Journal of Thermal Analysis, Vol. 47 (1996) 1299-1314

DSC ANALYSIS OF STARCH THERMAL PROPERTIES RELATED TO FUNCTIONALITY IN LOW-MOISTURE BAKED GOODS

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Abstract

We describe an application of DSC as an analytical 'fingerprinting' method that has been used to characterize the thermal properties of wheat starch in low-moisture, wheat-flour-based baked products, including cookies, crackers, and pretzels. This use of DSC has enabled us to relate starch thermal properties, on the one hand, to starch structure, and on the other hand, to starch functionality, in terms of baking performance and finished-product quality.

Keywords: baked goods, cookies, crackers, DSC, pretzels, starch

Introduction

A great deal has been published on the use of differential scanning calorimetry (DSC) to study the thermal properties of starches, as related to starch structure, in both food model systems and real food products, the latter including high-moisture baked goods such as bread (e.g. see [1–6] and refs therein). However, much less work has been reported on the use of DSC as a diagnostic tool to characterize the condition of wheat starch in low-moisture, wheat-flour-based baked products, such as cookies, crackers, and pretzels. Aside from two reports on the use of DSC to determine the behavior of the major ingredients during heating of typical high-sugar cookie doughs [7, 8], and one other on DSC analysis of the wheat starch isolated from baked wire-cut cookies [9], we are not aware of any other work reported on the application of DSC to other low-moisture baked goods, such as crackers or pretzels.

In this paper, we describe how: a) DSC can be applied as an analytical 'fingerprinting' method to characterize the thermal properties of wheat starch in cookies, crackers, and pretzels; b) these thermal properties can be related to both starch structure and function in such low-moisture baked goods; and c)

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0368–4466/96/ $ 5.00

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such DSC 'fingerprinting' can be used as an aid to successful product development efforts, by identifying matches between appropriate ingredient functionality/baking performance and superior finished-product quality.

Experimental

A Perkin-Elmer (PE) model DSC 7 differential scanning calorimeter, equipped with PE model TAC 7 Instrument Controller, PE model 7700 Professional Computer with PE TAS 7 Thermal Analysis Software, and Intracooler II (FTS Systems) subambient temperature controller, was used for all DSC mea-surements. Indium, benzophenone, and a series of National Bureau of Standards melting-point standards (52–164°C) were used to calibrate temperature and enthalpy of melting.

Samples for DSC analysis were prepared by grinding product (e.g. cookies, crackers, or pretzels with low 'as is' moisture contents) to a powder in a Krups coffee grinder, adding to the powdered product (or to samples of wheat flour of the type used to make the product) an equal weight of water (distilled, deionized) [3], and mixing powder and water together by hand with a spatula to the consistency of a homogeneously hydrated slurry. Slurry samples were immediately filled into PE large-volume, stainless steel DSC pans, which were then hermetically sealed and weighed (to 0.001 mg) on a PE AD-6 Autobalance. DSC sample weights were typically 35–45 mg. Duplicate sample pans were analyzed by DSC (against an empty stainless-steel reference pan) within one hour of sample preparation, in order to ensure reproducibility of experimental results [2]. After loading and temperature-equilibration of pans in the DSC 7, samples were heated from 15–130°C, at 10°C min^{-1}. In some experiments, after this initial scan, samples were immediately cooled (at 320°C min^{-1}, nominal instrumental rate) to 15°C and rescanned to 130°C, at 10°C min^{-1}.

Materials analyzed by DSC in this study included the following samples. Flours, of the types used to make the cookie, cracker, and pretzel products, were typical, commercial, soft-wheat-based, cookie/cracker flours with 'as is' moisture contents around 13%. The rotary-molded, high-sugar cookie was a typical commercial product (with a formula of a type similar to that of the standard AACC 'sugar-snap' cookie [10]), with a moisture content less than about 3%. The fat-free, fermented ('sponge-and-dough' type) saltine cracker was a patented commercial product [11]. The pretzel and full-fat, fermented ('sponge-and-dough' type) saltine cracker were typical commercial products with moisture contents below about 5%. For such baked goods, general aspects of formulation and processing are familiar to those skilled in the art. Proprietary aspects of the product and flour samples analyzed in our study are not germane to the subject of this paper.

Actual 'as is' moisture contents of all baked products and flours analyzed by DSC were determined by a standard method of vacuum-oven-drying at 70°C for 18–48 h. Throughout this paper, compositions expressed in % or by ratio represent weight percentages or ratios, unless otherwise indicated.

Results and discussion

DSC of wheat flour, cookies, and crackers

Figure 1 shows typical DSC curves for representative samples (1:1 mixtures with water) of a cookie/cracker flour, a commerical, rotary-molded, high-sugar cookie, and a commercial saltine cracker. Wheat flours of the type used to make such baked goods typically contain about 13% moisture (wet basis) and approximately 85% starch (dry basis), the latter in the native form of partially crystalline, partially amorphous granules containing the two starch polymers, amylopectin (Ap) and amylose (Am) [7]. Thus, the flour sample represented in Fig. 1A comprises a 40% starch-in-water slurry, and the appearance of the DSC

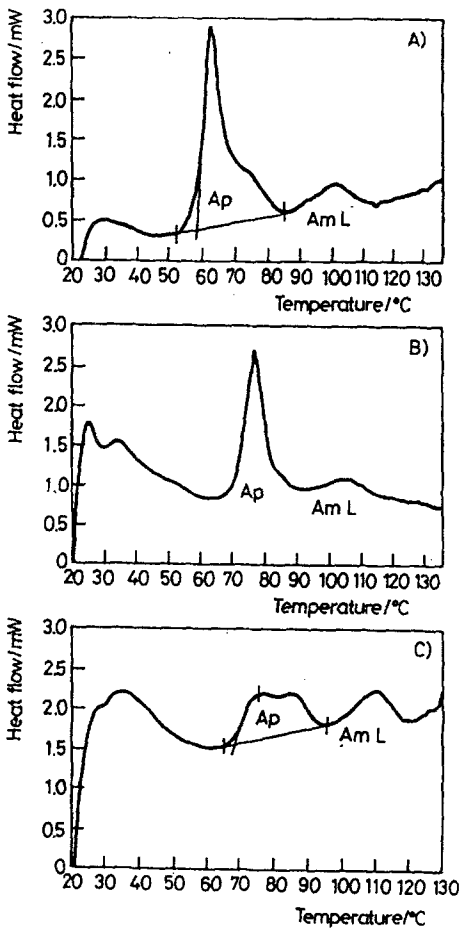

Fig. 1 Typical DSC curves for representative samples (1:1 mixtures with water) of: A) a cookie/cracker flour; B) a commercial rotary-molded high-sugar cookie; and C) a commercial saltine cracker. See text for explanation of peak labels

thermogram is that widely recognized to be typical of native granular wheat starch in mixtures of approximately 1:1 with water [1–3, 7 and refs therein]. The characteristic biphasic endotherm, with onset temperature (T) of 53°C, completion T of 88°C, peak T of 64°C, and shoulder at about 75°C, is generally acknowledged to represent a combination of glass transition, of water-plasticized amorphous regions, followed by non-equilibrium melting, of microcrystallites of the partially crystalline glassy Ap in the 'fringed-micelle' structure of the granules of native wheat starch, in a process known as starch gelatinization [1–6, 12–14, 16–18 and refs therein]. The appearance of this so-called 'gelatinization endotherm' in the thermogram in Fig. 1A signifies, as expected, that the starch in the flour was native, until it was gelatinized as a consequence of heating to 90°C during the DSC measurement. The characteristic higher-T endotherm, with onset T of 89°C, completion T of 117°C, and peak T of 104°C, is recognized to represent the melting of amylose-lipid (Am L) crystalline inclusion complex [1–6, 15 and refs therein].

In Fig. 1B, the DSC curve for the high-sugar cookie sample shows two principal endothermic events, aside from a pair of small fat-melting endotherms below 40°C (representing the fat ingredient in the cookie formula, which is not of interest in this discussion). The smaller of the two endotherms of interest, occurring above 100°C, had previously been observed in the DSC of wheat starch isolated from a wire-cut cookie, as reported by Kulp *et al.* (Fig. 6 in [9]). As described above for Fig. 1A, this endotherm represents the melting of crystalline Am L complex. The larger endotherm, with onset T of 66°C, completion T of 88°C, and peak T of 77°C, resembles the gelatinization endotherm in Fig. 1A (same completion T), although it is obviously narrower and shifted to higher peak T. In fact, the appearance of this endotherm is characteristic of that for the gelatinization of native granular wheat starch in the presence of sucrose-water solution rather than water alone [1]. Based on the known amounts of flour and sucrose in the cookie formula, and thus the corresponding known amounts of flour, sucrose, and water contained in the DSC sample pan, the appearance of this endotherm can be explained, to begin with, by recognizing that the sample pan contained, in essence, a 1:4 mixture of starch and 20% sucrose solution.

It is well known that the presence of sucrose causes the gelatinization temperature of starch (taken as the peak T of the gelatinization endotherm in Fig. 1A [1–4 and refs therein]) to be elevated [16–18]. This effect of sucrose has been explained by a concept of 'antiplasticization' (by sugar-water relative to water alone) [1], which has received wide support in recent years [14, 19 and refs therein]. According to this 'antiplasticization' mechanism [1], sugar, in the presence of native starch and excess water, behaves as a plasticizing co-solvent with water, such that the sugar-water co-plasticizer, of higher average molecular weight (MW) (and lower free volume, so higher glass transition temperature (T_g) [20]) than water alone, plasticizes (i.e. depresses the temperature of the glass transition of the amorphous regions, which immediately precedes the ge-

latinization of native, partially crystalline starch [1, 2, 12]) starch less than does water alone. Thus, the gelatinization temperature (as well as the T_g that precedes it) in the presence of sugar is elevated (hence, 'anti') relative to the gelatinization temperature of starch in water alone. Moreover, with increasing concentration of sugar in the three-component mixture (thus, a sugar-water co-plasticizer with increasing average MW, decreasing free volume, and increasing T_g, relative to water alone), the magnitude of the antiplasticizing effect increases, and so do T_g and the gelatinization temperature [1].

Thus, based on previously reported DSC results for native granular wheat starch in mixtures with sucrose solutions of varying concentration [1], the major endotherm in Fig. 1B for the cookie sample is interpreted as representing the gelatinization of starch in 20% sucrose solution. This interpretation was confirmed by DSC analysis of a sample of flour prepared so as to represent a 1:4 mixture of starch in 20% sucrose (DSC curve not shown). Once normalized for sample weight, that thermogram for flour (containing fully native starch) in 20% sucrose was found to be essentially identical in appearance to the one in Fig. 1B (except for the fat-melting peaks below 40°C) for the 1:1 mixture of high-sugar cookie in water, in terms of both areas and temperature ranges for both of the endothermic peaks (labeled Ap and Am L) in Fig. 1B. [It should be noted that we prefer to express peak area in terms of ΔQ (for the change in total heat uptake), rather than the conventional ΔH (change in enthalpy) terminology used by the PE DSC 7 software (and unavoidably listed as such in the printouts from the instrument), when a peak is known to comprise multiple thermal events, such as the glass and crystalline melting transitions represented within the gelatinization endotherm of starch [1, 2, 12].] Further comparison of the peak areas for the Ap and Am L endotherms {first normalized for total sample weight, and then further normalized for flour (and therefore starch) weight} in the DSC curve for flour:20% sucrose {or in the equivalent (after normalization) DSC curve in Fig. 1B} with the corresponding peak areas in the curve for flour:water in Fig. 1A demonstrated that both the Ap and Am L peak areas in Fig. 1B represent 100% of those for the native wheat starch represented in Fig. 1A. This result indicates that the starch in the baked cookie was completely native prior to DSC analysis, and was first gelatinized during DSC heating, thus demonstrating that the starch was not gelatinized at all during baking of this high-sugar cookie. This finding is in agreement with the conclusion reached previously in other studies [8, 9, 16–18, 21]. To anticipate a question about why, if the native starch represented in Fig. 1B could be completely gelatinized by heating to 88°C in the DSC, was it not gelatinized during baking of the cookie, wherein the internal temperature reached approximately 100°C, we point out that the gelatinization temperature of 77°C in Fig. 1B was measured for starch in a 1:4 mixture with 20% sucrose solution. Thus, for the 20% starch slurry, plasticization by the sucrose solution (present in 4-fold excess) depressed the gelatinization temperature

down to 77°C. In contrast, during baking of the cookie dough (with a dry-basis composition of 87:54:35 flour:sucrose:water), the native starch in the flour was in an aqueous environment composed of a small excess of total solvent (=sum of sucrose+water [22]) comprising a 61% sucrose solution. Under these conditions (i.e. less effective plasticization of the starch, by a lesser amount of a more concentrated sucrose solution), the gelatinization temperature would be expected, based on previously reported DSC results for starch:sucrose:water model systems, to be elevated to well above 100°C [1]. Therefore, the native starch of the flour in the cookie dough would be unaffected (i.e. not gelatinized at all) by the maximum temperature reached by the cookie during baking.

In Fig. 1C, the DSC curve for the saltine cracker sample shows two principal endothermic events, aside from a broad fat-melting endotherm, centered about 35°C (representing the fat ingredient in the cracker formula, which again is not of interest in this discussion). The smaller of the two endotherms of interest, with onset T of 96°C, completion T of 118°C, and peak T of 109°C, is again identified (as in Figs 1A and 1B) as that representing the melting of crystalline Am L complex. The larger endotherm, with onset T of 65°C, completion T of 95°C, and peak T of 75°C, again resembles the gelatinization endotherm in Fig. 1A, although it is obviously smaller in peak area and shifted to a higher temperature range. We can begin to explain these differences by first noting that a saltine cracker is typically formulated with no added sugars (the presence of which would elevate the starch gelatinization temperature), and with enough water (i.e. at least about 27 parts water to 73 parts dry wheat starch [1]) in the dough (at least, early in baking) to allow starch in the flour to gelatinize during baking of the cracker, wherein the internal temperature reaches at least about 100°C. If we assume that the peak labeled Ap in Fig. 1C represents what remained of the full gelatinization endotherm in Fig. 1A, after some but not all of the starch in the cracker was gelatinized during baking, we can calculate the % remaining native Ap structure, by comparing the Ap peak areas in Figs 1C (1.49 J g^{-1}) and 1A (3.92 J g^{-1}), and then normalizing first for total sample weight, and second for flour (and thus starch) weight. We obtain a value of 40%, indicating that the extent of starch gelatinization during backing of the cracker was 60%. Apparently, it could not reach 100%, because, as the content of plasticizing water in the dough decreased as baking progressed, the gelatinization temperature would have increased, evidently to well above 100°C by the end of baking. Since not all of the starch was gelatinized during baking, the portion remaining native was evidently subject to annealing (at temperatures within the range from T_g to T_m at the end of Ap crystallite melting), due to the heat-moisture treatment constituted by baking [1, 2, 6, 12]. The expected effect of this annealing treatment [23] is manifested by the Ap peak in Fig. 1C, which is narrower by about 5°C and up-shifted by about 10°C, relative to the corresponding Ap peak in Fig. 1A. As with the Ap peak areas, we can compare the Am L peak areas in Figs 1A (0.63 J g^{-1}) and 1C (0.71 J g^{-1}), and, after the same nor-

malizations as before, we obtain a value of 121% native Am L structure in the cracker sample represented in Fig. 1C. Thus, evidently as a consequence of gelatinization of some of the granular starch during cracker baking, some previously uncomplexed amylose was made available for forming additional Am L complex [15] in the cracker. The Am L peak in Fig. 1C is narrower by about 6°C and up-shifted by about 5°C, relative to the corresponding Am L peak in Fig. 1A, apparently as a consequence of the same annealing treatment during baking, which similarly influenced the Ap peak. As a final remark about the curve in Fig. 1C, we point out what we view as the salient DSC features of this cracker sample (which is taken to represent an excellent eating-quality, commercial product with optimum properties): 40% remaining native Ap structure and 121% native Am L structure. As will be developed further in the discussion of Fig. 2 that follows, these features illustrate the basis of our application of DSC analysis as a diagnostic 'fingerprinting' method that has allowed us to relate starch structure and thermal properties to starch function in, and associated finished-product quality of, low-moisture baked goods.

DSC of crackers

Figure 2 shows typical DSC curves for representative samples (1:1 mixtures with water) of a cracker flour (of the same type as described above with regard to Fig. 1A), a commercial full-fat saltine cracker of excellent eating quality (of the same type as described above with regard to Fig. 1C), a prototype no-fat saltine cracker of poor eating quality, and a patented [11], commercial no-fat saltine cracker of excellent eating quality. The critical aspect of Fig. 2 lies in the comparison among the 'fingerprint' thermograms in parts B, C, and D. When one tries to produce a no-fat version of the saltine cracker represented in Fig. 2B, by simply omitting from the formula the added fat (the presence of which would normally allow the cracker dough to be soft enough to be machined on commercial equipment), one must ordinarily add extra water, to obtain a dough of softness and machinability equal to that of its full-fat analog [11]. The result of adding extra water to the dough is revealed in the thermogram in Fig. 2C. Evidently, more of the starch in the flour is gelatinized during baking of the dough, because sufficient plasticizing water was present for a longer portion of the baking time, thus keeping the gelatinization temperature depressed, for a longer time, below the maximum temperature reached during baking. As a result, only 31% native Ap structure remained (to be detected by its DSC fingerprint) in the no-fat cracker after baking, rather than 40%, as in the full-fat cracker. Furthermore, less additional Am L complex was able to form in the no-fat dough during baking (resulting in 105% native Am L structure in the cracker), than that formed in the full-fat dough (resulting in 121% in the cracker), possibly because of time/temperature/moisture conditions during baking that were less favorable to the sequestering of solubilized Am in Am L crystalline complex [1, 5, 6]. The consequence of these differences in the re-

sulting starch structure – more Ap gelatinized and less Am sequestered in discrete crystallites of Am L complex, rather than free, within the gelatinized starch network, to contribute toughness to the matrix – was a deleterious effect on product texture, as assessed by sensory analysis. The no-fat cracker represented in Fig. 2C was less tender, more brittle, and tougher than the target full-fat cracker represented in Fig. 2B [11].

In contrast, when Nabisco's patented pentosanase-enzyme technology [24, 25] was applied in the commercial production of the no-fat saltine cracker [11], the DSC fingerprint of the resulting cracker (Fig. 2D: 39% native Ap structure, 119% native Am L structure) was found to be a virtual match for the fingerprint of the corresponding full-fat cracker (Fig. 2B: 40% native Ap structure, 121% native Am L structure). In the case of the cracker represented in Fig. 2D, even though the fat normally included in the formula was omitted, so that extra water was needed to produce a machinable dough, this extra water in the dough did not result in a significantly increased extent of Ap gelatinization, nor in a reduced extent of Am L complex formation, during baking, because of the beneficial effect of the pentosanase enzyme in the dough [11, 24, 25]. By hydrolyzing the highly-water-holding pentosans (non-starch polysaccharides) in

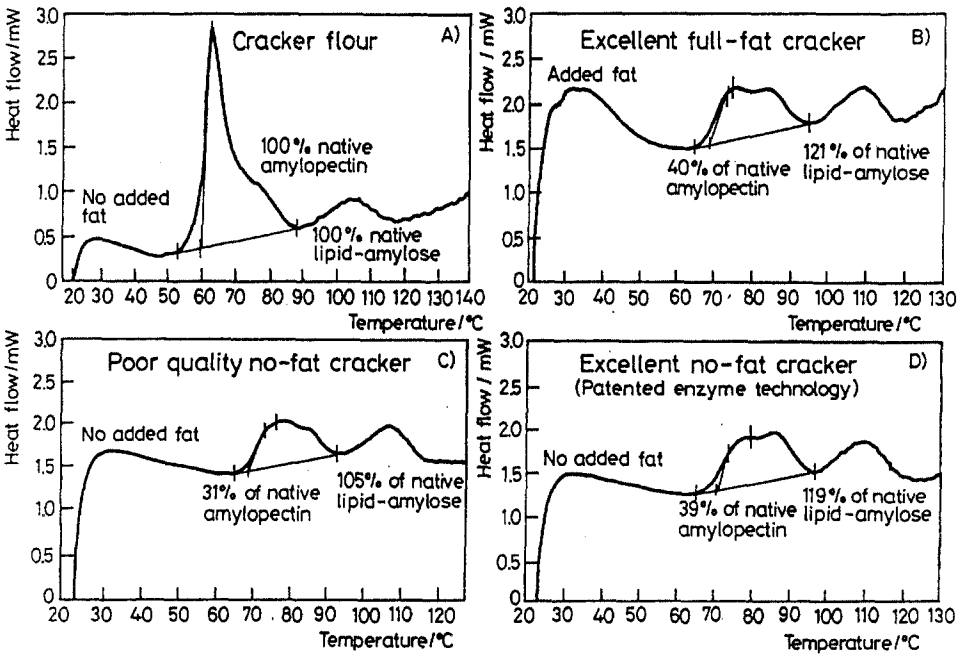

Fig. 2 Typical DSC curves for representative samples (1:1 mixtures with water) of: A) a cracker flour; B) a commercial full-fat saltine cracker of excellent eating quality; C) a prototype no-fat saltine cracker of poor eating quality; and D) a patented [11] commercial no-fat saltine cracker of excellent eating quality

the flour during dough mixing, and thereby markedly reducing the water-holding capacity of the resulting dough, this enzyme caused a facilitation of moisture loss from the dough during baking. Thus, more of the plasticizing water was removed, more rapidly, from the dough during baking, so that it was not available to make possible excessive Ap gelatinization or reduced Am L complex formation, and the deleterious effect on product texture, which would otherwise have resulted. In the absence of excessive starch gelatinization, the resulting no-fat cracker had a tender, non-brittle, non-tough texture, comparable to that of the full-fat target product [11].

As a final remark about Fig. 2, in the context of DSC as a 'fingerprinting' method, it is worth noting that, even if one did not know the identity or cause of the two principal endotherms in Fig. 2B, one would logically assume (and, at least in this case, turn out to be correct) that the DSC sample represented in Fig. 2D was a much closer match (in terms of its structure-thermal property relationships, and thus, presumably, in its functional characteristics) to the target represented in Fig. 2B, than was the DSC sample represented in Fig. 2C.

DSC of pretzels

Figures 3–5 illustrate the results of diagnostic DSC analysis of commercial pretzel doughs and products. The pretzel samples represented in Figs 3A and 3B were produced from a cookie/cracker flour of the type represented in Fig. 1A, and were formulated with added fat (i.e. not fat-free). Thus, the three endothermic peaks evident in the thermograms in both Fig. 3A and 3B can be assumed to correspond to the three similar endotherms in Fig. 2B for the full-fat cracker sample. The lowest-T, broad endotherm, centered around 35°C in Figs 3A and 3B, is again assigned to fat-melting. This peak is seen to reappear, with a slightly lower peak T and narrower width, in the immediate rescan in Fig. 3C. Such thermal behavior is well known to be characteristic of the kinds of polymorphic crystalline fats typically used in such baked goods. Since the same type and amount of fat was used in both pretzel formulas (in fact, the formulas were identical in all aspects), we must assume that fat played no direct role in distinguishing the good product (Fig. 3B) from the bad one (Fig. 3A). Therefore, we again turn our attention away from fat, and focus it on the two peaks – the one below 100°C, assigned earlier to Ap, and the one above 100°C, assigned earlier to Am L – arising from starch in the wheat flour. We note in passing that the Am L peak reappears in the immediate rescan in Fig. 3C, while the Ap peak does not. Such thermal behaviour is quite familiar and well-established for wheat starch:water mixtures, and has been explained in detail elsewhere [1–6, 15 and refs therein]. With the Ap peak completely absent in the rescan in Fig. 3C, the appearance that curved baseline in the 70–100°C range is revealed, thus demonstrating that the Ap peaks in Figs 3A and 3B, while small

in height and area, are unquestionably real. It is also worth mentioning that these Ap peaks are much smaller in area and somewhat narrower than the corresponding Ap peaks for the cracker samples represented in Figs 2B–D, thus indicating greater extents of starch gelatinization and annealing during baking of the pretzels. It is tempting to suggest that such differences in starch structure and thermal properties must correlate with functional differences, and must therefore be related to the obvious textural differences between pretzels and saltine crackers, both of which are produced from doughs formulated with flour and water (but little added fat and virtually no added sugars) as the predominant elements. However, as discussed further below, the Ap peaks may not tell the whole story.

The critical functional distinction between the pretzel samples represented in Figs 3A and 3B concerned eating quality. The product whose thermogram is shown in Fig. 3A had poor eating quality, as assessed by sensory panel evaluation; its texture was described as too hard, and it had a dry, mealy, pasty mouthfeel. In contrast, the product represented in Fig. 3B had good texture (crisp, but not too hard) and eating quality. Once again, if we examine the DSC

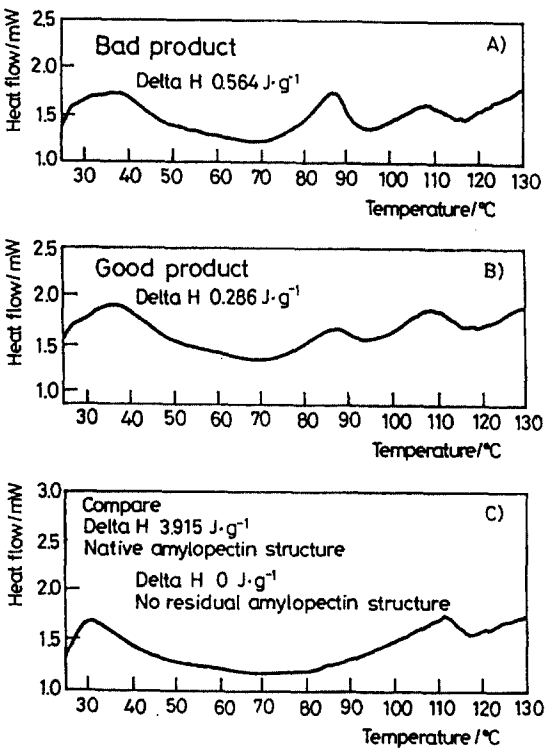

Fig. 3 Typical DSC curves for representative samples (1:1 mixtures with water) of: A) a prototype pretzel product of poor eating quality; and B) a commercial pretzel of good eating quality; C) an immediate rescan of the sample in (B)

curves in Figs 3A and 3B as fingerprints, whose differences might correlate with, and account for, the differences in texture and eating quality of the two products, we see immediately that the only obvious difference is that the Ap peak areas (normalized for sample weight) differ by a factor of about 2. Further rough comparison of these Ap peak areas (0.56 J g^{-1} in Fig. 3A, 0.29 J g^{-1} in Fig. 3B) with that for the flour in Fig. 1A (3.92 J g^{-1}≡100% native Ap structure) showed that the poor product had 14.4% remaining native Ap structure, while the good one had only 7.3% remaining native Ap structure after baking. The logical implication of these results is that the extent of starch gelatinization during production of the bad pretzel was insufficient (i.e. only 86%, rather than 93%) for optimum product texture and eating quality.

However, more careful examination of the curve in Figs 3A and 3B revealed that less obvious differences involving the Am L peaks may also have been instrumental in differentiating the good and bad products. It can be seen, even without consulting the ΔQs, that the Am L peaks are quite similar in area, but the one in Fig. 3B looks slightly larger. [This was verified by Fig. 4C, as discussed below.] Probably more important, and certainly more evident, is the fact that, in Fig. 3A, the Ap peak is much larger, in both height and area, than the Am L peak, while in Fig. 3B, in contrast, this is not the case. The Ap and Am L peaks are much more similar in size; in fact, the Am L peak is slightly larger in area. If we recall the earlier discussion about the crackers represented in Fig. 2, wherein a benefit to texture accrued from enhanced Am L complex formation during baking, such that the resulting Am L peak was both larger in area and closer in size to that of the optimum Ap peak, we may infer that the good pretzel represented in Fig. 3B, like the good crackers represented in Figs 2B and 2D, enjoyed a similar textural benefit arising from increased sequestering of available Am in Am L crystalline complex. We will return to this point again later. For now, it is important to also recall that the good and bad pretzels were formulated identically. Thus, differences in their finished-product quality were assumed to have arisen because of differences in their finished product qualitz were assumed to have arisen because of differences in their manufacturing process.

Typical pretzel production involves running a pretzel dough through a bath of hot caustic solution {lye (NaOH)} prior to baking. The caustic-bath treatment is responsible for the glossy brown surface appearance of a typical pretzel (hard, low-moisture type), by a process involving gelatinization of starch on the surface of the pretzel dough, via sufficient contact with the hot caustic solution [7]. Thus, in a typical pretzel dough, starch in the wheat flour can be gelatinized during caustic-bath treatment and also, of course, during baking. The curves in Fig. 4 (measured for DSC samples of virtually the same weight) reveal the progress, in two discrete but evidently additive processing steps, of increasing extents of starch gelatinization and annealing during manufacture of

a different sample of the same type of commercial pretzel product (with good texture and eating quality) as described before with regard to Fig. 3B. In Fig. 4A, the curve for the pretzel dough, prior to caustic-bath treatment, can be seen to resemble quite closely the one for flour in Fig. 1A. The reason for this was alluded to earlier; it is simply that a pretzel dough is, in essence (i.e. aside from a bit of fat and a few other minor ingredients that need not concern us here), a flour-water dough. Thus, the major biphasic endotherm with a peak T of 69°C can be assigned without question to Ap (as verified, in part, by the expected appearance of the immediate rescan), and its peak area, corresponding to a ΔQ of 4.22 J g^{-1}, can be taken to represent 100% native Ap structure. Applying the 'fingerprint' analysis to the DSC curves in Fig. 4, we see in Fig. 4B that, as a

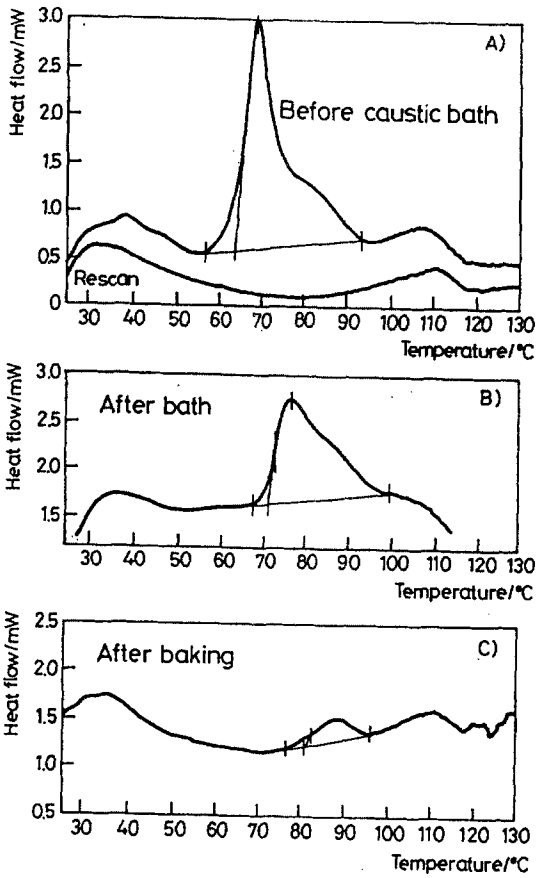

Fig. 4 Typical DSC curves for representative samples (1:1 mixtures with water) of: A) a commercial pretzel dough before caustic-bath treatment – scan and immediate re-scan; B) the same pretzel dough after caustic-bath treatment, but before baking; and C) the same pretzel dough after caustic-bath treatment and baking, representing a finished product of good eating quality

consequence of the caustic-bath treatment, the Ap peak area (2.26 J g^{-1}) was reduced to 53.6% of its original value for native Ap structure, for the in-process sample of dough taken prior to baking. For the finished product, after both caustic-bath treatment and baking, the area of the Ap peak (0.33 J g^{-1}) in Fig. 4C demonstrated that the remaining native Ap structure had reached a final value of 7.8%, in reasonable agreement with the value of 7.3% from Fig. 3B for a different sample of the pretzel with good eating quality. We also note that the Am L peak in Fig. 4C (in its characteristic location above 100°C) is slightly larger in area (8%) than the Ap peak as was also the case for the good-textured product represented in Fig. 3B.

The DSC curves in Fig. 5 reveal how the prototype pretzel, with poor texture and eating quality, had been subjected to a presumably less-than-optimal process of starch conversion (i.e. combination of gelatinization and annealing), via a processing path that contrasted significantly with the one followed by the pretzels (Figs 3B and 4C) with good eating quality. Again, by applying the 'fingerprint' approach to the DSC results in Fig. 5, in order to compare them to the corresponding results in Fig. 4, we see that, as a consequence of the progression from untreated dough (Fig. 5A) to dough after caustic-bath treatment but before baking (Fig. 5B) to finished product after caustic treatment and baking (Fig. 5C), the % remaining native Ap structure, as reflected by the Ap peak area, decreased from 100% (4.30 J g^{-1}) to 61.8% (2.66 J g^{-1}) to 15.8% (0.68 J g^{-1}), with the latter value of 15.8% again being in reasonable agreement with the earlier value of 14.4% obtained from Fig. 3A for a different sample of these same poor eating-quality pretzels. The values of 61.8% (Fig. 5B) and 15.8% (Fig. 5C) can be said to contrast significantly with the respective values of 53.6% and 7.8% obtained from Figs 4B and 4C. [That is, if we can infer a measure of significance from the reproducibility (actually, of one sample of commercial product to another) of experimental results compared above – 7.3 *vs.* 7.8% and 14.4 *vs.* 15.8%.] Thus, we are led to surmise that the inferior pretzel (represented in Fig. 5) had been subjected to too little starch conversion in the caustic bath, possibly resulting from a) too short a residence time, b) too cool a bath, and/or c) too low a NaOH concentration. Was this the direct and sole cause of its poor texture and eating quality? It seems clear from the DSC 'fingerprints' that the caustic-bath treatment was certainly a critical processing step that distinguished the good and bad products, in terms of their starch structure-thermal property relationships, on the one hand, and their starch functional characteristics and concomitant finished-product quality attributes, on the other hand.

But what about what happened during baking? Interestingly, the DSC 'fingerprint' results revealed that the extent of starch conversion caused by baking was essentially the same for the good and bad products, i.e. the change in % native Ap due to baking was 45.8% for the good product (53.6–7.8% – Figs 4B and 4C) *vs.* 46.0% for the bad product (61.8–15.8% – Figs 5B and 5C). How-

ever, as noted earlier with regard to the curve in Fig. 3A representing the other sample of bad product, the Am L peak in Fig. 5C is smaller (this time, obviously much smaller) than the Ap peak, which again contrasts with the situation for the good product, as illustrated in Fig. 4C. We conclude that the baking process for the bad product must also (like the caustic-bath treatment) have been deficient, at least in the sense that Am L complex formation (which would be expected to be favored by the higher product temperature reached in the oven [1], rather than in the caustic bath) was evidently not enhanced. But, what if the inferior product had been more optimally baked? For example, what if it had been baked more intensively (assuming this were possible, without burning it or causing its moisture content to be too low, even though its texture was already too hard), to a final 7.5% remaining native Ap structure (presumably, the target

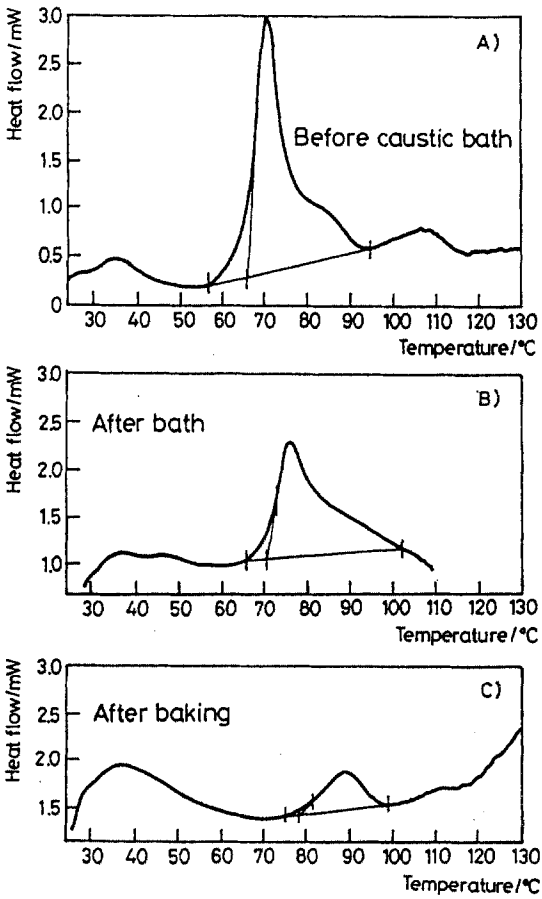

Fig. 5 Typical DSC curves for representative samples (1:1 mixtures with water) of: A) a prototype pretzel dough before caustic-bath treatment; B) the same pretzel dough after caustic-bath treatment, but before baking; and C) the same pretzel dough after caustic-bath treatment and baking, representing a finished product of poor eating quality

value), in an attempt to compensate for insufficient starch conversion in the caustic bath? Could its texture and eating quality have been salvaged in this way? Fortunately (and in contrast to what usually happens in the 'real world' of commercial baked-goods production), we were able to obtain the appropriate product samples required to answer these questions. And the answer was no; after insufficient starch conversion in the caustic bath, even baking of product down to about 7.5% remaining native Ap structure appeared (curve not shown) to be insufficient to produce a significantly enlarged Am L peak in the curve, and the quality of this product was still inferior. The unavoidable conclusion from this part of the study was that both the caustic-bath treatment and baking must be optimal, with respect to both starch conversion and Am L complex formation, in order to produce a pretzel with optimal texture and eating quality.

Conclusions

In this paper, we have demonstrated that: a) DSC can be applied as an analytical 'fingerprinting' method to characterize the thermal properties of wheat starch in cookies, crackers, and pretzels; b) these thermal properties can be related to both starch structure and function in such low-moisture baked goods; and c) such DSC 'fingerprinting' can be used as a valuable time- and labor-saving research aid to successful product development efforts, by screening prototype products by DSC, rather than by more traditional trial-and-error methods (referred to in the food industry as 'cook-and-look'), in order to identify promising matches between appropriate ingredient functionality/baking performance and superior finished-product quality, which can be used to help guide subsequent development work.

Nevertheless, as is always the case when a new or different research approach is advocated, the interpretations and conclusions expressed in this paper are still open to further research, and to new challenges to the claimed utility of this DSC 'fingerprinting' method.

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