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Non-Equilibrium Melting of Native Granular Starch: Part I. Temperature Location of the Glass Transition Associated with Gelatinization of A-Type Cereal Starches

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ABSTRACT

The temperature location of the effective glass transition (T_g), which immediately precedes the non-equilibrium melting transition of amylopectin microcrystallites and controls the melting process associated with starch gelatinization, was identified for native granular wheat and waxy corn starches, heated at 10 °C min^{-1} in the presence of water added to 55% (by weight) total moisture to facilitate temporal resolution of the thermal events. Definitive differential scanning calorimetry experiments, involving partial initial heating scans to intermediate temperatures in the range from 30 to 130 °C, followed by quench-cooling and immediate complete rescans, revealed the operational location of T_g for wheat starch (above 54 °C and completed by 63 °C) and waxy corn starch (above 63°C and completed by 71·5 °C). Corresponding effective 'end of melting' temperatures (T_m) for the non-equilibrium melting transition of amylopectin microcrystallites in normal wheat (about 92 °C) and waxy corn (about 95 °C) starches were also identified. Results of this study were used to (1) deconvolute the contributions of amylopectin and amylose to the non-equilibrium melting behavior of native granular starches; (2) explain the kinetically controlled relationship (based on the dynamics of plasticization by water) between the operative temperature, T_a, at which a non-equilibrium process of annealing can occur in native granular starches subjected to various heat/moisture/time treatments, and the effective T_g and T_m relevant to gelatinization; and (3) demonstrate that the effective T_g associated with gelatinization of native granular starch, most readily resolved by heating in limited added moisture, depends on the instantaneously operative conditions of moisture content, temperature and time, because the glass transition represents a rate-limiting stage of a relaxation process, for which the spectrum of relaxation rates depends on the

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instantaneous magnitude of the free volume and/or local effective viscosity. This magnitude in turn depends on the relative values of experimental moisture content compared to the moisture content (W_g) of the operative glass, experimental temperature compared with the instantaneous T_g, and experimental timeframe compared with the instantaneous relaxation rate. Such a relaxation process, described by Williams–Landel–Ferry free volume theory for glass-forming systems, underlies various functional aspects of starch, such as gelatinization, crystallite melting, annealing, and recrystallization.

INTRODUCTION

The temperature location of the glass transition (T_g) associated with gelatinization of native starch is a point of contention in the current literature. Normal starch is not a homopolymer, but a mixture of two glucose polymers, predominantly linear amylose (of molecular weight (MW) 10^5–10^6 daltons) and highly branched amylopectin (MW 10^8–10^9 daltons), typically in a weight ratio of ~25:75 amylose:amylopectin, arranged in a supramolecular structure in the form of a layered granule (Whistler & Daniel, 1984). Even mutant starch, such as waxy corn starch which contains only amylopectin, is not best described as a homopolymer of glucose, but as a special type of block copolymer in which backbone segments with their branch points (e.g. intercrystallite segments of B2 and B3 chains (Hizukuri, 1986)) exist in amorphous domains and the crystallizable branches exist in microcrystalline domains (Wunderlich, 1980; French, 1984; Whistler & Daniel, 1984). These amylopectin branches also account for the characteristic low extent of crystallinity, ~15–42% (Zobel, 1984; Blanshard, 1986; Biliaderis *et al.*, 1986*a*), in normal granular starches (French, 1984). The native granule of normal starch is not a polymer spherulite (Wunderlich, 1973), but a layered structure in which space-filling is achieved by amylopectin branching with radial alignment of the branches in crystalline regions (French, 1984). Each of the glucose polymers may be partially crystalline (French, 1984), and their amorphous components may each manifest a distinctive T_g (at a temperature dependent on MW (Billmeyer, 1984) as well as on local moisture content) characteristic of a predominant amorphous domain (Slade & Levine, 1987*a*).

Despite this microscopic and macroscopic structural complexity of starch, many workers since 1980 have usefully discussed the physicochemical effect of water, acting as a plasticizer of the amorphous regions in the native granule, on the T_g of starch (van den Berg, 1981, 1986; van den Berg & Bruin, 1981; Slade, 1984; Slade & Levine, 1984*a,b*, 1987*a,b*; Biliaderis *et al.*, 1985, 1986*a,b,c*; Maurice *et al.*, 1985; Ablett *et al.*, 1986; Blanshard, 1986; Yost & Hoseney, 1986; Biliaderis & Vaughan, 1987; Chungcharoen & Lund, 1987; Levine & Slade, 1987; Zeleznak & Hoseney, 1987). We have advanced a food polymer science approach to this subject, as part of a basic research program on structure/property relationships of starch and starch hydrolysis products (Slade, 1984; Slade & Levine, 1987*a*; Levine & Slade, 1986, 1987). Our group has used thermal analysis by differential scanning calorimetry (DSC) to demonstrate that native granular starches, both normal and waxy, exhibit non-equilibrium melting (Wunderlich, 1981), annealing, and recrystallization behavior characteristic of a kinetically metastable, water-plasticized, partially crystalline polymer system with a small extent of crystallinity (Slade, 1984; Slade & Levine, 1984*a,b*, 1987*a,b*; Biliaderis *et al.*, 1985, 1986*a,b,c*; Maurice *et al.*, 1985; Levine & Slade, 1987). DSC results showed, and we have stressed the significance of the conclusion, in which others concur (Reid & Charoenrein, 1985; Blanshard, 1986; Chungcharoen & Lund, 1987), that gelatinization (Blanshard, 1979; Lund, 1984; Zobel, 1984) is a non-equilibrium melting process, actually a continuum of relaxation processes that occurs during heating of starch in the presence of plasticizing water, in which crystallite melting is indirectly controlled by the kinetically constrained, continuous amorphous surroundings. That is, melting of microcrystallites, which are hydrated clusters of amylopectin branches (French, 1984; Whistler & Daniel, 1984), is controlled by prerequisite plasticization ('softening') of randomly coiled, possibly entangled (Graessley, 1984) chain segments in the interconnected amorphous regions of the native granule, for which the local structure is conceptualized according to the classic 'fringed micelle' (Flory, 1953; Wunderlich, 1973, 1976; Billmeyer, 1984) morphological model of partially crystalline, three-dimensional polymer networks (Slade, 1984; Slade & Levine, 1984*a,b*, 1987*a,b*; Maurice *et al.*, 1985; Levine & Slade, 1987). Such non-equilibrium melting in metastable, partially crystalline polymer systems, in which the crystalline and amorphous phases are neither independent of each other nor homogeneous, is an established concept for synthetic polymers (Wunderlich, 1981). Previous attempts (e.g. Lelievre, 1976; Donovan, 1979; Biliaderis *et al.*, 1980) to use the Flory–Huggins thermodynamic treatment to interpret the effect of water content on the crystalline melting temperature (T_m), observed during gelatinization of native starch, failed to provide a mechanistic model, because Flory–Huggins theory (Flory, 1953) only applies to the melting of polymers in the presence of diluent under the conditions of the equilibrium portion of the solidus curve (Slade, 1984; Slade & Levine, 1984*a,b*, 1987*a,b*; Biliaderis *et al.*, 1985, 1986*a,b*,c; Maurice *et al.*, 1985; Levine & Slade, 1987).

Although the Flory–Huggins treatment is inappropriate, and the effect of water on T_m is not the direct effect experienced in equilibrium melting (i.e. dissolution) along the solidus, water as a plasticizer does affect indirectly the T_m, and directly the T_g, of partially crystalline, water-compatible polymers such as those of starch (Levine & Slade, 1987; Slade & Levine, 1987). The direct plasticizing effect of increasing moisture content at constant temperature, which is equivalent to the effect of increasing temperature at constant moisture, leads to increased segmental mobility of chains in amorphous regions of glassy and partially crystalline polymers, which in turn allows a primary structural relaxation transition at decreased T_g (Rowland, 1980; Sears & Darby, 1982; Flink, 1983; Karel, 1985). State diagrams recently presented by van den Berg (1986) and Zeleznak & Hoseney (1987) for gelatinized and native starch–water systems, respectively, illustrated the extent of this T_g-depressing effect. In both cases, smooth curves of T_g vs. weight % (w%) water showed the dramatic effect of water on starch T_g, especially at low moisture, such that T_g decreases about 5–10°C/w% water. This same extent of plasticization at low moisture has been found to apply to many amorphous and partially crystalline, water-compatible polymers, as well as to various monomeric and oligomeric carbohydrates (Bair *et al.*, 1981; Batzer & Kreibich, 1981; Franks, 1982; Levine & Slade, 1987; Slade & Levine, 1987*b*).

According to one modern view in the synthetic polymers literature, the predominant contribution to the mechanism of plasticization of water-compatible glassy polymers by water derives from a free volume effect (Ellis *et al.*, 1984; Jin *et al.*, 1984). Free volume theory (Ferry, 1980) provides the general concept that free volume is proportional to inverse number-average MW ($\bar{M}n$), so that the presence of plasticizing diluents of low MW leads to increased free volume, allowing increased backbone chain segmental mobility, which in turn results in decreased T_g (Moy & Karasz, 1980; Nakamura *et al.*, 1981; Bone & Pethig, 1982; Carfagna *et al.*, 1982; Sears & Darby, 1982). It is well known that ability of a diluent to depress T_g decreases with increasing diluent MW (Boyer *et al.*, 1985), as predicted by free volume theory. Recent reports have contended that the effectiveness of water as a plasticizer of synthetic polymers primarily reflects its low molar mass (Jin *et al.*, 1984; Ellis *et al.*, 1984). These workers discounted older concepts of specific interactions, such as disruptive water–polymer hydrogen bonding in polymer hydrogen-bonded networks or plasticizing molecules becoming 'firmly bound' to polar sites along a polymer chain, in explaining water's plasticizing ability. To negate the older arguments for site-specific hydrogen bonding, they cited nuclear magnetic resonance (NMR) results which clearly indicated that water molecules in polymers with polar sites have a large degree of mobility (Jin *et al.*, 1984). NMR was also used to test the accessibility of water with reduced mobility in retrograded starch gels, and results showed that all the water in the gel could be freely exchanged with deuterium oxide (Wynne-Jones & Blanshard, 1986).

In partially crystalline polymers, the fact that water plasticization occurs only in amorphous regions (Mohajer *et al.*, 1980; Starkweather, 1980; van den Berg, 1981; Gaeta *et al.*, 1982; Jin *et al.*, 1984) is critical to understanding how control by amorphous regions leads to the nonequilibrium melting behavior of crystalline regions. For normal native starches, composed of partially crystalline polymers with hydrated crystalline regions, hydrolysis by aqueous acid ('acid-etching') or enzymes, at $T < T_m$, can occur initially only in amorphous regions (French, 1984). Similarly, acid-etching of retrograded starch progresses in amorphous regions, leading to increased relative crystallinity (or even increased absolute crystallinity, by crystal growth) of the residue (French, 1984). Dehumidification of granular starch proceeds most readily from initially mobile amorphous regions, leading to nonuniform moisture distribution (van den Berg, 1981). We reported (Slade, 1984; Maurice *et al.*, 1985; Levine & Slade, 1987; Slade & Levine, 1987*a*;) that the 'effective' T_g, which immediately precedes and thereby determines the temperature of gelatinization (T_{gelat}) in native starch, depends on the extent and type (B vs. A vs. V polymorphs) of crystallinity in the granule (but not on amylose content), and on total moisture content and moisture distribution. T_{gelat} increases with increasing percentage of crystallinity (Julians, 1982), an indirect effect due to the disproportionation of mobile short branches of amylopectin from amorphous regions to crystalline 'micelles', thereby increasing the average MW and effective T_g of the residual amorphous constituents. Two other related phenomena are observed in situations of overall low moisture content for partially crystalline polymers with hydrated crystalline regions, such as starch (Slade, 1984; Slade & Levine, 1984*a,b*, 1987*a,b*; Maurice *et al.*, 1985; Biliaderis *et al.*, 1986*b*; Levine & Slade, 1987): (1) atypically high T_g/T_m (in K) ratios $\geq 0{\cdot}80$, but, of course, $< 1{\cdot}0$ (Wunderlich, 1980; Soesanto & Williams, 1981), in contrast to the characteristic range 0·5–0·8 for many partially crystalline synthetic polymers (Brydson, 1972; Wunderlich, 1980; Batzer & Kreibich, 1981; Franks, 1982); and (2) a pronounced apparent depressing effect of water on T_m (Lelievre, 1976) as well as T_g, such that both T_g and T_m decrease with increasing moisture content.

We reported (Slade, 1984; Slade & Levine, 1984*a*,*b*, 1987*a*) that the explanation for these phenomena in starch gelatinization lies in the non-equilibrium nature of the melting process and the indirect effect of plasticizing water on T_m. The existence of contiguous microcrystalline regions (the crystallizable short branches) and amorphous regions (backbone segments plus branch points) covalently linked (Wunderlich, 1981) in individual amylopectin molecules creates a 'fringed micelle' network. Relative dehydration of the amorphous regions at an initial, low overall moisture content leads to the kinetically stable condition where the effective T_g (which is influenced by the extent of mobility of amylopectin branches) is higher than the 'equilibrium' T_m of the crystalline regions. Consequently, the 'effective' T_m is elevated and observed only after softening of the amorphous regions at T_g. Added plasticizing water acts directly on the continuous glassy regions, leading to the kinetically metastable condition where their effective T_g is depressed. Thus, the 'fringe' becomes an unstable rubber at $T > T_g$, and sufficient mobility and swelling by thermal expansion and water uptake is allowed for the interconnected microcrystallites, embedded in the 'fringed micelle' network, to melt (by dissociation, with concomitant volume expansion and further water uptake) on heating to a less kinetically constrained T_m only slightly above the depressed T_g. In contrast to the case of limited moisture, in an excess-moisture situation such as a retrograded wheat starch gel with greater than about 27 w% water, where the amorphous matrix would be fully plasticized and ambient temperature would be $> T_g$ (i.e. $T_g' \sim -5$ °C), the fully hydrated and matured crystalline junctions would show the actual, lower (and closer to equilibrium) T_m (~ 60°C for retrograded B-type starch). Once starch gelatinization was established as such a non-equilibrium melting process, for which the Flory–Huggins treatment would have no theoretical basis (Lelievre, 1976; Wunderlich, 1981; Alfonso & Russell, 1986), and which is described by Williams–Landel–Ferry (1955) (WLF), rather than by Arrhenius, kinetics (Reid & Charoenrein, 1985; Bhattacharya & Hanna, 1987; Levine & Slade, 1987), our coworkers (Biliaderis *et al.*, 1985, 1986*a*,*b*,*c*) and others (Chungcharoen & Lund, 1987) subsequently reported additional corroborating experimental results for non-equilibrium melting of granular starches and amylose–lipid crystalline complexes.

We previously reported (Slade, 1984; Slade & Levine, 1984*a*,*b*) and later published (Levine & Slade, 1987; Slade & Levine, 1987*a*) DSC results for native wheat and waxy corn starches, with water added to a final moisture content of 55 w%. Because the added water is outside the granules, and so initially non-plasticizing, this system demonstrated a major glass transition and subsequent superimposed crystalline transition(s) in the temperature range 50–90°C, which comprise the events of gelatinization (initial swelling) and pasting (second-stage swelling) of a starch granule (Zobel, 1984). The glass transition of the amorphous regions of amylopectin was observed at the leading edge of the first melting peak, between 50 and 60°C. This near superposition of the glass transition on the crystalline melt, due to the imbalance of moisture contents inside (10 w%) and outside (100 w%) the granules and to heating rate, was revealed by the expected characteristic shift in heat capacity (Wunderlich, 1981; Yost & Hoseney, 1986) shown by extrapolated baselines and by derivative thermal curves (Levine & Slade, 1987; Slade & Levine, 1987*a*). This important basic insight into starch thermal properties was subsequently corroborated by DSC results for granular rice starches (Biliaderis *et al.*, 1986*a*; Chungcharoen & Lund, 1987), which likewise demonstrated that melting of the microcrystallites was governed by the requirement for previous softening of the glassy regions of amylopectin. After gelatinization by heating to 130°C, and quench-cooling to 25°C, an immediate rescan of wheat starch at 55 w% moisture showed no transitions in the temperature range 30–100°C. However, when this completely amorphous (i.e. no remaining amylopectin microcrystals) sample was allowed to recrystallize (at uniformly distributed 55 w% moisture) for 55 days at 25°C, it showed a major T_m at ~ 60°C (as a symmetrical endothermic peak, with essentially no baseline shift), which was not immediately preceded by a T_g. This T_m characterizes the melting transition observed in retrograded wheat starch gels with excess moisture (which are partially crystalline and contain hydrated B-type crystals) and in staled bread and other high-moisture wheat starch-based baked goods (Kulp & Ponte, 1981; Longton & LeGrys, 1981; Fearn & Russell, 1982; Lund, 1983; Russell, 1983; Eliasson, 1985).

We reported results of complementary low-temperature DSC analysis (published here as Fig. 1 (Slade, 1984; Slade & Levine, 1984*a*,*b*)) which revealed why no T_g was observed in the above sample of freshly gelatinized wheat starch rescanned from room temperature to 130°C, or immediately before T_m in the above sample of recrystallized starch. Native wheat starch, at 55 w% total sample moisture, showed only a T_m of ice at the instrumental sensitivity used for the thermogram in Fig. 1. In contrast, a gelatinized sample, at the same water content and instrumental sensitivity, showed a major (and reversible) glass transition of fully plasticized amorphous starch at ~ −5°C, preceding and superimposed on the ice melt. This T_g is actually T_g' for gelatinized wheat starch in excess moisture, which is defined by $W_g' \sim 27$ w% water (Levine & Slade, 1987). The critical conclusion was that knowledge of total sample moisture alone cannot reveal the state of plasticization of

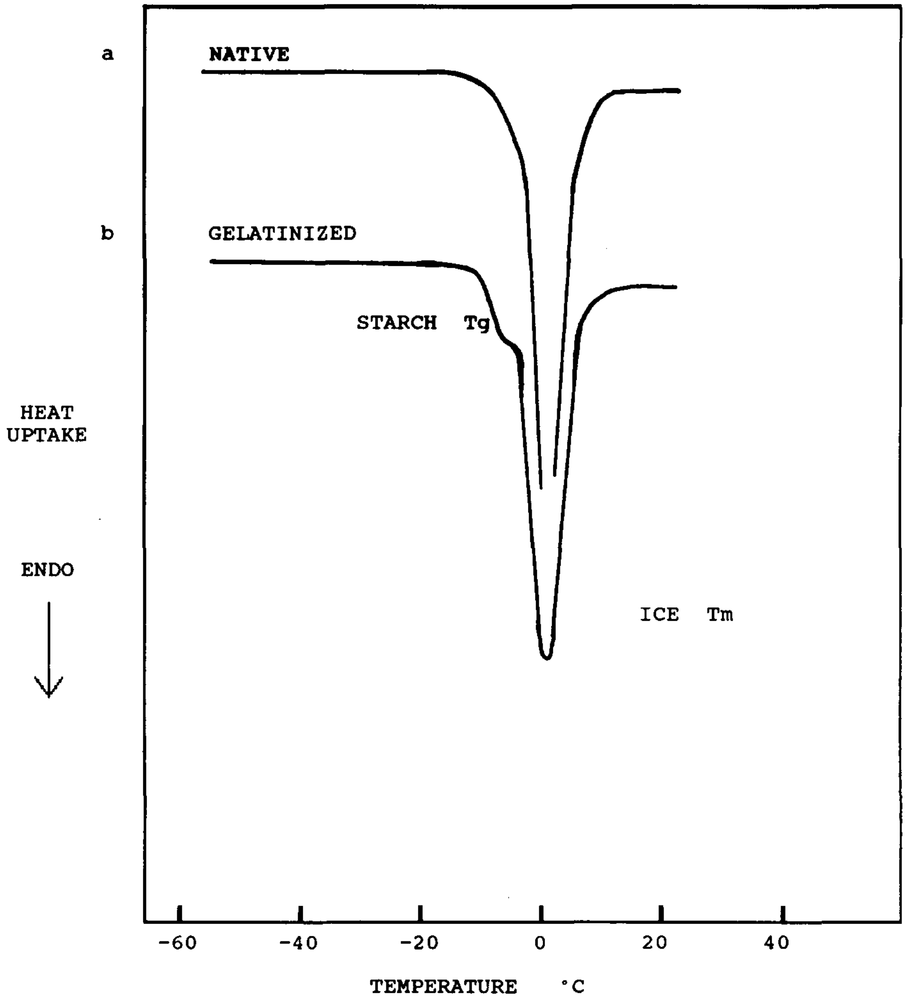

Fig. 1. DuPont 990 DSC heat flow curves of wheat starch:water mixtures (45:55 w/w): (a) native granular; (b) immediate rescan after gelatinization of sample in (a).

amorphous regions of a starch granule (Slade & Levine, 1987*a*). Amorphous regions of a native granule are only partially plasticized by excess water in a sample at room temperature, so that softening of the glassy matrix must occur at ~ 50–60°C (during heating at 10°C min^{-1} in the DSC), before microcrystallites can melt. After gelatinization, the homogeneously amorphous starch is fully and uniformly plasticized at 55 w% moisture, and the metastable amorphous matrix exists at room temperature as a mobile, viscoelastic rubber in which diffusion-controlled recrystallization, governed by WLF rather than by Arrhenius kinetics

(Levine & Slade, 1987), can proceed with rates proportional to $\Delta T \sim 30°C$ about T_g, as defined by WLW free volume theory (Ferry, 1980). Another insight revealed by these DSC results concerned the dynamic effects on starch caused by the DSC measurement itself (Slade & Levine, 1987*a*). During a DSC heating run, plasticizer (water) content increases dynamically from the initial 6–10 w% in a native sample before heating to the final 55 w% at the end of melting, and this kinetically constrained moisture uptake leads to dynamic swelling of starch granules above T_g, which is not reversible on cooling. The same behavior is manifested in volume expansion measurements on starch–water systems performed by thermomechanical analysis (Maurice *et al.*, 1985; Biliaderis *et al.*, 1986*a*). The major contribution to the experimentally observed increase in volume above T_g is a typical polymer swelling process, characteristic of compatible polymer–diluent systems (Sears & Darby, 1982), which is linear with the amount of water taken up. Thermal expansion of amorphous starch is also allowed above T_g, but it represents only a minor contribution to the observed volume increase, about 0.1% K^{-1} for typical polymers (Ferry, 1980). Thus, the predominant mechanism, swelling, is indirectly related to the role of water as a plasticizer of starch, while the minor mechanism is directly related.

Two recent reports (Yost & Hoseney, 1986; Zeleznak & Hoseney, 1987) explored the validity of our model in which the thermal behavior of native starch at 55 w% total moisture in the temperature range 50–100°C represents the superposition of a 'second-order' glass transition followed by a first-order crystalline melting transition. Yost & Hoseney (1986) presented DSC results for gelatinization and annealing by heat-moisture treatment of wheat starch in water at 50 w% total sample moisture content. They concluded that annealing occurred (in samples previously kept for 24 h at room temperature) at temperatures 3–8°C below the gelatinization T_m for wheat starch, but not at lower temperatures. These results did not contradict previous DSC results and conclusions (Slade, 1984; Slade & Levine, 1987*a*) about the relative locations of T_g and T_m for gelatinization of starch, especially when the following knowledge about annealing of synthetic polymers is considered. With respect to the crystalline domains in a metastable partially crystalline polymer, annealing is a crystal growth and/or perfection process (Wunderlich, 1976), which occurs at T_a, a temperature above T_g but below T_m, typically 0·75–0·88 T_m (K) (Brydson, 1972), for polymers with T_g/T_m ratios of 0·5–0·8. In this metastable rubbery domain defined by WLF theory (Williams *et al.*, 1955) and often from T_g to $T_g + 100$ K, within the temperature range between T_g and T_m, annealing is another diffusion-controlled, non-equilibrium process for which rate is governed by WLF, rather than by Arrhenius, kinetics (Nakazawa *et al.*, 1984; Levine & Slade, 1987). As demonstrated for various native granular starches in limited moisture situations (Nakazawa *et al.*, 1984; Maurice *et al.*, 1985; Yost & Hoseney, 1986; Krueger *et al.*, 1987; Slade & Levine, 1987*a*), the time required to achieve a measurable and comparable (in a reasonable and similar experimental timeframe) extent of annealing is shortest at T_a just below T_m (greatest ΔT above T_g) and longest at T_a just above T_g (smallest ΔT). The minimum value of the T_g/T_m ratio for wheat starch (at a uniformly distributed excess moisture content of greater than about 27 w%) is ~ 0·80 (i.e. T_g'/T_m), and the ratio increases with decreasing moisture content to an anomalously high value > 0·9. This anomalous situation corresponds to conditions of the non-equilibrium gelatinization or annealing of native starch upon heating in the presence of water added to 50 w%. Consequently, the temperature range which encompasses the effective locations of T_g, T_a and T_m for native starch heated with excess added water is quite narrow, a conclusion also suggested by the DSC results of Nakazawa *et al.* (1984). Zeleznak & Hoseney (1987) investigated the T_g of both native and pregelatinized wheat starches as a function of moisture content, and concluded, in seeming conflict with the annealing results previously reported (Yost & Hoseney, 1986), that their findings 'contradicted the suggestion that T_g immediately precedes melting in starch'. In both papers, Hoseney and coworkers based their argument, in large part, on the failure to observe a glass transition (in the form of a discontinuous change in heat capacity) in a rescan after gelatinization of native starch in excess added moisture in the DSC. Unfortunately, their DSC measurements were not extended below 0°C, and so the major T_g at $T_g' \sim -5°C$ for gelatinized starch, illustrated in Fig. 1, was not observed.

In the context of the considerable background information presented in this Introduction, the aims of the present DSC study of representative A-type cereal starches were to: (1) verify and further quantify the temperature location of the effective glass transition that controls the T_m associated with gelatinization in the presence of excess added moisture; (2) thereby confirm that the location of T_a 3–8°C below T_m is not inconsistent with a T_g immediately preceding melting; and (3) achieve a deconvolution of the contributions of amylopectin and amylose to the non-equilibrium melting behavior of native granular starches, through DSC analyses of normal wheat and waxy corn starches.

A further aim of this paper was to clarify the absence of a single, absolute value of T_g for starch (or any other amorphous material), by illustrating the established fact (Ferry, 1980) that the operational designation of any specific T_g value is only relevant to the particular conditions of its measurement. In other words, 'the' T_g of native granular starch heated in limited moisture will depend on the instantaneously operative conditions of moisture content, temperature and time.

MATERIALS AND METHODS

Commercial samples of native granular starches from normal wheat (Aytex P from Grain Processing Corp., Muscatine, IA) and waxy corn (Amaizo Amioca from American Maize Products, Hammond, IN) were used as received (i.e. approximate 'as is' moisture contents of 10 w%). Samples for DSC analysis were prepared outside the DSC pans by hand-mixing starch powder with distilled, deionized water to the consistency of a homogeneously hydrated slurry, at weight ratios of 10:8 starch:water (to obtain final 50 w% total moisture) and 1:1 (to obtain final 55 w% total moisture). DSC sample pans (aluminum, from DuPont Instrument Products) were immediately filled with 20–25 mg of homogeneous slurry (weighed on a Cahn Microbalance, Cahn Instruments Inc., California) and hermetically sealed (using a DuPont encapsulation press). Sample pans were analyzed by DSC (against an empty aluminum reference pan) within 1 h of sample preparation, in order to ensure the reproducibility of experimental results by maximizing the definition of sample history. As is typically the case with non-equilibrium systems, sample history (path dependence) may be more important than the equilibrium thermodynamic properties of a system for prediction of its behavior in technical applications. While it may be of value to explore the effects of longer holding times, it is not practical to attempt to 'equilibrate' non-equilibrium systems prior to DSC analysis.

DSC measurements (described below) were made with a Perkin-Elmer (PE) DSC-2C, equipped with an Intracooler II (plus FTS Systems TCH-10 temperature controller) and a Thermal Analysis Data Station (TADS). Benzophenone and indium standards were used to calibrate temperature and enthalpy of melting. Complementary low-temperature DSC measurements, shown in Fig. 1 and already described, had been made with a DuPont 990 Thermal Analyzer, combined with a DuPont 910 DSC, by a previously published method (Levine & Slade, 1986).

Preliminary DSC measurements, modeled after those of Yost & Hoseney (1986), were made with Aytex P at 50 w% moisture. Duplicate sample pans were heated, at 10°C min^{-1}, from 20 to 130°C ($\equiv$ complete initial scan), then immediately cooled (at 320°C min^{-1}, nominal instrumental rate) to 20°C and rescanned (at 10°C min^{-1}) to 130°C. Other pairs of pans were subjected to only partial initial scanning (from 20°C to

57, 63, 72, 82, 87, 89, 92 or 100°C), before cooling and immediate complete rescanning. The latter sample thermograms were analyzed to determine, from the thermal events evident in the complete rescan, what events must have previously occurred during the partial initial scan.

Subsequent DSC measurements were made with both Aytex P and Amioca at 55 w% moisture. Again, duplicate sample pans were heated, at 10°C min^{-1}, from 20 to 130°C ($\equiv$complete initial scan), then immediately cooled (at 320°C min^{-1}) to 20°C and rescanned (at 10°C min^{-1}) to 130°C. Other pairs of pans were subjected to only partial initial scanning (for Aytex P, from 20°C to 37, 47, 54, 63, 70, 77, 83, 89, 100 or 117°C; and for Amioca, from 20°C to 63, 71·5, 76, 82, 88 or 94°C), before cooling and immediate complete rescanning.

RESULTS AND DISCUSSION

The composite diagram of PE DSC-2C heat flow curves for Aytex P wheat starch, shown in Fig. 2, demonstrated conclusively that initial heating to at least 92°C was required (for a heating rate of 10°C min^{-1}, to a final sample moisture content of 50 w%) to complete the non-equilibrium melting process associated with gelatinization and pasting of native wheat starch (Zobel, 1984). The familiar $T_m \sim 115$°C for amylose–lipid crystalline complex (Biliaderis *et al.*, 1985) was evident in every curve in Fig. 2. Partial initial scanning to temperatures ≥ 72°C, but < 92°C, resulted in only partial melting, as evidenced in the rescans by a remnant of the melting profile, compared with the thermal profile of the complete melting process shown at the top of Fig. 2. This remnant decreased in area with increasing maximum temperature (in the range 72–92°C) of the partial initial scan, but only disappeared completely (yielding a featureless thermogram, as evidenced by a flat baseline, from 30–100°C) after initial heating to ≥ 92°C. From these preliminary DSC measurements, we concluded that 92°C represents the effective T_m at the '*end* of melting' (Lelievre, 1976; Nakazawa *et al.*, 1984) for native wheat starch heated at 10°C min^{-1} with 50 w% total moisture. The temperature at which melting begins was deduced from the DSC results shown in Fig. 3, which also revealed the temperature location of the effective glass transition that must precede the onset of this non-equilibrium melting process for Aytex P with water added to 55 w% total moisture. On the time scale of the DSC measurement, these two temperatures were essentially identical.

The composite diagram of PE DSC-2C heat flow curves for wheat starch with 55 w% water in Fig. 3 shows the complete non-equilibrium

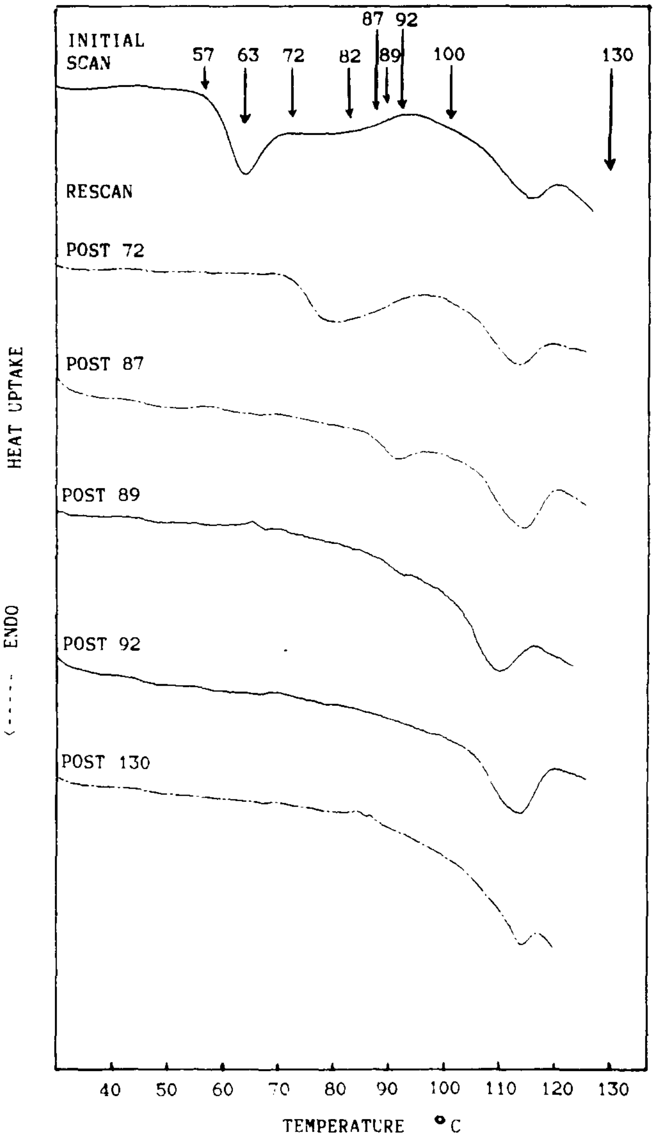

Fig. 2. Perkin-Elmer DSC-2C heat flow curves of wheat starch : water mixtures (50 : 50 w/w): top — initial scan at 10°C min^{-1} for native starch; others — rescans at 10°C min^{-1}, immediately following partial initial scanning, at 10°C min^{-1}, from 20°C to maximum temperatures indicated and then immediate cooling, at nominal instrument rate of 320°C min^{-1}, to 20°C.

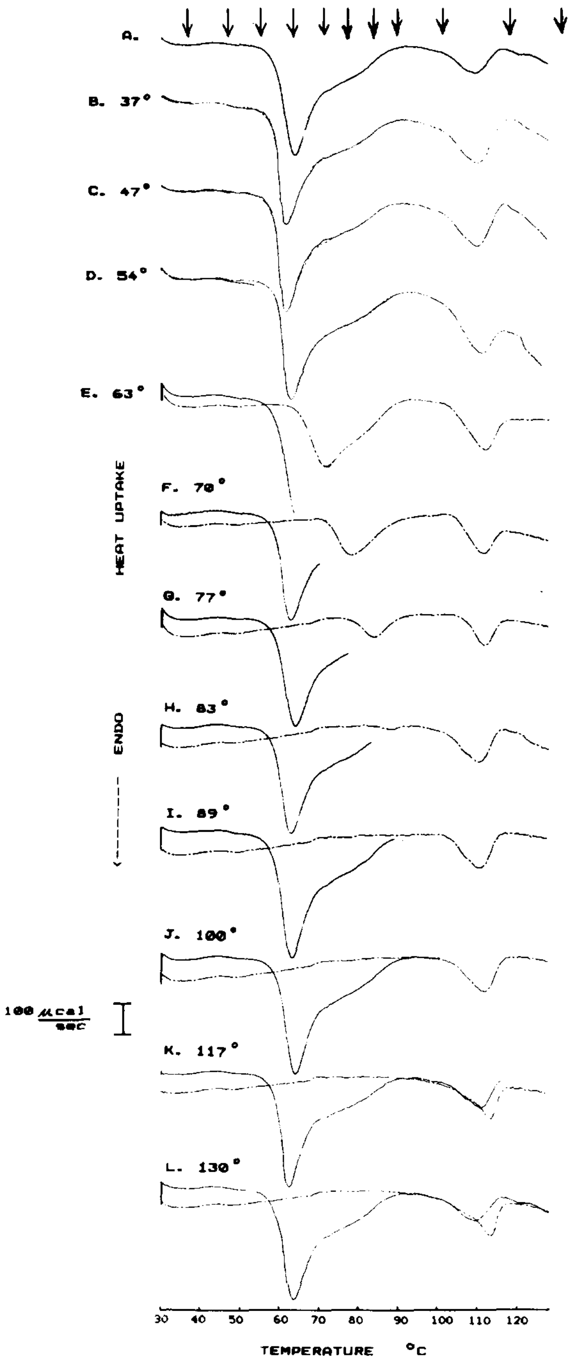

Fig. 3. Perkin-Elmer DSC-2C heat flow curves of wheat starch:water mixtures (45:55 w/w): A, initial scan at 10°C min^{-1} for native starch; B–L, solid lines = partial initial scans for native starch, at 10°C min^{-1}, from 20°C to maximum temperatures indicated dashed lines = rescans at 10°C min^{-1}, immediately following partial initial scanning and then immediate cooling, at 320°C min^{-1}, to 20°C.

melting process as an initial scan in curve A; the partial initial scans, with their maximum temperatures indicated, as solid lines in parts B–K; and the complete rescans as dashed lines in parts B–L. For parts B–L, the TADS computer was instructed to display simultaneously the initial scan and rescan and allowed to confirm that the same instrumental baseline response of heat uptake (in mcal s^{-1}) at the 'equilibrated' starting temperature of 20°C occurred in both scans. This data-processing step evidenced successful experimental execution by the near-perfect superposition of the 20–50°C baseline portions of the initial scans and corresponding rescan segments in parts B, C and D, and the 90–100°C baseline portions of the scans and rescans in parts J, K and L. This step was critical to the subsequent identification of the effective T_g which governs gelatinization of native starch in excess moisture during heating from room temperature to 100°C. The results in Fig. 3 were used to deduce the location of the effective T_g as the temperature by which there had occurred, in the initial scan, a characteristic and diagnostic change (baseline shift) in heat capacity, during the time scale of the experimental measurement, for heating at 10°C min^{-1}. As an example, within the temperature range 30–100°C in part L, comparison of the 30–60°C baseline portions of the initial scan and rescan demonstrates such a diagnostic difference in heat capacity, thereby documenting that a glass transition had occurred during the initial scan. Because of the previous occurrence of the change in heat capacity, the featureless (at $T < 100°C$) rescan was superimposed on the initial scan only after the latter returned to baseline after the end of the endothermic melting process at $T_m \sim 92°C$. As expected, this effective end-of-melting T_m was the same as shown before in Fig. 2, since both 50 and 55 w% water represent conditions of large excess moisture for gelatinized starch. This effective end-of-melting T_m was also suggested by Fig. 3(I), for which the initial thermal profile, upon heating to 89°C, stopped just short of a return to baseline. The reason for the apparent absence of a T_g in the rescan of part L was explained earlier by reference to Fig. 1. After complete gelatinization upon heating to 130°C and 55 w% final moisture content, $T_g = T'_g \sim -5°C$.

The effective T_g preceding and controlling the non-equilibrium melting process associated with gelatinization was identified as that minimum, narrow temperature span in the initial scan, below which the change in heat capacity had not yet occurred (as reflected by superimposed baselines for scan and rescan), but at and above which it already had occurred (as reflected by a displacement of baselines, at $T < T_g$, between scan and rescan). We see in parts B, C and D that the scans and corresponding rescan segments were essentially identical up to 54°C, and the heat capacity change had not yet occurred before the rescans, because initial heating to 37, 47 or 54°C had not yet reached T_g. In contrast, in parts E–K, the scan and rescan baselines, at $T < T_g$, were displaced, because initial heating to $T \geqslant 63$°C had allowed the amorphous regions of the native granules to undergo a glass transition. By the convention described above, the effective 'end of softening' T_g preceding crystallite melting was thus identified as 63°C, as illustrated in Fig. 3(E). This T_g corresponds to the temperature at the 'peak minimum' in the characteristic DSC thermal profile for wheat starch gelatinization shown in Fig. 3(A). The narrow temperature span of the effective T_g is seen to occur within the range 55–63°C (i.e. along the leading edge of the 'gelatinization endotherm'). Figure 3(E) represents a temporal and thermal deconvolution of the melting transition of microcrystalline regions from the preceding glass transition of amorphous regions of water-plasticized starch. Nakazawa *et al.* (1984) alluded to a similar differentiation between the mobile amorphous regions and immobile crystalline regions with respect to the timeframe of their DSC results for normal rice starches analyzed at 50 w% total moisture, but they implausibly suggested that the elevated T_m observed in annealed starches is due to increased stability in the amorphous regions. Rather, for this case of starch in excess moisture, annealing allows a relaxation in the amorphous regions from a more to a less stable (kinetically metastable) state, while the crystalline regions perfect from a less stable (metastable) state to a more stable state with higher T_m (Wunderlich, 1981). The rescan of part E exhibits the following features (compared with the typical appearance of curve A below 100°C): a more symmetrical melting endotherm with essentially no baseline shift, an onset temperature (essentially coincident with the initial effective T_g) of 63°C, a peak minimum of 70°C, and an effective end-of-melting T_m of 92°C. The appearance of the thermal profile in the region of the glass transition is analogous in shape to an endothermic hysteresis peak, a common characteristic manifested by partially crystalline polymers (Wunderlich, 1981). An endothermic hysteresis peak is indicative of some jump, during the sample history, in temperature, plasticizer content or pressure at a rate exceeding the relaxation rate of the appropriate process, and is observed during subsequent DSC analysis as a 'stress relief' via 'enthalpic relaxation' (Wunderlich, 1981). The apparent enthalpic relaxation of starch (Zeleznak & Hoseney, 1987), with a peak minimum at 63°C, is superimposed on the universal step-change in heat capacity. We can further imagine summing the glass and melting transitions, superimposed on one another in the temperature range 50 to 100°C, by adding together the scan and rescan in part E, thus reconstituting, with no discernible loss of total heat below the baseline, the characteristic DSC thermal profile (curve A) for wheat starch gelatinization in excess water.

Figure 4 contains the analogous composite diagram of PE DSC-2C heat flow curves for waxy corn starch with 55 w% total moisture. As in Fig. 3, Fig. 4 shows the complete non-equilibrium melting process as an initial scan in curve A; the partial initial scans, with their maximum temperatures indicated, as solid lines in parts B–G; and the complete rescans as dashed lines in parts B–H. In contrast to Fig. 3, amylose–lipid melting transitions above 100°C are absent for this amylose-free starch. Based on the same analysis and logic described for Fig. 3, and equally successful superposition of the instrumental baseline response of initial and rescans (e.g. part B in the temperature range from 30–60°C and H from 95–130°C), the following results were obtained from Fig. 4. Parts C–H manifested displaced baselines, in the temperature range 30 to less than about 65°C, for the initial scan and rescan, while part B showed superimposed baselines in the same temperature range. Accordingly, the effective end-of-softening T_g preceding crystallite melting was identified as 71·5°C from Fig. 4(C). As for wheat starch in Fig. 3, this T_g corresponds to the temperature at the 'peak minimum' in the typical DSC thermogram for waxy corn starch gelatinization shown in Fig. 4(A). The narrow temperature span of this T_g occurred within the range 64–71·5°C, along the leading edge of the endotherm. Part H revealed an effective end-of-melting $T_m \sim 95$°C, where the initial scan returned to baseline after gelatinization. This was corroborated in part G, where the thermal profile, upon initial heating to 94°C, stopped just short of a return to baseline. As in Fig. 3(E), we suggest that Fig. 4(C) illustrates a separation of the melting transition of A-type microcrystallites from the glass transition that must precede it. However, in this case, the melting transition can be unambiguously assigned to the microcrystalline, clustered amylopectin branches, and the glass transition to the contiguous amorphous regions of water-plasticized amylopectin. The rescan of Fig. 4(C) shows a nearly symmetrical melting endotherm with the following features: onset temperature of 71·5°C, coinciding with T_g; peak minimum of ~ 78°C; and end-of-melting T_m at 95°C. Waxy corn starch in Fig. 4(C), like normal wheat starch in Fig. 3(E), showed an undetectably small baseline shift from its leading to trailing end for the isolated melting transition associated with gelatinization in excess moisture. Thus, these new DSC results demonstrated conclusively that the change in heat capacity, illustrated in Figs 3 and 4, was associated entirely with the glass transition which immediately preceded the crystalline melting endotherm. In contrast, Yost & Hoseney (1986) also observed such a change

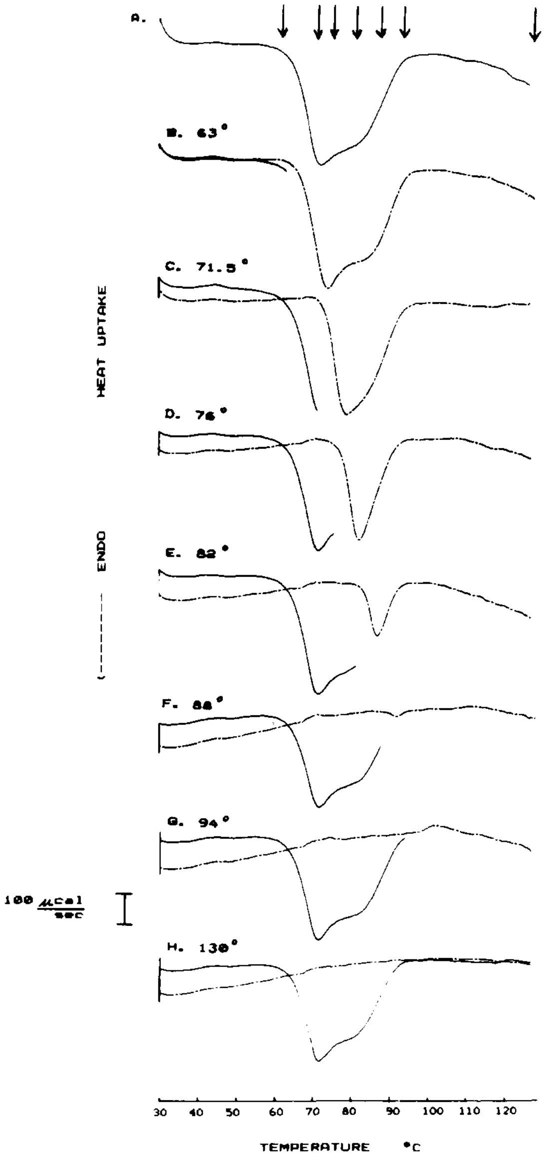

Fig. 4. Perkin-Elmer DSC-2C heat flow curves of waxy corn starch:water mixtures (45:55 w/w): A, initial scan at 10°C min^{-1} for native starch; B–H, solid lines = partial initial scans for native starch, at 10°C min^{-1}, from 20°C to maximum temperatures indicated, dashed lines = rescans at 10°C min^{-1}, immediately following partial initial scanning and then immediate cooling, at 320°C min^{-1}, to 20°C.

in heat capacity for native wheat starch in 50 w% water, but, because they did not observe a T_g (at the subzero T_g') in the DSC rescan, Zeleznak & Hoseney (1987) suggested instead that it 'merely indicates that the heat capacity of a starch–water suspension is lower than that of gelatinized starch'. Our Figs 3(E) and 4(C) demonstrated the actual explanation for their observation.

With the aim of deconvoluting the contributions of amylopectin and amylose to the non-equilibrium melting behavior of native granular wheat and waxy corn starches in 55 w% moisture, as determined in the present study, we can compare effective values of T_g and end-of-melting T_m: for wheat starch, $T_g \sim 63°C$ and $T_m \sim 92°C$, while for waxy corn starch, $T_g \sim 71{\cdot}5°C$ and $T_m \sim 95°C$. We have chosen to compare these effective end-of-melting T_m values (rather than the corresponding onset or peak values), because they would represent melting of the largest and/or most perfected microcrystals (Wunderlich, 1980), and so would be most relevant to the comparison of T_g/T_m ratios (Lelievre, 1976). For both starches, the T_m values were similar. In contrast, the effective T_g for wheat starch was significantly lower than the value for waxy corn starch.

The values of the ratio of effective T_g/end-of-melting T_m, relevant to gelatinization of these native granular starches in 55 w% water by DSC heating at 10°C min^{-1}, were 0·92 for wheat and 0·94 for waxy corn. For pure synthetic homopolymers, T_g/T_m ratios $> 0{\cdot}8$ have been attributed to highly unsymmetrical molecular structure (Brydson, 1972; Wunderlich, 1980). For water-compatible polymers other than starch, T_g/T_m ratios $> 0{\cdot}9$ have been attributed to the influence of a metastable supramolecular structure with nonuniform moisture distribution. For those carbohydrate–water systems which are spatially homogeneous due to uniform moisture content and compositionally homogeneous with well-defined $\bar{M}n$ and $\bar{M}w$, we have found that increasing T_g/T_m ratio (above 0·8) correlated with increasingly anomalous relaxation behavior, due to contributions of excess free volume (i.e. high mobility and free volume) or decreased 'local effective viscosity' in a glass at its T_g and in concentrated solutions above T_g (Slade & Levine, 1987*b*).

The effective values of T_g identified in this study, which are associated with first-stage swelling of native granular starches heated in 55 w% water, do not represent the T_g of amorphous regions of native granules at ~ 10 w% total moisture. Recent evidence has suggested that the value for that operative T_g is $> 100°C$ for several different normal and waxy cereal grain starches (Maurice *et al.*, 1985; Biliaderis *et al.*, 1986*a*; Zeleznak & Hoseney, 1987). Nor do they represent the T_g of completely amorphous gelatinized starch at 55 w% moisture, which is actually T_g' of $\sim -5°C$, as illustrated in the state diagram for starch–water presented by van den Berg (1986). The values of T_g reported here are manifested by the amorphous regions of native granules *during* the dynamic process of plasticization by heat (increasing at 10°C min^{-1} in the temperature range from 20 to 130°C) and moisture uptake (increasing in the range from 10–55 w%) and represent particular, intermediate values, within a continuum, which depend on the instantaneous temperature and content of plasticizing water.

As discussed above, when the experimental history with respect to heating rate, temperature range and total sample moisture content was the same, the thermal profiles of amylose-containing normal wheat starch in Fig. 3 and essentially amylose-free waxy corn starch in Fig. 4 did not differ qualitatively below 100°C. The major qualitative difference was the presence of a melting transition above 100°C for the crystalline lipid–amylose complex in the initial scans of normal wheat starch (also seen in immediate rescans as a result of recrystallization from the self-seeded melt), and the absence of this transition in the thermal profiles for waxy corn starch. The qualitative similarity of the thermal behavior of normal and waxy starches below 100°C indicated that the thermal profiles represented non-equilibrium melting of microcrystals composed of hydrated clusters of amylopectin branches in both cases, with no significant contributions from amylose. Thus, the quantitative differences between the values of the operative end-of-softening T_g and end-of-melting T_m for normal wheat vs. waxy corn starch should be explained on the basis of structure/property differences in their amylopectin components. As remarked earlier, sample history (path dependence, such as jumps in moisture, temperature or pressure) is often more important than inherent equilibrium thermodynamic properties, and as important as chemical structure for the explication of structure/property differences in non-equilibrium systems. Moreover, the starch–water system is neither spatially nor molecularly homogeneous, and the greater anomaly in T_g/T_m ratio for waxy corn starch compared with normal wheat starch will also depend highly on contributions of sample history as well as the structural biochemistry of the starch.

For a similar initial operative level of water plasticization in both the normal wheat and waxy corn starch systems, the quantitative differences seen for T_g, non-equilibrium T_m and T_g/T_m ratio associated with gelatinization and pasting, can be explained by the established structure/property principle for synthetic polymers that, for homologous amorphous polymers, T_g increases with increasing average MW (Billmeyer, 1984). Significantly lower average MW of the amorphous regions of the starch granule would allow a greater rate of water uptake and greater values for the instantaneous extent of water-plasticization at each time point in the DSC experiment. The underlying basis for the difference in operative average molecular weight of the amorphous regions of the native amylopectins was described in the Introduction. Disproportionation of more mobile branches with lower linear DP to the microcrystalline domains leads to higher average MW in the residual amorphous regions, and consequently, to higher effective values of T_g and kinetically constrained T_m (Slade & Levine, 1987*a*). For this reason, the relative extents of crystallinity, ranging from 15 to 42% (Zobel, 1984), of native starches from various sources and with both A- and B-type diffraction patterns, are inversely related to their gelatinization temperatures (Zobel, 1984; Snyder, 1984). The 'high amylose' starches which result from the amylose-extender mutation, and which give misleading blue value determinations of 60% amylose content (Shannon & Garwood, 1984), are an apparent exception to this rule of thumb. But even in the case of this so-called high-amylose starch, it is the anomalous amylopectin, with its long, unclustered, non-crystalline branches, that produces the dramatically elevated values of T_g and, indirectly, of T_m, in spite of the inherently low T_m of (isolated) B-type crystals. (B-type crystals, isolated to remove kinetic constraints on melting due to amorphous surroundings, would melt at a lower temperature than isolated A-type crystals.) Like the silo-aging process for rice and high-humidity drying process for potato (Snyder, 1984), the wet-milling process for corn provides an opportunity for annealing of starch (Krueger *et al.*, 1987) and concomitant elevation in extent of crystallinity, average MW of residual disproportionated amorphous regions of amylopectin, and gelatinization T_g.

This study of the gelatinization process has dealt exclusively with A-type cereal grain starches rather than B-type tuber and root starches, such as from potato. The same was true of the previously published studies (cited above); (1) by us and our group at General Foods, (2) of T_g and annealing by Hoseney's group, and (3) of annealing by Krueger *et al.* and Nakazawa *et al.* In addition to possible differences in extent of crystallinity (Zobel, 1984) due to process variations (Snyder, 1984), B-type granular starches often have higher 'as is' moisture contents in both the amorphous and crystalline regions than A-type starches (i.e. overall, but likewise heterogeneously distributed, moisture contents of ~18–20 w% for B-type vs. ~6–10 w% for A-type) (French, 1984; Whistler & Daniel, 1984). Thus, the initial instantaneously operative extent of plasticization of the continuous amorphous matrix, which subsequently governs the non-equilibrium melting of the disperse microcrystalline regions, can be significantly different for B- vs. A-type starches (Slade & Levine, 1987*a*) and can contribute to the observed lower gelatinization temperature of potato starch (Snyder, 1984). However, the generic description of the gelatinization process for cereal starches is still valid for potato starch. Greater initial moisture content in the amorphous regions increases initial free volume and decreases effective initial T_g, and in the crystalline regions, decreases effective end-of-melting T_m. The functional attributes and physical properties, including extent of crystallinity and X-ray diffraction pattern, of potato starch can be altered by deliberate drying (Donovan, 1979; Snyder, 1984) or heat-moisture treatment (Donovan *et al.*, 1983; Snyder, 1984) to resemble those of cereal starches. As a consequence of lower initial T_g, greater initial mobility and lower end-of-melting T_m, the entire heating profile of the gelatinization of native potato starch is sharper and narrower than for cereal-like, treated potato starch (at the same average total moisture content) and is centered at a lower temperature. A follow-up study, as a companion piece (Part II) to the present work, of the glass transition which controls the gelatinization of potato starch in limited added moisture, by the DSC partial-heating technique described in this paper, is in progress.

CONCLUSIONS

In closing, it cannot be overemphasized that this glass transition in starch, as in any other amorphous or partially crystalline material, represents a rate-limiting stage of a relaxation process (Ferry, 1980), for which the spectrum of relaxation rates depends on the instantaneous magnitude of the free volume and/or local effective viscosity, which in turn depends on the relative values of experimental moisture compared with W_g of the operative glass, experimental temperature compared with instantaneous T_g, and experimental timeframe compared with the instantaneous relaxation time. Thus, when DSC heating rates approach the operative relaxation rates for a measured process, a lower heating rate would result in observation of a lower T_g value. Theoretically, heating at 1° rather than 10°C min^{-1} would result in a T_g lower by about 3°C, as calculated from the WLF equation (Williams *et al.*, 1955) for 'well-behaved' polymers with T_g/T_m (in K) near 0·67. T_g differences of 3–5°C per order of magnitude are expected over broader ranges of experimental rates (or frequencies) for such well-behaved polymers, since the relaxation spectrum changes gradually from WLF to Arrhenius kinetics over a temperature interval of about 100°C below T_m. Experimentally, this expectation was confirmed in the case of polystyrene, for which the value of T_g was lower by 15°C when the heating rate was decreased from 1° s^{-1} to 1° h^{-1}, a factor of 3600 (Wunderlich, 1981). DSC experiments with slow heating rates of less than 0·5°C min^{-1}, for very dilute aqueous potato starch suspensions of about 2% solids, have allowed a very small scale micro-reversibility, which was misinterpreted as the ability to achieve and maintain equilibrium throughout the gelatinization process (Shiotsubo & Takahashi, 1986). Loss of temporal resolution of the thermal events due to the greatly excess moisture content accounted for part of the apparent micro-reversibility. Actually, isothermal treatment of aqueous rice starch slurries with excess moisture (50% solids), for more than 100 h at various temperatures between 40–85°C (equivalent to infinitely slow heating rates), was not sufficient to approach an equilibrium state (Nakazawa *et al.*, 1984), as expected, since the melting of partially crystalline systems is never an equilibrium process (Wunderlich, 1981). The dynamic nature of the glass transition is also reflected in the non-equilibrium annealing process for native starches in limited moisture. For example, recently reported results for annealing (to measurable, but not necessarily equal, extents, for different granular starches) at different temperatures and times have included the following: (1) waxy corn at 55 w% moisture, 70°C for 10 min or 65°C for 30 min (Maurice *et al.*, 1985); (2) wheat at 50 w% moisture, 72°C for 30 min or room temperature for 24 h (Yost & Hoseney, 1986); (3) dent corn in excess added water, 60°C for 15 min, 55°C for 2 h, or 50°C for 48 h (Krueger *et al.*, 1987); (4) normal and waxy rices at 50 w% moisture, from 85°C for 5 min to 40°C for 140 h (Nakazawa *et al.*, 1984); and (5) wheat at 55 w% moisture, 25°C for 55 days (Slade, 1984; Slade & Levine, 1987*a*). Comparison of these results leads to the conclusion that significant annealing at lower temperatures for longer times is apparently controlled by a much lower operative T_g (resulting from a longer experimental timeframe) than the T_g which precedes crystallite melting by heat-moisture treatment in the DSC. In other words, the operative T_g relevant to annealing at $T_g < T_a < T_m$ decreases with increasing holding time in excess added moisture at lower temperatures, due to the effect of dynamic plasticization. The unifying explanation lies in the fact that the progressively resultant events of plasticization, relaxation above the glass transition, and functional manifestation (including starch gelatinization, crystallite melting, annealing, and recrystallization) are all dynamic, non-equilibrium processes, the kinetics of which are governed by WLF theory for glass-forming systems.

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