GmbH & Co, Haan, Germany) and packed into gas proof bags. The moisture content of the milled pasta powder was immediately determined by drying ≈ 2 g with an infrared dryer (LP16, Mettler-Toledo, Greifensee, Switzerland) at 120°C for 10 min. The time interval between removal of the samples from the dryer and DSC measurement was <6 hr. For DSC measurements, milled pasta powder was mixed with deionized water to obtain a moisture content of 70 g water/100 g. Thus, the thermal behavior of starch was characterized at excess moisture conditions to minimize secondary crystallization processes during the measurements. The moist samples were allowed to equilibrate for 15 min before DSC measurements to attain an even distribution of water. Moist samples (35-45 mg) were weighed into DSC pressure pans (Perkin Elmer Ltd., Norwalk, CT).

DSC measurements were also conducted on semolina samples at different moisture levels for the determination of the starch-water state diagram. Moisture levels were adjusted between 20 and 80 g/100 g. The samples were equilibrated for 15 min and weighed into DSC pressure pans as described above.

The measurements were made on a DSC system (Thermal Analyst 2000, DSC 2910, TA Instruments Ltd., Newcastle, UK) calibrated with indium, and an empty pan was used as reference. The samples were heated at a rate of 4°C/min from 4 to 140°C with nitrogen flushing (40 cm³/min). The dry matter content was determined in each individual pan after DSC scan by puncturing and drying the pan at 105°C for 16 hr.

The temperature and the enthalpy of the melting transition M_1 and M_2 , which are attributed to the disorganization of starch crystallites in excess water and limited water conditions, respectively, and of the melting transition M_3 , which corresponds to the reversible dissociation of the preexisting amylose-lipid complexes, were evaluated and termed according to Biliaderis (1998). For each endotherm, onset (T_o), peak (T_p), and conclusion (T_c) temperatures were evaluated using the TA instruments analysis software program. Furthermore, the melting ranges ($\Delta T = T_c - T_o$) were calculated. The T_o of the phase transitions was determined by the usual tangent method. For the construction of the state diagram, the effective onset of starch melting ($T_{o1 \text{ effective}}$) is the lower limit of the peak where a deviation from the baseline is recognizable. The enthalpies were expressed as ratios to the corresponding enthalpy changes of the raw material:

$$\text{Relative gelatinization enthalpy:} \quad \Delta H_1/\Delta H_{01}$$

$$\text{Relative enthalpy of the melting of amylose-lipid complex:} \quad \Delta H_3/\Delta H_{03}$$

where: ΔH_1 = gelatinization enthalpy of pasta sample (J/g, db), ΔH_{01} = gelatinization enthalpy of semolina, ΔH_3 = melting enthalpy of the amylose-lipid complex of pasta, ΔH_{03} = melting enthalpy of the amylose-lipid complex of semolina.

All data represent the mean of at least two measurements of two to three productions of pasta. Standard deviations of the enthalpies and transition temperatures were generally within 5% of the mean.

Wide Angle X-ray Powder Diffraction

Samples were milled to pass through a 0.5-mm mesh screen on a centrifugal mill (Typ ZW1, Retsch GmbH & Co, Haan, Germany). The milled pasta samples were conditioned over saturated BaCl₂ solution to obtain a moisture content of 12 g/100 g, wb. The samples were compressed into thin disks of 1-2 mm thickness and

a diameter of 13 mm and were subsequently mounted on a sample holder. The wide-angle X-ray diffraction measurements were made at ambient conditions in the transmission mode on a powder diffractometer (Siemens Kristalloflex D500, Karlsruhe, Germany) equipped with a monochromator that selects $\text{CuK}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$) with 35 mA and 40 kV. A divergence slit of 2 mm and a receiving slit of 1° were selected. The relative intensity was recorded in a scattering angle (2θ) range of $5\text{--}30^\circ$ with a scintillation counter at a scanning speed of $0.05^\circ/\text{min}$.

RESULTS

State Diagram of Starch in Semolina and Temperature-Humidity Conditions During Pasta Processing

Starch transformations are primarily governed by temperature, moisture and time conditions. To understand and predict the changes in the starch fraction during drying of pasta, it is convenient to analyze the temperature-moisture conditions during pasta processing. For this purpose, the thermal behavior of semolina at various moisture levels was assessed by DSC. Based on the thermal data, which primarily reflect the behavior of starch, a state diagram for the binary starch water system was plotted (Fig. 2). T_{p1} and T_{p2} are presented including the onset (T_{o1} and $T_{o1 \text{ effective}}$) and conclusion (T_{c1}), respectively. Additionally, T_{p3} is presented in the state diagram. Furthermore, literature values for glass transition temperatures (T_g) of wheat starch as a function of moisture content (Zeleznaek and Hosenev 1987) are also shown. Finally, the temperature and the sample moisture conditions at various stages of the pasta process were also plotted.

The state diagram of starch in Fig. 2 shows that transformation during heating is determined by the availability of water as shown by other authors (Donovan 1979, Biliaderis et al 1980, Cooke and Gidley 1992, Garcia et al 1996). Wheat starch transformation at excess water conditions ($>60 \text{ g}/100 \text{ g}$) is characterized by a large M_1 endotherm with a melting temperature T_{p1} at $\approx 63^\circ\text{C}$. At intermediate water conditions ($35\text{--}60 \text{ g}/100 \text{ g}$) endotherms M_1 and M_2 are observable. The two-stage melting process reflects the first rapid melting of crystallites (M_1) followed by a HT melting of remaining crystallites (M_2). At limited water conditions ($<35 \text{ g}/100 \text{ g}$), the M_2 transition becomes dominant and T_{p2} increases strongly as the water content decreases. On the other hand, the effective onset

of starch melting ($T_{o1 \text{ effective}}$) is $\approx 50\text{--}55^\circ\text{C}$ and is almost independent of moisture conditions down to water content of $30 \text{ g}/100 \text{ g}$. It should be noted that $T_{o1 \text{ effective}}$ is $5\text{--}10^\circ\text{C}$ lower than T_{o1} as determined by the usual tangent method (Eerlingen et al 1996). The latter method has the advantage of having a better reproducibility. Similarly to the melting of the native amylopectin, the melting temperatures of amylose-lipid complexes (T_{p3}) are depressed by increasing availability of water, and remain constant at excess water conditions. The glass transition T_g is lowered from $\approx 140^\circ\text{C}$ to ambient temperature by increasing the moisture content $6\text{--}23 \text{ g}/100 \text{ g}$, which confirms that water is a very effective plasticizer for natural semicrystalline polymers (Bair 1981, Zeleznaek and Hosenev 1987).

With regard to starch, pasta is processed at limited water conditions at temperatures that favor plasticization but prevent substantial

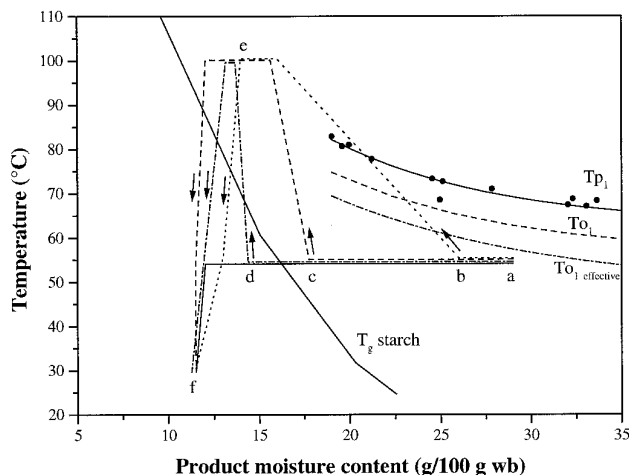


Fig. 3. Temperature-moisture conditions during spaghetti drying for four drying cycles: reference at 55°C (a, f), and drying profiles with a high temperature (HT) phase at 100°C : early HT phase 100°C (a, b, e, f), intermediate HT phase 100°C (a, c, e, f), and late HT phase 100°C (a, d, e, f) in relation to the onset (T_{o1} and $T_{o1 \text{ effective}}$), melting (T_{p1}) and glass transition of starch (T_g). Data on T_g were obtained from literature (Zeleznak and Hosenev 1987).

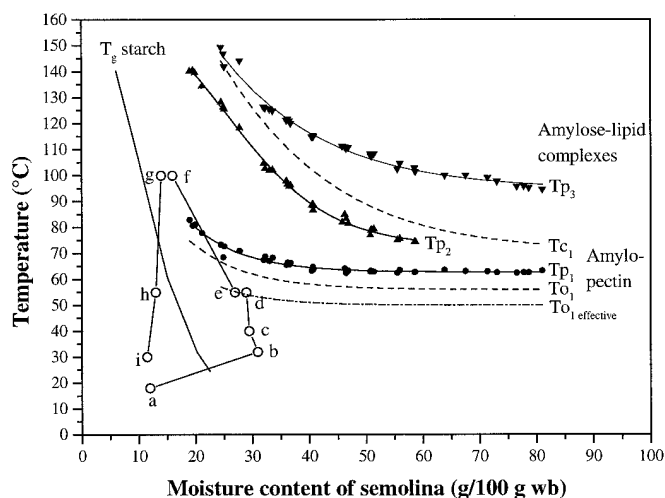


Fig. 2. State diagram of starch in semolina and temperature-moisture conditions during pasta processing: (a) semolina, (b) pasta dough, (c) freshly extruded spaghetti, (d) start of the drying cycle, (e) onset of high temperature (HT) phase, (f, g) HT phase at 100°C , (h) back to 55°C , (i) dried pasta. Starch melting temperatures T_{p1} and T_{p2} include onset (T_{o1} and $T_{o1 \text{ effective}}$), conclusion (T_{c1}) and melting temperatures of amylose-lipid complexes (T_{p3}). Data on T_g were obtained from literature (Zeleznak and Hosenev 1987).

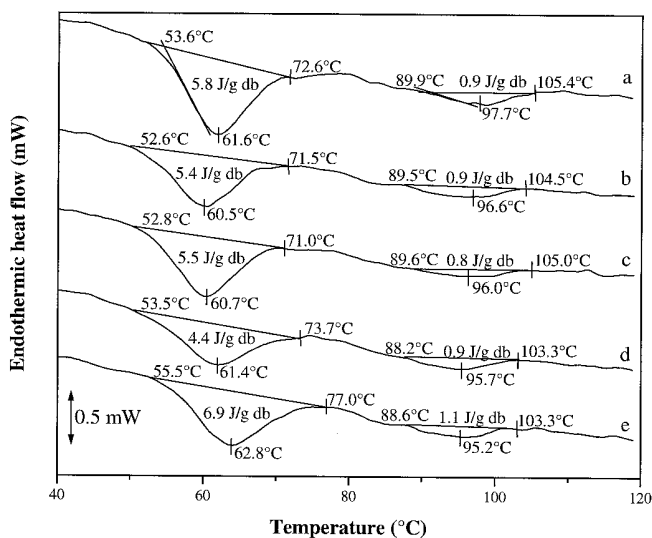


Fig. 4. Representative differential scanning calorimetry (DSC) thermograms of semolina (a), freshly extruded spaghetti (b), and of pasta dried with an early high temperature (HT) phase at 100°C after 15 min at 55°C (c), after 75 min at 100°C (d), and at the end of the drying profile (e). Onset temperatures were calculated by analysis software (example in a). Moisture of samples adjusted to $70 \text{ g}/100 \text{ g}$, wb.

melting. The temperature and moisture conditions during processing of pasta are marked into the state diagram of starch in Fig. 2 by the line from a to i. The temperature-moisture conditions correspond to a drying at 100°C with an early HT phase. During the first processing step (a to b), semolina is mixed with water to a level of 31 g/100 g at 30°C. Although plasticization of the protein fraction is the technological objective, the amorphous regions of starch also become mobile ($T > T_g$) if equal moisture distribution is assumed. During the extrusion of pasta (b to c), the temperature increases to 40°C while the moisture conditions remain almost unchanged. The aim of the subsequent drying (d to i) is the stabilization of pasta by transforming the product from the rubbery to the glassy state.

The presentation of the four different drying profiles in a state diagram of starch in Fig. 3 reveals that starch is plasticized by water, and maintained between T_g and T_p (T_{p1} or T_{p2}) in limited water during the drying process.

Based on the thermodynamics of semicrystalline polymers, it can be expected that thermal treatments between glass transition (T_g) and melting temperature (T_m) favor structural rearrangements of the polymers toward lower free energy (Wunderlich 1976, Biliaderis 1992, Stute 1992).

Changes in Thermal Properties of Starch During Pasta Drying

Representative DSC thermograms of semolina, freshly extruded spaghetti, and spaghetti at different stages of drying are presented in Fig. 4. The two distinct, symmetrical endotherms can be attributed to the gelatinization with excess water (M_1) and the reversible dissociation of the preexisting amylose-lipid complexes (M_3). In general, melting temperature (T_p), melting range (ΔT), and melting enthalpy values (ΔH) are in good agreement with similar studies on pasta (Cunin 1995, Vansteelandt and Delcour 1998, Yue et al 1999). Although pasta contains an appreciable amount of protein, transformation of the protein fraction during heating involves only small enthalpy changes that are not measurable as phase transition (Eliasson and Hegg 1980, Arntfield and Murray 1981). This allowed a characterization of starch in presence of protein without extraction that would otherwise increase the risk of artifacts (Grant 1998).

The freshly extruded spaghetti (Fig. 4, curve b) showed a slightly lower gelatinization peak temperature (60.5°C) and enthalpy (5.4 J/g) as compared with the raw material (61.6°C, 5.8 J/g) (Fig. 4, curve a). One characteristic of the DSC thermograms of spaghetti in a drying process with an early HT phase at 100°C is the progressive increase of the gelatinization temperature T_{p1} in the course of drying (Fig. 4, curves b to e). Over the drying period, the tem-

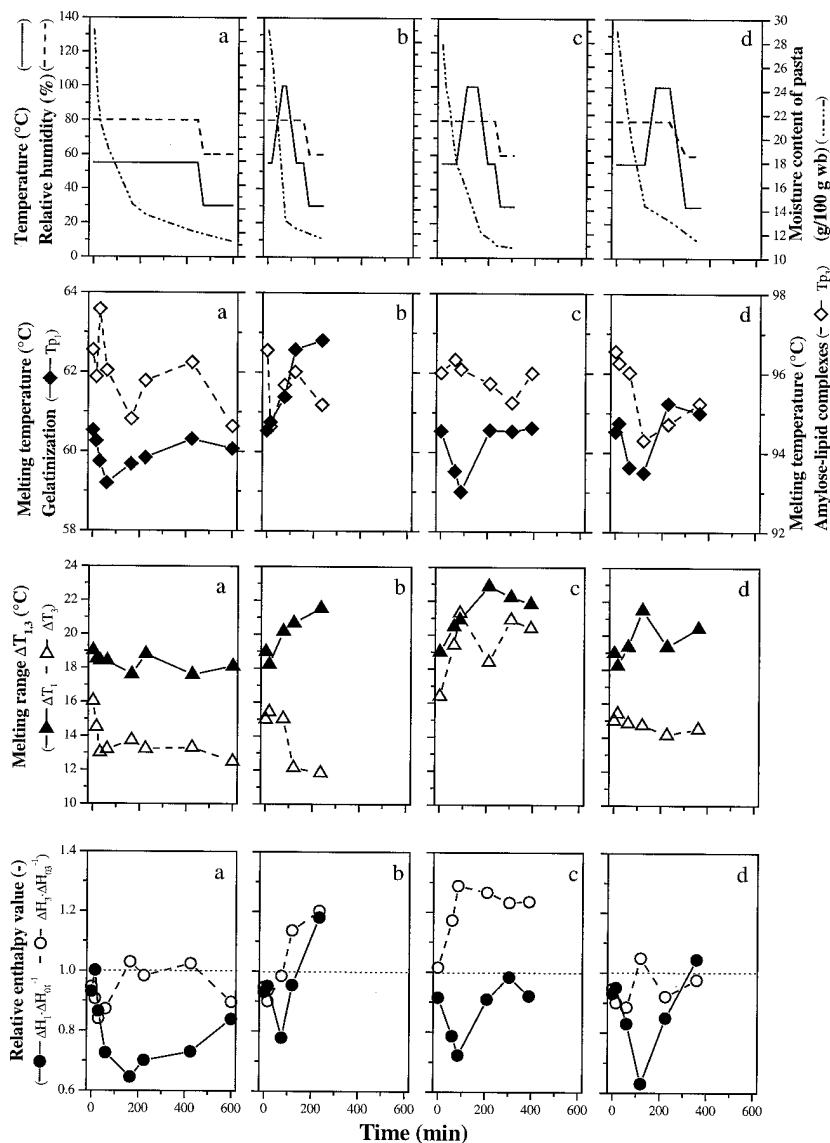


Fig. 5. Changes of melting temperature (T_p), melting range (ΔT), and relative enthalpy values of gelatinization ($\Delta H_1/\Delta H_{01}$) and melting of amylose-lipid complexes ($\Delta H_3/\Delta H_{03}$) of starch fraction of four differently dried spaghetti during drying. Reference (a), early high temperature (HT) phase 100°C (b), intermediate HT phase 100°C (c), and late HT phase 100°C (d). Moisture of samples adjusted to 70 g/100 g, wb.

perature increased by 2.3°C, and the melting range ΔT_1 ($T_c - T_o$) increased by 2.6°C. The shift of T_{p1} was accompanied by a decrease of the gelatinization enthalpy (ΔH_1) from 5.4 to 4.4 J/g during the first drying interval of 75 min, in which the temperature increased from 55 to 100°C. As the dehydration of spaghetti progressed, the gelatinization enthalpy increased again, and the melting enthalpy ΔH_1 of the final product was higher than that of the raw material (6.9 J/g). In addition, the endothermic transition (M_3) exhibited melting temperatures (T_{p3}) at $\approx 96^\circ\text{C}$ and melting ranges (ΔT_3) of 12–16°C. The enthalpy values of the latter transition were 0.8–1.1 J/g.

The changes in the thermal properties of starch during drying were dependent on the drying conditions. The effect of four different drying programs on the thermal properties of starch is summarized in Fig. 5 (reference at 55°C; drying at 100°C with an early, intermediate, and late HT phase). To compare the enthalpy changes of the starch fraction during drying of pasta, the enthalpy values ΔH_1 and ΔH_3 were expressed as ratios to the corresponding enthalpy changes of the raw material (ΔH_{01} , ΔH_{03}).

In all cases, the gelatinization temperature and enthalpy of freshly extruded spaghetti was lower than the raw material. Other authors (Cunin 1995, Vansteelandt and Delcour 1998) did not observe these changes in the DSC characteristics of freshly extruded spaghetti. During the first 2 hr of drying at 55°C (reference), the gelatinization temperature decreased by 1.3°C, and the relative gelatinization enthalpy was reduced by 30%. During subsequent drying, the trend was reversed, but the final values were still lower than those of the freshly extruded spaghetti. For all HT drying programs, the relative gelatinization enthalpy first decreased until the beginning of the HT phase similarly to the reference. After this point, the relative gelatinization enthalpy started to increase and, in contrast to the reference, the final enthalpies were close to (intermediate and late HT phase) or higher (early HT phase) than the values at the beginning of drying. The changes of the gelatinization peak temperature (T_{p1}) and the corresponding relative enthalpy values as a function of time are almost parallel for all drying profiles. This can be explained by the fact that the more thermostable the granule to gelatinize, the higher the energy required to melt its structure (Biliaderis 1990). In general, HT drying of pasta induced a broadening of the gelatinization range (ΔT_1). The properties of the amylose-lipid complexes were also affected by drying. The melting temperature (T_{p3}) tended to be lowered during drying, whereas the melting range (ΔT_3) was either narrowed (reference, early HT phase), broadened (intermediate HT phase) or was not affected (late HT phase). The melting enthalpy of the amylose-lipid complexes was not clearly affected by HT drying except for the early and intermediate drying, where an increase in the range of 20–30% was observed.

Changes in the Crystalline Structure of Starch

The DSC measurements of samples during processing have been complemented by wide-angle X-ray powder diffraction measurements to investigate whether the large differences in the gelatinization enthalpies, which were induced by drying, were the result of differences in starch crystallinity. X-ray diffraction on semolina was made as a reference. In addition, X-ray diffraction measurements of freshly extruded pasta and two pasta samples with large differences in the relative enthalpy of gelatinization were characterized (reference after a drying time of 165 min [$\Delta H_1 = 4.0$ J/g] and spaghetti dried with the early HT phase at 100°C at the end of the drying process [$\Delta H_1 = 6.9$ J/g]). The X-ray diffractograms are presented in Fig. 6. All samples showed reflections at 15, 17, 18.1, and 23.3° which are typical for A-type patterns (Le Bail et al 1993). A slight decrease in crystallinity was observed by comparing the raw material with freshly extruded pasta, but no major changes were found between pasta at different stages of drying. Similar diffractograms were obtained by Cunin (1995), who did not find differences between differently dried pasta.

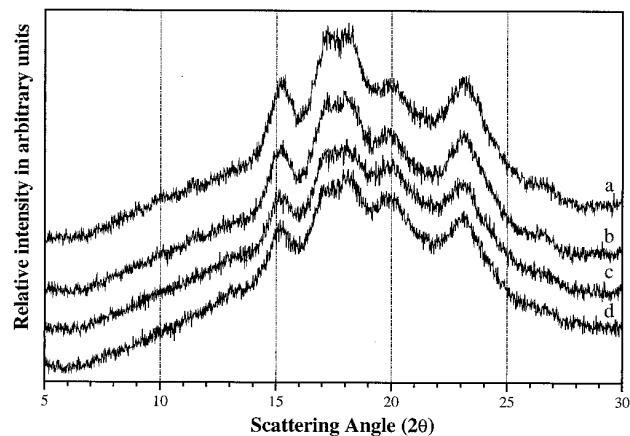


Fig. 6. X-ray diffractograms of semolina (a), freshly extruded spaghetti (b), spaghetti dried with the reference drying program (sample measured after 165 min of drying time) (c), and of the final product of spaghetti dried with the early high temperature (HT) phase 100°C drying program (d).

DISCUSSION

By considering the temperature-moisture conditions during pasta processing based on a state diagram of starch, one can expect that processing conditions favor physical modifications of starch in the granular state. However, a state diagram contains nonequilibrium information and all transformations are influenced by kinetics. The fact that the time scale of the DSC measurements and of the drying processes are different makes quantitative predictions difficult. A further restriction is that the moisture content presented in the state diagram does not necessarily represent the water available for starch transformation. Protein binds part of the water and, furthermore, water is not homogeneously distributed within the starch granules (Grzybowski and Donnelly 1977, Resmini and Pagani 1983). According to Donald et al (1997), water initially penetrates the amorphous growth rings of native starch, followed by hydration of the intercrystalline amorphous phase as heating proceeds. Thus, the plasticization of starch is a diffusion-controlled process and partial melting of starch crystallites contributes to relieve the constraints imposed by ordered regions and further reduces T_g (Biliaderis et al 1986, Slade and Levine 1988, Slade and Levine 1991). The melting of starch crystallites, on the other hand, is T_g dependent, since a previous softening (relaxation) of the amorphous zones facilitates crystal melting (Biliaderis et al 1986, Slade and Levine 1988).

Interpretation of DSC data may be difficult due to the fact that the thermal changes are the result of different, often superimposed molecular events, that is, the dynamic plasticization and the decrease and increase of molecular order at the double helical or crystalline level. For instance, it may be questioned whether the decrease of the temperature and enthalpy of starch gelatinization in the initial stage of drying at 55°C can be attributed to plasticization or to partial melting of starch. The latter is most likely, since control experiments with semolina revealed that increasing hydration time before DSC measurements tended to increase T_{p1} and ΔH_1 (data not shown). A partial melting of starch during drying at 55°C is conceivable because the effective T_{o1} effective is $\approx 53^\circ\text{C}$ for semolina at moisture levels of 30 g/100 g (Fig. 2).

Clearly, the HT phase favors molecular rearrangements as evidenced by an increase of the temperature and enthalpy of starch gelatinization. Other authors also showed that HT drying increases the thermal stability of starch (Cunin 1995, Vansteelandt and Delcour 1998, Yue et al 1999). The properties of semicrystalline polymers can be influenced by thermal treatments between the glass transition (T_g) and the melting temperature (T_m) termed annealing. According to the definition of Wunderlich (1976), annealing of semicrystalline

polymers may involve a partial melting of polymer crystals followed by a recrystallization of the molten materials using the remaining crystals as substrate. Physical modifications of starch in the granular state by hydrothermal treatments are well documented in literature (Sair and Fetzer 1944, Stute 1992, Jacobs and Delcour 1998). In starch, the literature distinguishes between hydrothermal treatments at limited and intermediate or excess water conditions. The treatments are heat-moisture treatment and annealing, respectively. Both treatments increase the thermal stability of starch. The main difference between annealing and heat-moisture treatment is that the former decreases the temperature range of melting while the latter broadens the endothermic transition. However, the current categorization of hydrothermal treatments for physical modification of starch in the granular state, heat-moisture treatment and annealing, are not applicable to pasta processing. The starch fraction of HT-dried pasta presents features of annealed and heat-moisture treated starch (Cunin 1995, Vansteelandt and Delcour 1998). This may be explained by the fact that the conditions change from intermediate to limited moisture conditions in the course of drying. Therefore, and by analogy with synthetic polymers, it is more appropriate to designate all treatments between T_g and T_p as annealing, keeping in mind that the type and extent of structural rearrangements may vary depending on the temperature, time, and availability of water.

Pasta processing at 80–100°C at moisture levels of 20–30 g/100 g favor an annealing of starch involving a partial melting, as evidenced by the state diagram of starch (Fig. 2) and DSC measurements of pasta. An annealing of starch without partial melting would require a treatment at temperatures far below the T_o of starch gelatinization as shown by Tester et al (1998). The annealing rate was highest when high temperatures were applied at relatively high product moisture (at 27 g/100 g, in early HT phase). This is in agreement with the theory that predicts the annealing rate is lowest close to T_g and highest close to melting of polymers (T_m) (Wunderlich 1976).

In thermodynamics, annealing moves starch closer to an equilibrium structure. However, the exact changes in the amorphous and crystalline fraction on annealing of starch, which, in turn, increase the thermal stability of starch, are not fully understood. Garcia et al (1996) suggested that a partial melting increases the mobility of the chain segments in the amorphous zones, leading to crystallization by propagation in the regions of remaining crystallites. In pasta, no clear differences in crystallinity were detectable by X-ray diffraction. The crystallinity of the sample with the larger enthalpy of gelatinization was not enhanced. Furthermore, no changes from A- to B-type diffraction pattern was found, which could be expected for recrystallized starch. Preliminary experiments using polarized light microscopy did not reveal changes regarding the birefringence of starch in pasta (micrographs not shown). Similar observations using X-ray diffraction and polarized light microscopy have been reported by several authors (Kulp and Lorenz 1981, Hoover and Vasanthan 1994, Cunin 1995). It is important to note that polarized light microscopy, X-ray diffraction, and DSC reflect different levels of ordered structures. Neither the long range order as revealed by birefringence, nor the crystalline register of starch was significantly altered by HT drying. The fact that changes in the starch fraction can be detected by DSC but not by X-ray diffraction is an indication that structural rearrangements on annealing, that is melting and increase of molecular order, take place at the double helical level. According to Cooke and Gidley (1992), the endothermic enthalpy reflects the loss of double helical order rather than the loss of crystalline register.

CONCLUSIONS

Based on DSC measurements, we can conclude that the modifications in the starch fraction occur during processing of pasta, in particular during the drying step. The changes in the thermal prop-

erties of starch during drying were dependent on the drying conditions. Low temperature drying (reference, 55°C) of pasta induces a decrease in the enthalpy of gelatinization due to a partial melting of starch. In contrast, HT drying (100°C) increases the molecular order of starch, as concluded from increased gelatinization temperature and enthalpy. Moreover, an early or intermediate HT phase increases the melting enthalpy of amylose-lipid complexes that eventually contribute to a stabilization of starch granules. Analyses of the drying conditions based on the physical states of starch as a function of moisture content confirmed that HT drying favors an annealing of starch at limited moisture conditions. Based on DSC and X-ray diffraction, the molecular order of starch is increased at the double helical level whereas the crystallinity is not affected. It is reasonable to assume that an increased thermostability of starch has a positive influence on the cooking properties of pasta. The selection of drying conditions based on a state diagram of starch could allow to control the resulting structural properties of pasta. However, the relative importance of starch and protein on the structural and textural properties of pasta remains to be clarified.

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