

# ACCEPTED MANUSCRIPT

The ‘Food Polymer Science’ Approach to the Practice of Industrial R&D, Leading to Patent Estates Based on Fundamental Starch Science and Technology

LOUISE SLADE and HARRY LEVINE\*

Food Polymer Science Consultancy, Morris Plains, New Jersey, USA

\*Author for correspondence at LevineHarry@optonline.net

## ABSTRACT

This paper reviews the application of the ‘Food Polymer Science’ approach to the practice of industrial R&D, leading to patent estates based on fundamental starch science and technology.

The areas of patents and patented technologies reviewed here include: a) soft-from-the-freezer ice creams and freezer-storage-stable frozen bread dough products, based on ‘cryostabilization technology’ of frozen foods, utilizing commercial starch hydrolysis products (SHPs); b) glassy-matrix encapsulation technology for flavors and other volatiles, based on structure-function relationships for commercial SHPs; c) production of stabilized whole-grain wheat flours for biscuit products, based on the application of ‘solvent retention capacity’ technology to develop flours with reduced damaged starch; d) production of improved-quality, low-moisture cookies and crackers, based on pentosanase enzyme technology; e) production of ‘baked-not-fried’, chip-like, starch-based snack products, based on the use of commercial modified-starch ingredients with selected functionality; f) accelerated staling of a starch-based food product from baked bread crumb, based on the kinetics of starch retrogradation, treated as a crystallization process for a partially crystalline glassy polymer system; g) a process for producing an enzyme-resistant

# ACCEPTED MANUSCRIPT

starch, for use as a reduced-calorie flour replacer in a wide range of grain-based food products, including cookies, extruded expanded snacks, and breakfast cereals.

## KEYWORDS

Glass transition, Tg, state diagram, SHPs, biscuit products, flour functionality, SRC, pentosanase enzyme, resistant starch

# ACCEPTED MANUSCRIPT

## INTRODUCTION

The ‘Food Polymer Science’ (FPS) approach, created and developed by Louise Slade and Harry Levine in the early 1980s at General Foods, has been the basis of the technical subject matter of two previous review papers published in this Journal (Slade and Levine, 1991; Kweon et al., 2014). Unlike those, the present paper focuses on a review of the application of the FPS approach to the practice of industrial R&D, leading to patent estates based on fundamental starch science and technology. In this review, the underlying context of the subject matter described is “Why patents are important to....?”: a) the local company that owns them; b) the global locations of the company that owns them; c) the companies that do not own them; and d) the entire technical community. The answer to (a) -- patents covering industrially commercialized, new and novel food ingredients, processes, and products can create and generate huge business and financial value for the local company that owns them -- will be made obvious from the technical material emphasized throughout the main text. But the answers to (b)-(d) will wait to be explicitly addressed in a Conclusions section at the end of this paper.

The underlying principles of the FPS approach have been reviewed in detail previously elsewhere (Levine and Slade, 1988a). Suffice it to say here that they include the following key elements: a) the importance of the glass transition and its temperature, T<sub>g</sub>; b) the critical role of water as a plasticizer of amorphous food materials; c) the effect of water on T<sub>g</sub> and resulting diffusion-limited behavior; and d) the significance of non-equilibrium glassy and rubbery states in ‘real world’ food products and processes, and their effects on processibility, quality, and storage stability. Early on, the applicability of the FPS approach to starch was usefully demonstrated (Slade, 1984; Maurice et al., 1985; Slade and Levine, 1987a). Figure 1 (Slade and

Levine, 1987a) illustrates the primary structural and functional aspects of the FPS approach with reference to starch. This structural aspect is described in terms of the T<sub>g</sub> and the crystalline melting temperature, T<sub>m</sub>, of the classic Fringed Micelle model, and how the sequential T<sub>g</sub> and T<sub>m</sub> transitions control the non-equilibrium melting of starch, viewed as a partially crystalline glassy, water-compatible polymer system. The primary functional aspect of the FPS approach is described in terms of a schematic ‘state diagram’ of temperature vs. water content, utilized as a ‘mobility map’ for starch. The underlying message here is that starch’s structural and functional properties dictate the many structure-function relationships of starch, which have served as a basis for industrial R&D efforts that have led to many practical food ingredient, process, and product applications and patentable opportunities since the early 1980s (Slade and Levine, 2017).

In the spirit of the concept of “standing on the shoulders of giants”, it is important to point out that the FPS approach was built on a foundation of seminal works by earlier pioneers. For example, nearly 90 years ago, G.S. Parks and co-workers (Parks et al., 1928, 1929, 1930, 1934a,b,c) published the first known studies on glasses, the glassy state, and the T<sub>g</sub> of a food material, exemplified by glucose, as illustrated by the compilation in Fig. 2 (Slade and Levine, 2009). Another example was the work of Felix Franks and co-workers (Franks et al., 1977) at Cambridge University in the 1970s, who were the first to explicitly recognize and study the particular T<sub>g</sub>’ of frozen aqueous systems, as illustrated by the compilation in Fig. 3 (Slade and Levine, 2009). And a third example was the doctoral thesis work by Cornelius van den Berg (van den Berg, 1981, 1986), wherein the amorphous regions of native granular starches, their T<sub>g</sub> value as a function of moisture content, and the resulting glass curve and state diagram for starch, were

first explicitly discussed in 1981, as illustrated by the compilation in Fig. 4 (Slade and Levine, 2009).

Continuing with the theme of the Tg of starch, a novel concept that was new to the field of food science and technology in the early 1980s, it was at that same time that the FPS approach was first applied to the study of starch's Tg. As illustrated in Fig. 5 (Slade, 1984; Slade and Levine, 1988), definitive evidence, from differential scanning calorimetry (DSC) analysis, of the characteristic change in heat capacity at the glass transition of native granular wheat starch in excess water was first presented in 1984 (Slade, 1984). As illustrated further in Fig. 6 (Slade, 1984; Slade and Levine, 1987a; Slade and Levine, 1988), the temperature location of that Tg was shown to coincide with the onset of the non-equilibrium melting temperature, Tm, which coincided in turn with the onset temperature of the so-called gelatinization endotherm for native starch in water, for both normal wheat starch, as shown in Fig. 7 (Slade and Levine, 1988), and waxy (i.e. all-amylopectin) corn starch, as shown in Fig. 8 (Slade and Levine, 1988). The schematic state diagram shown in Fig. 9 (Slade and Levine, 1991), viewed as a conceptual representation of whole-grain processing, illustrated how the Tg and associated glass curve for starch control the two stages of swelling (2, 3, 4) and ultimate gelatinization (3), as involved in various starch cooking processes, such as parboiling (5) or ordinary cooking of rice (4), or puffing or popping of, e.g., popcorn (6).

#### CRYOSTABILIZATION TECHNOLOGY OF FROZEN FOODS

Cryostabilization technology is the part of the FPS approach that deals with the freezer-storage stability of frozen food systems. As illustrated in Fig. 10 (Levine and Slade, 1988b), this

technology is based on the temperature location of  $T_g'$  for the maximally freeze-concentrated aqueous glass surrounding the ice crystals in a frozen product, relative to the freezer-storage temperature,  $T_f$ . In simplest terms, when  $T_g'$  of the ice-containing product is above  $T_f$ , the food would be in a partially glassy solid state that could be stable indefinitely. But if  $T_g'$  is below  $T_f$ , the non-ice portion of the frozen product would be in a viscous or rubbery liquid state, and the food would have much more limited freezer-storage stability.

The plot of  $T_g'$  vs.  $W_g'$ , the amount of unfreezable water in the glass at  $T_g'$ , shown in Fig. 11 (Levine and Slade, 1988b) illustrates the ‘cryostabilization technology’ spectrum of ingredients that might be found in fabricated frozen foods. These ingredients range from ‘polymeric cryostabilizers’ such as commercial starch hydrolysis products (SHPs), including e.g. low-DE (dextrose equivalent) maltodextrins, with characteristic high  $T_g'$  and low  $W_g'$  values, at the top left, to ‘monomeric cryoprotectants’ such as low-molecular-weight (MW) carbohydrates, including e.g. monosaccharide sugars and polyhydric alcohols, with characteristic low  $T_g'$  and high  $W_g'$  values, at the bottom right. Figure 12 (Levine and Slade, 1988b) is a simplified version of Fig. 11, showing the  $T_g'/W_g'$  locations for a spectrum of commercial SHPs, other carbohydrate sugars, and polyols, again ranging from higher  $T_g'/lower W_g'$  cryostabilizers at the upper left to lower  $T_g'/higher W_g'$  cryoprotectants at the lower right. What’s particularly noticeable is a specific 36-DE Corn Syrup Solid (CSS) commercial ingredient, at the upper right, with an unusual combination of higher  $T_g'$  and higher  $W_g'$ . As illustrated in the compilation shown in Fig. 13 (Slade and Levine, 2009), this unusual 36-DE CSS, with its unique high  $T_g'/W_g'$  functionality, was a key commercial SHP ingredient used to formulate a novel soft-from-the-freezer, extrudable ice cream product with good freezer-storage stability against ice

crystal growth. Product formulations in the ‘atypical’ area highlighted in the lower-left quadrant of the lower-right diagram in Fig. 13, representing ‘stable/easy to extrude’ products, proved to be patentable. These formulations led to a pair of U.S. Patents (Cole et al., 1983, 1984), assigned to General Foods, for industrially commercialized ‘Soft, Frozen Dessert Formulation’ products with ready extrudability and good freezer-storage textural stability. Cryostabilization technology was also shown to be applicable, as illustrated in Fig. 14 (Levine and Slade, 1990a), through the use of a 10-DE maltodextrin commercial SHP as an effective polymeric cryostabilizer for a frozen bread dough product, specifically a novel ‘freezer-to-oven, proofed-before-frozen’ freezer-storage-stable bread dough product. A related application of this technology led to another pair of General Foods patents, one U.S. and one European (Lindstrom and Slade, 1983, 1987), for such novel ‘freezer-to-oven, proofed-before-frozen’ bread dough bakery products with good freezer-storage stability of their baking and textural characteristics.

#### STRUCTURE-FUNCTION RELATIONSHIPS FOR COMMERCIAL SHPs

The FPS approach was applied in the construction of a ‘map’, shown in Fig. 15 (Levine and Slade, 1986), of the structure-function relationships for a large family of commercial SHPs. This  $T_g$ ' vs. MW/DE plot was utilized as a basis in the development of a novel four-component glassy matrix for the encapsulation of flavors and other volatile or labile liquid food components. This glass-encapsulation technology, keyed by the use of several commercial SHPs with selected  $T_g$  functionality, led to three U.S. Patents (Levine et al., 1991, 1992; Gimmier et al., 1996), assigned to Nabisco.

APPLICATIONS OF FLOUR ‘SOLVENT RETENTION CAPACITY’ (SRC) TECHNOLOGY  
FOR DEVELOPMENT OF WHEAT FLOURS WITH IMPROVED BAKING  
FUNCTIONALITY

Wheat flour for baking is composed mainly of native granular starch. But the portion of that starch that impacts the biscuit-baking functionality of a flour is the relatively small amount of the starch that is damaged (i.e. granules broken open) during flour milling, thereby exposing the interior starch polymers to excessive, detrimental interaction with water or other aqueous solvent during dough mixing and baking. Thus, as shown in Fig. 16 (Slade and Levine, 1993), damaged starch is one of the three key polymeric components of wheat flour, along with gluten protein and pentosans, which controls the functional specifications of a flour. Alveography is one of the preferred flour functional specification methods for soft wheat flours for biscuit-baking applications (Kweon et al., 2014). The alveogram shown in Fig. 17 (Kweon et al., 2011) suggests how the damaged starch component of a wheat flour detrimentally impacts the flour’s rheological and viscoelastic properties and resulting biscuit-baking functionality, by contributing to an increased Pmax value that signifies the increased resistance of a flour-water dough to bubble formation and expansion.

In the context of flour performance for baking, the functional properties of the three polymeric components of wheat flour -- damaged starch, gluten protein, and pentosans -- depend on how these polymers interact with water or other aqueous solvent in a dough to become hydrated or solvated and then swelled. As suggested in Fig. 18 (Sears and Darby, 1982; Slade and Levine, 2009), the nature of this polymer-solvent interaction -- involving solvation and swelling, but not dissolution, as could be the contrasting case for small molecules -- can be usefully characterized

in terms of a ‘Solubility Parameter’ approach adopted from synthetic polymer science (Slade and Levine, 1994), wherein solvent retention capacity is the standard method used to measure the Solubility Parameter of polymers. Thus, a Solvent Retention Capacity or so-called SRC method was created and developed (Slade and Levine, 1994; Kweon et al., 2011), as a new functional specification method complementary to alveography, for evaluating wheat flour quality and functionality in a wide range of baking applications, deliberately not limited to soft wheat flours for cookie- and cracker-making. The SRC profile or pattern of values for the three functional polymeric components of flour, as defined by what has become the AACC Method 56-11 (AACC International, 2009), was conceived on the basis of a Solubility Parameter approach to characterize the maximum extent of solvation and swelling of each individual polymeric component of a flour in a different, specifically selected swelling solvent. The individual solvent chosen for use to reveal the swelling behavior due to the damaged starch in a flour, and its consequent impact on baking functionality -- which would be detrimental to biscuit baking, but could be beneficial to other baking applications such as bread-making, for which a product’s increased water-holding capacity could be a quality plus (Kweon et al., 2011) -- is a 5 w% solution of sodium carbonate in water at pH 11. Such sodium carbonate SRC values, which increase with an increasing contribution to overall flour swelling due to damaged starch in a series of sample flours, have been shown to correlate well with corresponding alveogram results showing increasing Pmax values for the same flour series (Slade and Levine, 2009; Kweon et al., 2011). This new SRC technology led to the development and commercialization in 2004 of a new cultivar of Washington soft white spring wheat (SWSW), named ‘Louise’ by its breeder (Kidwell et al., 2006; see Fig. 19 (Slade and Levine, 2009)). ‘Louise’ wheat is a high-quality,

biscuit-friendly, Pacific northwest SWSW, whose breeding development was guided by the SRC flour quality testing methodology that had been created at Nabisco in the late 1980s. SRC testing of the biscuit flour milled from ‘Louise’ wheat demonstrated that its superior baking performance was critically due in part to reduced levels of detrimental damaged starch and pentosans in the flour, resulting from this wheat’s enhanced kernel softness (Kweon et al., 2011). As a further complement to alveography and the new SRC method, a new wire-cut cookie test-baking formula/method was also created and developed (Levine and Slade, 1993), which has become the AACC Method 10-53 shown in Fig. 20 (AACC International, 2009), for the practical evaluation of flour quality and functional performance for commercial cookie and cracker baking.

Part of the Global Biscuit Flour Science and Technology R&D program, carried out by Nabisco’s long-standing Flour Performance Task Force, led to a Kraft-Nabisco patent estate of five U.S. Patents (Wilhelm et al., 2003; Haynes et al., 2012a,b, 2013a,b) and one International Patent Application (Haynes et al., 2007), for ‘Production of Stabilized Whole-Grain Wheat Flour for Biscuit Products’. These patents describe novel, industrially commercialized milling processes for whole-grain wheat (Graham) flours with improved biscuit-baking functionality, due to reduced levels of detrimental damaged starch, as assayed by SRC methodology, and consequently beneficial reduced water-holding capacity and thus (always desirable) reduced water requirements for dough-making, along with concomitant facilitation of moisture bake-out (Slade and Levine, 1994; Kweon et al., 2011, 2014).

PENTOSANASE ENZYME TECHNOLOGY FOR PRODUCTION OF IMPROVED-  
QUALITY, LOW-MOISTURE COOKIES AND CRACKERS

A new pentosanase enzyme technology R&D program was initiated at Nabisco in the late 1980s. The alveograms shown in Fig. 21 (Slade and Levine, 1993; Levine and Slade, 2004) illustrate the remarkable beneficial effects of Nabisco's so-called PEN enzyme (aka PEN), an endo-xylanase enzyme capable of hydrolyzing the water-accessible arabinoxylans (aka 'pentosans') in a typical soft wheat-based biscuit flour. Such pentosans, in the absence of endo-chain-breakage by PEN, would otherwise be three-dimensional gel network-forming and thereby extremely highly water-holding during dough-mixing and -baking. PEN's action, on the pentosans present -- even in a high-quality, Ohio soft red winter wheat (SRW)-based biscuit flour of modest gluten strength -- and otherwise highly detrimentally interactive with added water, enabled a flour-water dough to be made with 15% less than the normal amount of added water required for processability of such a dough in the alveograph, or analogously, for acceptable machinability of a dough in commercial manufacturing. 15% less formula water, added to produce a machinable biscuit dough, would translate to that much less water: a) available to the flour for the detrimental swelling of its damaged starch during dough-mixing; or b) available in a dough for the potentially excessive starch gelatinization during baking, which would ordinarily be detrimental to finished-product texture; or c) present and therefore needing to be fully baked-out, otherwise often resulting in too-high finished-product moisture content, which would typically be detrimental to overall baked-product quality and shelf-life (Levine and Slade, 2004).

Figure 22 (Levine and Slade, 1990b) shows diagnostic DSC results for samples, each mixed 1:1 by weight with water, of Nabisco's typical soft wheat-based flour for cookies and crackers, a baked wire-cut cookie, and a baked lean cracker, both products made with that same flour. The top thermogram is entirely predominated by the two primary thermal transitions -- endotherms for the gelatinization of amylopectin and the melting of amylose-lipid crystals -- for the initially raw native granular wheat starch in the flour. The middle thermogram shows the same two primary endothermic transitions for the baked cookie as for the raw flour. And after appropriate normalization of the two peak areas for sample size -- as well as recognition of slight annealing of the amylopectin, and notice of a small fat-melting endotherm at lower temperature -- it can be seen that the baked cookie still manifested 100% native amylopectin and amylose-lipid crystals, because its high sugar content completely prevented any gelatinization of the wheat flour starch during baking (Slade and Levine, 1994). In contrast, as shown in the bottom thermogram, the baked lean cracker, with much higher formula water than for the cookie, but no added formula sugar, evidenced that ~60% of the wheat flour starch (based on comparison of peak areas) was gelatinized during baking. It's worth mentioning here that this large difference, in the extent of flour starch gelatinization during baking of such low-moisture cookies and crackers, accounts in part for the resulting 'night-and-day' difference in their product textures. Figure 23 (Levine and Slade, 1990b, 2004) shows the definitive results from a diagnostic DSC study on crackers. The top two thermograms are for the same cracker flour and excellent-quality full-fat saltine cracker as in Fig. 22. But the bottom-left thermogram in Fig. 23 reveals the result of a failed attempt to produce a no-fat version of the full-fat control saltine cracker represented at the top right. When the tenderizing fat was completely left out of the bottom-left prototype, additional (necessary for

plasticizing) formula water had to be used to enable the no-fat dough to be normally machinable. But the presence of this extra water allowed additional amylopectin (~69% in total) to be detrimentally gelatinized during baking (Slade and Levine, 1994), resulting in a poor-quality prototype that had a cardboard-like texture. The solution to this Product Development problem, as illustrated by the bottom-right thermogram in Fig. 23, was the addition of PEN enzyme to the no-fat cracker formula. This introduction of PEN enabled a machinable no-fat cracker dough to be produced using the control level of formula water. That improvement resulted in no significant additional starch gelatinization (~61% in total) during baking, compared to that in the full-fat control, and thereby yielded an excellent-quality no-fat cracker with a consumer-preferred tender texture matching that of the full-fat saltine cracker (Craig et al., 1992).

Figure 24 (Slade and Levine, 1991) illustrates principles of ‘brown color development and stability’, as applicable and applied to color formation during cookie baking, and baked-color stability and the resulting absence of color fading during product shelf-life. The plot in Fig. 24 shows that color development and stabilization depend on the critical variables of moisture content, temperature, and time. As applied to cookie baking, the key to a successful baking process is a temperature/time baking profile that results in a desired moisture-loss profile and sufficiently low finished-product moisture content. These key process aspects enable the ultimate formation of final stable brown-colored compounds at low moisture, late in baking, from unstable brown-colored intermediates produced at higher moisture contents earlier in baking. Such stable brown color of low-moisture baked products can be shown to resist color fading indefinitely during shelf-life. And in this context, the use of PEN: a) to enable machinable dough-making with (always desirable) minimized formula water addition (Kweon et al., 2011,

2014); b) to facilitate sufficient moisture loss during baking, without surface burning or excessive heating to gelatinize too much starch; and c) to inhibit any fading-promoting moisture regain during product storage, has been demonstrated to be extremely beneficial in commercial manufacturing practice (Slade et al., 1989, 1993).

Nabisco's pentosanase enzyme technology R&D program led to a patent estate of one 1989 European Patent Application (Slade et al., 1989) and five subsequent U.S. Patents (Craig et al., 1992; Slade et al., 1993, 1994; Zimmerman et al., 1996a,b), for 'Enzyme-Treated Low Moisture Content Comestible Products', encompassing a proprietary endo-xylanase enzyme technology for the industrially commercialized production of improved-quality cookies and crackers. This enzyme technology enabled minimized formula water usage for the production of machinable biscuit doughs, thus avoiding a) excessive, detrimental (to product texture) starch gelatinization during cookie/cracker baking, and b) too-high finished-product moisture content, detrimental to biscuit product quality and shelf-life. Nabisco was able to apply this patented pentosanase technology to a) the commercial production of Fat-Free Premium Saltine crackers with consumer-acceptable tender texture (Craig et al., 1992), b) Chips Ahoy! chocolate chip cookies with desirable baked-product color and reduced color fading during shelf-life (Slade et al., 1993), c) crackers with reduced 'checking' and breakage during shelf-life (Slade et al., 1994), d) calcium-enriched crackers with consumer-acceptable tender texture (Zimmerman et al., 1996a), and e) reduced-fat, low-fat, or no-added-fat crackers with tenderized texture (Zimmerman et al., 1996b), owing to a reduced extent of starch gelatinization during baking.

PRODUCTION OF ‘BAKED-NOT-FRIED’, CHIP-LIKE, STARCH-BASED SNACK PRODUCTS

Figure 25 (Colonna and Buleon, 1992; figure on the right (Biliaderis, 1991); Slade and Levine, 2009) illustrates two ‘Food Polymer Science’-based treatments of structure-property relationships of starch. Colonna’s figure on the left represents a spectrum of modified-starch ingredients, like the commercial ones that were identified and selected for use in the development of the unique ‘bubbles and crunch’ characteristics of Nabisco’s commercial line of ‘Air Crisps’ products. That starch-ingredient technology led to a patent estate of six U.S. Patents (Addesso et al., 1995, 1996; Hnat et al., 1997; Carey et al., 1998, 1999, 2002), encompassing Nabisco’s proprietary formulation technology, based on key commercial modified-starch ingredients with specially selected functional properties, for the production of the ‘Air Crisps’ product line of baked-not-fried, crispy snack chips with unique surface bubbles. This industrially commercialized line of products included Nabisco’s Mr. Phipps Tater Crisps, Potato Air Crisps, Crispers/Crack-Ups, Ritz Air Crisps, Wheat Thins Air Crisps, Cheese Nips Air Crisps, and Ritz Chips.

ACCELERATED STALING OF A STARCH-BASED FOOD PRODUCT FROM BAKED BREAD CRUMB

The FPS approach adopted, from synthetic polymer science, the crystallization kinetics theory and mechanism described in Fig. 26 (Levine and Slade, 1990a) for partially crystalline glassy polymers. As illustrated in this Figure, the mechanism has three sequential steps: 1) nucleation (or seed crystal nucleus formation), with a rate increasing with decreasing temperature, down to

Tg; 2) propagation (or crystal growth), with a rate increasing with increasing temperature, up to Tm; and 3) maturation (or slow further crystal growth and/or perfection). According to this mechanism, a single holding temperature midway between Tg and Tm would result in an intermediate overall crystallization rate. In 1948, John Ferry, a well-known academic polymer chemist of the time, applied this crystallization kinetics theory and mechanism to the gelation of gelatin (Ferry, 1948). Ferry was able to demonstrate that he could produce a partially crystalline gelatin gel from a completely amorphous gelatin-water sol, using a two-step time/temperature protocol to first maximize the rate of nucleation, by holding for a minimal time at a low temperature (i.e. above gelatin's relevant Tg,  $Tg' = -12^{\circ}\text{C}$  (Slade and Levine, 1987b; Levine and Slade, 1988a)), and then to maximize the rate of propagation, by holding for another minimal time at a higher temperature (i.e. just below gelatin's relevant Tm of  $37^{\circ}\text{C}$  (Slade and Levine, 1987b)). Importantly, the resulting high- moisture gelatin gel showed a much greater initial gel strength, due to its greater extent of crystallization, achieved in a much shorter setting time, and no tendency toward maturation over subsequent storage time. In contrast, another gelatin gel, formed conventionally by holding at a single setting temperature midway between Tg and Tm for a much longer time, had a much weaker initial gel strength, but a more typical tendency to mature over storage time to a much more rubbery final texture.

35 years after Ferry's seminal study on gelatin, his unique crystallization protocol was adopted, modified, and then applied to starch, in the development of a novel industrial process to accelerate the staling, by maximizing the rate of starch retrogradation, in freshly baked white bread crumb. It is well known that native granular, partially crystalline wheat flour starch is completely gelatinized during the baking of white pan bread. As illustrated in Fig. 27 (Levine

and Slade, 1990a), the kinetics of the crystallization process underlying starch retrogradation in as-is moisture baked bread could be optimized, using a similar two-step time/temperature protocol to first maximize the rate of nucleation, by holding the completely amorphous, gelatinized aqueous starch network for a minimized time at a low temperature just above starch's applicable  $T_g$  (of  $T_g' = -5^\circ\text{C}$  (Slade and Levine, 1987a)), and then to maximize the rate of propagation, by holding for another minimized time at a higher temperature just below starch's applicable  $T_m$  (of  $60^\circ\text{C}$  for recrystallized B-type amylopectin (Slade and Levine, 1987a)). In this case, the resulting retrograded starch network, created in the as-is moisture baked bread crumb, showed a much greater extent of staling, achieved in a much shorter storage time, in contrast to the same baked bread staled conventionally by holding at a single storage temperature between  $T_g$  and  $T_m$ , such as room temperature, for a much longer time. It is of practical processing importance to note here that the rate curve for overall crystallization, shown in Fig. 27, is not symmetrical, but rather is skewed toward lower temperature, because the process of starch retrogradation has been found to be nucleation-limited (Slade and Levine, 1987a).

The DSC results shown in Figs. 28-30 (Slade and Levine, 1987a) revealed and confirmed the nucleation-limited aspect of this crystallization protocol underlying starch retrogradation, and the ultimate success of this accelerated staling process. As shown in thermogram A of Fig. 28, ordinary staling of freshly baked, as-is moisture bread crumb, at  $25^\circ\text{C}$  room temperature for 39 days of storage, produced a melting endotherm of relatively smaller area for retrograded amylopectin. In contrast, thermogram C of Fig. 28 showed a melting endotherm of much larger area, representing a far greater extent of staling, achieved in just less than two days of total storage time, via 42 hours of nucleation at  $0^\circ\text{C}$ , followed by 2.5 hours of propagation at  $40^\circ\text{C}$ .

The DSC thermograms shown in Fig. 29 identified and illustrated the optimum time/temperature conditions for the accelerated creation of an extensively staled starch network, based on the two-step crystallization kinetics mechanism described above. Thermogram G revealed those optimized conditions to be 2 hours at 4°C, followed by 6.5 hours at 40°C. It is also worth noting that no staling at all was possible or observed in any of the gelatinized wheat starch-water samples stored below starch's  $T_g'$  of -5 °C, and thereby 'cryostabilized' (Slade and Levine, 1987a; Levine and Slade, 1988b). The thermograms shown in Fig. 30 illustrated the predominant effect of increased nucleation time at 0 °C on the accelerated extent of starch staling in gelatinized wheat starch-water samples. For all those samples, initially gelatinized and lastly propagated under identical time/temperature/moisture conditions, the overall extent of starch retrogradation clearly increased systematically with increasing nucleation time, from 10 minutes to 5 hours, at 0 °C.

This new starch processing technology ultimately led to a U.S. Patent (Slade et al., 1987), assigned to General Foods, for a novel process to accelerate the staling of a starch-based food product (e.g. GF's Stove Top stuffing mix) produced from freshly baked bread crumb. This industrial process to accelerate the retrogradation of gelatinized starch was based, as described above, on optimizing the crystallization kinetics for a partially crystalline glassy polymeric starch system. It enabled an extent of staling, required for consumer-preferred product texture, which was achievable in as little as 5-8 hours of total storage time after baking, in contrast to the same overall extent of staling, conventionally achieved by room temperature storage of the same baked bread loaves (or extruded ropes) for at least three days -- of more costly storage time.

PROCESS FOR MAKING AN ENZYME-RESISTANT STARCH FOR USE AS A  
REDUCED-CALORIE FLOUR REPLACER

A further (and later) extension of the novel starch processing technology described above (from the mid-1980s at General Foods) led to a case study (described in Fig. 31 (Slade and Levine, 1987a, 2009)), and an R&D program at Nabisco, which put theory into practice, with the goal to create a unique enzyme-resistant starch (RS), a food ingredient with enhanced thermomechanical stability in commercial baking and extrusion processes. Such an RS needed to have a crystalline melting T<sub>m</sub> above 140°C, even in high-water-content systems, and needed to be produced by an industrially commercializable manufacturing process that deliberately avoided the recrystallization of typical staled starch (of T<sub>m</sub> ~ 60°C) and amylose-lipid crystals (of T<sub>m</sub> ~ 110°C). As illustrated in Fig. 32 (Slade and Levine, 2009), the RS that resulted from this R&D program, Nabisco's so-called X-150 enzyme-resistant starch, was a unique Type-3 RS comprised of retrograded amylose. It had a T<sub>m</sub> of 150°C, for exceptional heat stability in baking and extrusion processes, and superior cookie-baking characteristics, due to its highly desirable, unusually low water-holding capacity, browning capability, and crisp-texture attributes. Furthermore, X-150 assayed as 50% insoluble fiber by AOAC Method 991.43 (AOAC International, 2005), so it was 50% calorie-reduced, compared to normal starch. Thus, X-150 was shown to be capable of functioning as a wheat flour-replacer ingredient in a wide range of grain-based food products.

Figure 33 (Slade and Levine, 2009) shows the three-stage Process Flow Chart for the pilot-plant manufacture of X-150. The key aspects of the sequential process steps, which were critical to the

production of the ultimate X-150 final product, were as follows: stage 1 -- complete gelatinization, by heating to 130°C, of the initial starting-material 40:60% w/w mixture of native granular, 70% high-amylose corn starch and water; stage 2 -- treatment of the gelatinized starch-water mixture by an optimized series of four sequential time/temperature cycles of nucleation at 60-80°C, in order to nucleate only high-T<sub>m</sub> retrograded amylose, while deliberately preventing the otherwise typical recrystallization of B-type amylopectin of T<sub>m</sub> = 60°C, followed by propagation at 120-130°C, in order to propagate only retrograded amylose of T<sub>m</sub> = 150°C, while deliberately preventing any otherwise typical recrystallization of amylose-lipid crystals of T<sub>m</sub> ~ 110°C; and stage 3 -- heat-moisture treatment, at 130°C, of the product of stage 2, in order to promote the maturation, and thereby further increase and perfect the (enzyme-resistant) crystallinity of the portion of the material with crystalline T<sub>m</sub> = 150°C, as well as to increase the density of the non-crystalline portion of the stage-2 product, thereby further increasing the enzyme resistance of this starch material.

Figure 34 (Haynes et al., 2000; Slade and Levine, 2009) shows Modulated DSC results for two X-150 samples. The top thermogram shows a small but clearly evident melting endotherm at 149°C, for the retrograded amylose portion of the stage-3 product of the X-150 manufacturing process, but the complete absence of any other crystalline melting endotherms, such as at T<sub>m</sub> ~ 60°C for typical staled starch or at T<sub>m</sub> ~ 110°C for amylose-lipid complex. And the bottom thermogram in Fig. 34 shows even more clearly the much larger melting endotherm at T<sub>m</sub> = 151°C, for an isolated RS crystalline component of the stage-3 X-150 product, but no other melting endotherms at lower temperatures.

As shown in Fig. 35 (Slade and Levine, 2009), the superior cookie-baking functionality of X-150, as a 50% flour-replacer ingredient, was demonstrated using the standard wire-cut cookie test-baking method AACC 10-53 (AACC International, 2009). The desired extent of spread and baked color of the control cookie (at top-left), made with 100% of Nabisco's high-quality, Ohio SRWW-based cookie flour, was clearly matched only by the 50% X-150 sample cookie (at top-right), but not by any of the National Starch commercial Type-2 (cookies at bottom-left and bottom-center) or Type-3 (cookie at bottom-right) RS ingredients tested, all of which showed unacceptably reduced cookie spread and too-pale baked color, symptomatic of inferior cookie-baking functionality, due to their much lower T<sub>m</sub> values and much higher water-holding capacities, compared to X-150 (Haynes et al., 1999; Slade and Levine, 2009).

The R&D program on X-150 led to a Nabisco-Kraft patent estate of one International Patent Application (Haynes et al., 1999) and ten U.S. Patents (Haynes et al., 2000, 2002, 2003, 2009, 2011, 2013c; Squire et al., 2010; Zimeri et al., 2010, 2012, 2013), for a new Type-3 enzyme-resistant starch (RS) ingredient, a novel technological process for its production, and for its various uses in baked, breakfast cereal, and extruded-snack food products. This new "health & wellness" ingredient, Nabisco's so-called X-150 (for its 150°C crystalline melting temperature of its retrograded amylose), had a dietary fiber content of up to 60% and a resulting caloric content of as low as 1.6 calories/gram. Its novel functionality related, e.g., to its cookie-baking performance -- when used as a reduced-calorie, 50%-level wheat flour replacer -- which was superior to any previously available commercial RS ingredient, and to its high-temperature extrudability, owing to its 150°C melting temperature. Under exclusive license from Kraft-Nabisco for its X-150 ingredient and process patents, this RS ingredient was ultimately

# ACCEPTED MANUSCRIPT

industrially commercialized, produced, and sold for a time by Tate & Lyle, as its ‘Promitor’-branded RS ingredient.

## CONCLUSIONS

Why are patents important to the global locations of the company that owns them? Within a company that owns an active patent, the original research behind the patent can be translated to technical advances for education and training of product developers and marketing teams, in addition to global technology transfer, to create targeted consumer-preferred products appropriate for different cultures and consumer groups.

Why are patents important to the companies that do not own them? For companies that do not own a particular active patent, the process of creating actionable research findings, and making them useful for product development and process optimization, can be learned from the patents of others, for creation of inventions that are more relevant to the market needs of those other companies.

Why are patents important to the entire technical community? Industrial research that has demonstrated superiority by its patentability, and by its ability to create a marketing competitive advantage, can teach, both within the company that owns the patent and throughout the outside world of corporate and academic and government research, because each organization or entity has different and non-overlapping end-product goals. Patents do not claim the ‘research’ that enabled the invention, so that research is available for anyone to study and use, as applied to their own ingredient/process/product/shelf-life inventions. Patents teach that research can be successfully and valuably translated to marketplace reality, and other scientists and companies

# ACCEPTED MANUSCRIPT

can use that learning to create their own novel and useful inventions. The learning from the process of conducting actionable research and translating it to successful products with patent protection, with education and training at each step of that process, is the major benefit of patents to the entire technical community.

## ACKNOWLEDGEMENTS

We wish to acknowledge the following individuals, who were our closest and most important collaborators in the work described in this paper: Darrell Medcalf, Rhoda Oltzik, and Terry Maurice at General Foods; Hamed Faridi, John Finley, Jim Ievolella, Martha Wang, Meera Kweon, Diane Gannon, Lynn Haynes, Denise Deming, Ana Bravo, and Susan Saunders at Nabisco.

# ACCEPTED MANUSCRIPT

## REFERENCES

- AACC International. (2009). Approved Methods of the American Association of Cereal Chemists. 11<sup>th</sup> ed. Method 10-53.01, Baking quality of cookie flour - Macro wire-cut formulation. Approved 11/3/99;
- Method 56-11.02, Solvent retention capacity. Approved 6/3/09. AACC International, St. Paul, MN. Addesso, K., Dzurenko, T., Moisey, M., Levine, H., Slade, L., Manns, J., Fazzolare, R., Ievolella, J., and
- Wang, M. Production of chip-like starch-based snacks. U.S. Patents 5,429,834 (1995) and 5,500,240 (1996).
- AOAC International. (2005). Official Methods of Analysis of the Association of Official Analytical Chemists. 18<sup>th</sup> ed. Method 991.43, Total, Soluble, and Insoluble Dietary Fibre in Foods. AOAC International, Rockville, MD.
- Biliaderis, C.G. (1991). The structure and interactions of starch with food constituents. *Can. J. Physiol. Pharmacol.* **69**: 60-78.
- Carey, J., Moisey, M., Levine, H., Slade, L., Dzurenko, T., McHugh, K., and Zimmerman, E. Production of crispy wheat-based snacks having surface bubbles. U.S. Patents 5,747,092 (1998) and 5,980,967 (1999).
- Carey, J., Moisey, M., Levine, H., Slade, L., Dzurenko, T., and McHugh, K. (2002). Production of crispy wheat-based snacks having surface bubbles. U.S. Patent 6,479,090.

# ACCEPTED MANUSCRIPT

Cole, B., Levine, H., McGuire, M., Nelson, K., and Slade, L. (1983). Soft, frozen dessert formulation. U.S. Patent 4,374,154.

Cole, B., Levine, H., McGuire, M., Nelson, K., and Slade, L. (1984). Soft, frozen dessert formulation. U.S. Patent 4,452,824.

Colonna, P., and Buleon, A. (1992). New insights on starch structure and properties. In: Symposium on 'Cereal Chemistry and Technology: A Long Past and a Bright Future', 9th International Cereal and Bread Congress, Paris, 6/1-5.

Craig, S., Mathewson, P., Otterburn, M., Slade, L., Levine, H., Deihl, R., Beehler, L., Verduin, P., and Magliacano, A. (1992). Production of crackers with reduced or no added fat. U.S. Patent 5,108,764.

Ferry, J. (1948). Mechanical properties of substances of high molecular weight. *J. Am. Chem. Soc.* **70**: 2244-2249.

Franks, F., Asquith, M., Hammond, C., Skaer, H., and Echlin, P. (1977). Polymeric cryoprotectants in the preservation of biological ultrastructure. I. *J. Microscopy* **110**: 223-238.

Gimmler, N., Levine, H., Slade, L., Faridi, H., and Sauer, R. (1996). Juice-based expanded snacks and process for preparing them. U.S. Patent 5,523,106.

Haynes, L., Gimmler, N., Locke, J., Kweon, M., Slade, L., and Levine, H. (1999). Process for making enzyme-resistant starch for reduced-calorie flour replacer. WIPO Patent Application WO/1999/022606A1.

# ACCEPTED MANUSCRIPT

Haynes, L., Gimmler, N., Locke, J., Kweon, M., Slade, L., and Levine, H. Process for making enzyme- resistant starch for reduced-calorie flour replacer. U.S. Patents 6,013,299 (2000), 7,531,199 (2009), 7,972,643 (2011), and 8,367,139 (2013c).

Haynes, L., Gimmler, N., Locke, J., Kweon, M., Slade, L., and Levine, H. Enzyme-resistant starch for reduced-calorie flour replacer. U.S. Patents 6,352,733 (2002) and 6,613,373 (2003).

Haynes, L., Levine, H., Slade, L., Zhou, N., Manns, J., Gannon, D., Howey, E., Mihalos, M., Epperson, C.W., Gabriel, S., Cassone, D., and Zimeri, J. (2007). Production of stabilized whole grain flour and products thereof. WIPO Patent Application WO/2007/149320A1.

Haynes, L., Levine, H., Slade, L., Zhou, N., Manns, J., Gannon, D., Howey, E., Mihalos, M., Epperson, C.W., Gabriel, S., and Cassone, D. Production of stabilized whole grain wheat flour and products thereof. U.S. Patents 8,133,527 (2012a) and 8,455,036 (2013a).

Haynes, L., Levine, H., Slade, L., Zhou, N., Manns, J., Gannon, D., Howey, E., Mihalos, M., Epperson, C.W., Gabriel, S., Cassone, D., and Zimeri, J. Production of stabilized whole grain flour and products thereof. U.S. Patents 8,173,193 (2012b) and 8,455,037 (2013b).

Hnat, D., Levine, H., Slade, L., Maitland, R., Brown, W., and Mozeke, P. (1997). Production of chip- like durum wheat-based snacks. U.S. Patent 5,695,804.

Kidwell, K., Shelton, G., Demacon, V., Burns, J., Carter, B., Chen, X., Morris, C., and Bosque Perez, N. (2006). Registration of ‘Louise’ wheat. *Crop Sci.* **46**: 1384-1386.

# ACCEPTED MANUSCRIPT

Kweon, M., Slade, L., and Levine, H. (2011). Solvent retention capacity (SRC) testing of wheat flour: Principles and value in predicting flour functionality in different wheat-based food processes, as well as in wheat breeding -- a review. *Cereal Chem.* **88**: 537-552.

Kweon, M., Slade, L., Levine, H., and Gannon, D. (2014). Cookie- versus cracker-baking – What's the difference? -- Flour functionality requirements explored by SRC and alveography. *Crit. Rev. Food Sci. Nutr.* **54**: 115-138.

Levine, H., and Slade, L. (1986). A polymer physico-chemical approach to the study of commercial starch hydrolysis products (SHPs). *Carbohydr. Polym.* **6**: 213-244.

Levine, H., and Slade, L. (1988a). Water as a plasticizer: Physico-chemical aspects of low-moisture polymeric systems. In: Water Science Reviews, Vol. 3, pp. 79-185. Franks, F., Ed., Cambridge University Press, Cambridge.

Levine, H., and Slade, L. (1988b). Principles of cryostabilization technology from structure/property relationships of water-soluble food carbohydrates - A review. *Cryo-Letters* **9**: 21-63.

Levine, H., and Slade, L. (1990a). Influences of the glassy and rubbery states on the thermal, mechanical, and structural properties of doughs and baked products. In: Dough Rheology and Baked Product Texture: Theory and Practice, pp. 157-330. Faridi, H., and Faubion, J., Eds., Van Nostrand Reinhold/AVI, New York.

Levine, H., and Slade, L. (1990b). Effects of glassy and rubbery states on rheological properties of dough and texture of finished products. In: AACC Dough Rheology and Baked Product Texture short course, Short Hills, NJ, 7/18.

# ACCEPTED MANUSCRIPT

Levine, H., Slade, L., Van Lengerich, B., and Pickup, J. (1991). Glassy matrices containing volatile and/or labile components, and processes for preparation and use thereof. U.S. Patent 5,009,900.

Levine, H., Slade, L., Van Lengerich, B., and Pickup, J. (1992). Double-encapsulated compositions containing volatile and/or labile components, and processes for preparation and use thereof. U.S. Patent 5,087,461.

Levine, H., and Slade, L. (1993). The glassy state in applications for the food industry, with an emphasis on cookie and cracker production. In: The Glassy State in Foods, pp. 333-373.

Blanshard, J., and Lillford, P., Eds., Nottingham University Press, Loughborough.

Levine, H., and Slade, L. (2004). Influence of hydrocolloids in low-moisture foods - a food polymer science approach. In: Gums and Stabilisers for the Food Industry 12, pp. 425-436.

Williams, P., and Phillips, G., Eds., Royal Society of Chemistry, Cambridge, UK.

Lindstrom, T., and Slade, L. (1983). Frozen dough for bakery products. U.S. Patent 4,374,151.

Lindstrom, T., and Slade, L. (1987). A frozen dough for bakery products. European Patent EP0114451B1.

Maurice, T., Slade, L., Page, C., and Sirett, R. (1985). Polysaccharide-water interactions – Thermal behavior of rice starch. In: Properties of Water in Foods, pp. 211-227. Simatos, D., and Multon, J., Eds., Martinus Nijhoff, Dordrecht.

Parks, G.S., Huffman, H., and Cattoir, F. (1928). Studies on glass. II. The transition between the glassy and liquid states in the case of glucose. *J. Phys. Chem.* **32**: 1366-1379.

# ACCEPTED MANUSCRIPT

Parks, G.S., and Gilkey, W. (1929). Studies on glass. IV. Some viscosity data on liquid glucose and glucose-glycerol solutions. *J. Phys. Chem.* **33**: 1433-1437.

Parks, G.S., Thomas, S., and Gilkey, W. (1930). Studies on glass. V. Heat capacity data for some complex organic glasses and liquids. *J. Phys. Chem.* **34**: 2028-2034.

Parks, G.S., Snyder, L., and Cattoir, F. (1934a). Studies on glass. XI. Some thermodynamic relations of glassy and alpha-crystalline glucose. *J. Chem. Phys.* **2**: 595-598.

Parks, G.S., and Thomas, S. (1934b). The heat capacities of crystalline, glassy, and undercooled liquid glucose. *J. Am. Chem. Soc.* **56**: 1423.

Parks, G.S., Barton, L., Spaght, M., and Richardson, J. (1934c). The viscosity of undercooled liquid glucose. *Physics* **5**: 193-199.

Sears, J., and Darby, J. (1982). The Technology of Plasticizers. Wiley-Interscience, New York.

Slade, L. (1984). Starch properties in processed foods: Staling of starch-based products. In: American Association of Cereal Chemists Annual Meeting, abs. #112, Minneapolis, MN, 9/30-10/4.

Slade, L., and Levine, H. (1987a). Recent advances in starch retrogradation. In: Industrial Polysaccharides -- The Impact of Biotechnology and Advanced Methodologies, pp. 387-430.

Stivala, S., Crescenzi, V., and Dea, I., Eds., Gordon and Breach Science Publishers, New York.

# ACCEPTED MANUSCRIPT

Slade, L., and Levine, H. (1987b). Polymer-chemical properties of gelatin in foods. In: Advances in Meat Research, Vol. 4 - Collagen as a Food, pp. 251-266. Pearson, A., Dutson, T., and Bailey, A., Eds., AVI Publishing, Westport.

Slade, L., Oltzik, R., Altomare, R., and Medcalf, D.G. (1987). Accelerated staling of starch-based food products. U.S. Patent 4,657,770.

Slade, L., and Levine, H. (1988). Non-equilibrium melting of native granular starch: Part I. Temperature location of the glass transition associated with gelatinization of A-type cereal starches. *Carbohydr. Polym.* **8**: 183-208.

Slade, L., Finley, J., Levine, H., Craig, S., Faridi, H., Smith, K., Arciszewski, H., Saunders, S., Mathewson, P., Menjivar, J., Ievolella, J., Baumann, B., and Wang, M. (1989). Enzyme-treated low moisture content comestible products. European Patent Application EP0338787A2.

Slade, L., and Levine, H. (1991). Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. *Crit. Rev. Food Sci. Nutr.* **30**: 115-360.

Slade, L., and Levine, H. (1993). Aspects of soft wheat quality of current interest to a cookie/cracker baker. In: 40th Annual Research Review Conference, USDA-ARS Soft Wheat Quality Lab, Wooster, OH, 4/15.

Slade, L., Levine, H., Craig, S., Arciszewski, H., and Saunders, S. (1993). Enzyme-treated low moisture content comestible products. U.S. Patent 5,200,215.

# ACCEPTED MANUSCRIPT

Slade, L., and Levine, H. (1994). Structure-function relationships of cookie and cracker ingredients. In: The Science of Cookie and Cracker Production, pp. 23-141. Faridi, H., Ed., Chapman and Hall, New York.

Slade, L., Levine, H., Craig, S., and Arciszewski, H. (1994). Reducing checking in crackers with pentosanase. U.S. Patent 5,362,502.

Slade, L., and Levine, H. (2009). Food Polymer Science short course manual. In: Food Polymer Science website, online at <http://www.foodpolymerscience.com/home.html>; <http://www.foodpolymerscience.com/fpscource2009.html>.

Slade, L., and Levine, H. (2017). A 37-year retrospective on Slade/Levine's 'Food Polymer Science' approach to the practice of industrial R&D, leading to U.S. patent estates based on fundamental starch science and technology. In: AACCI Annual Meeting, San Diego, CA, 10/8-11.

Squire, G., McPherson, A., Larue, E., Slade, L., and Haynes, L. (2010). Fiber-containing rice-based cereals and methods of preparation. U.S. Patent 7,740,894.

van den Berg, C. (1981). Vapour sorption equilibria and other water-starch interactions; a physico-chemical approach. Doctoral Thesis, Agricultural University, Wageningen, the Netherlands.

van den Berg, C. (1986). Water activity. In: Concentration and Drying of Foods, pp. 11-36. MacCarthy, D., Ed., Elsevier Applied Science, London.

# ACCEPTED MANUSCRIPT

Wilhelm, C., Adrianson, T., Gannon, D., Howey, E., Levine, H., Mozeke, P., and Slade, L. (2003). Method of stabilizing graham flour, and cracker produced from said flour. U.S. Patent 6,616,957. Zimeri, J., Haynes, L., Olson, A., Arora, V.K., Slade, L., Levine, H., and Kweon, M. Production of low calorie, extruded, expanded foods having a high fiber content. U.S. Patents 7,648,723 (2010), 8,163,324 (2012), and 8,563,065 (2013).

Zimmerman, E., Carey, J., Slade, L., and Levine, H. (1996a). Calcium-enriched baked good production and method of making. U.S. Patent 5,514,387.

Zimmerman, E., Carey, J., Slade, L., and Levine, H. (1996b). Tenderized baked good production with reduced fat, low fat, or no added fat. U.S. Patent 5,514,404.

# FOOD POLYMER SCIENCE OF STARCH

## STRUCTURAL ASPECT FRINGED MICELLE MODEL OF PARTIALLY CRYSTALLINE STARCH

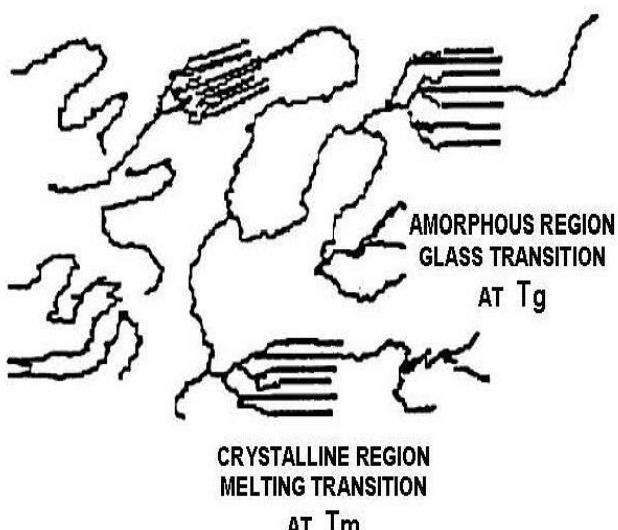


Figure 1

## FUNCTIONAL ASPECT STARCH MAP

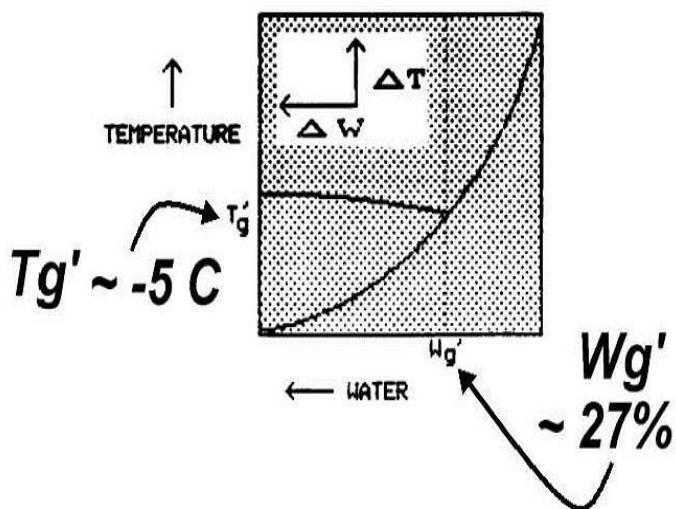


Figure 1 An illustration of the primary structural and functional aspects of the FPS approach with reference to starch (Slade and Levine, 1987a).

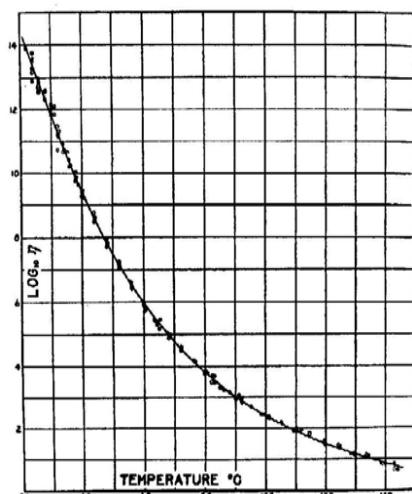
# SEMINAL STUDIES ON GLUCOSE GLASSES

1928-1934

G.S. Parks et al.

## EFFECT OF TEMPERATURE ON VISCOSITY OF GLUCOSE

PURE GLUCOSE FLUID  
EXCEEDS  $10^{13}$  POISE AND  
BECOMES A GLASSY SOLID  
AT ROOM TEMPERATURE



## THERMAL ANALYSIS OF PURE ONE-COMPONENT GLASSES AND THEIR TWO- AND THREE-COMPONENT GLASSES

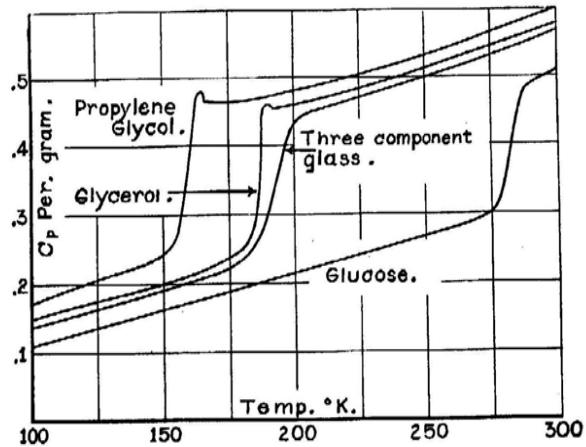
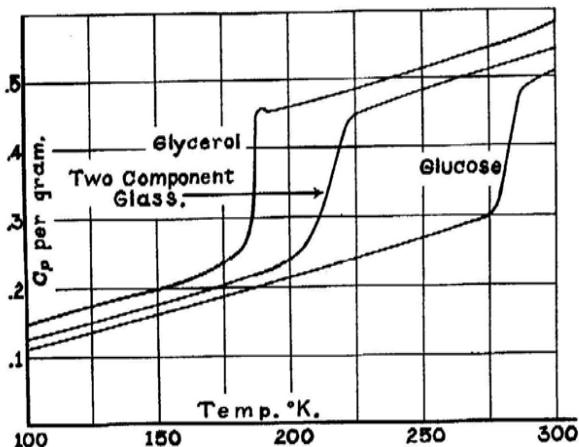
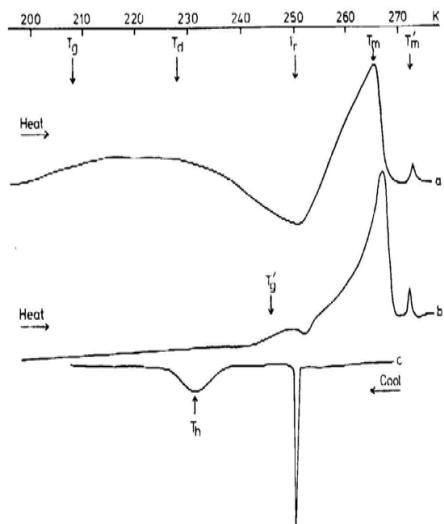


Figure 2

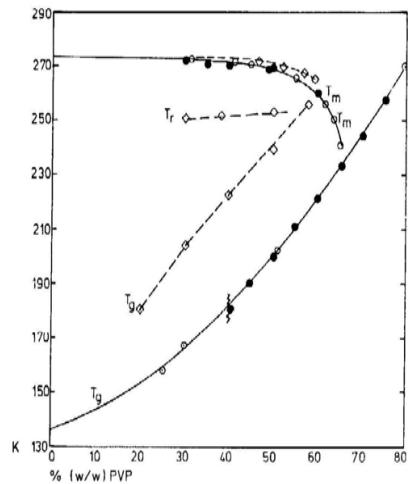
Figure 2 A compilation illustrating results from the seminal studies on glucose glasses published nearly 90 years ago by G.S. Parks et al. (Slade and Levine, 2009).

SEMINAL WORK:  $T_g'$  ( $\approx T_r$ ) SHOWN  
FOR FIRST TIME ON DSC THERMOGRAM  
AND SOLUTE-WATER STATE DIAGRAM

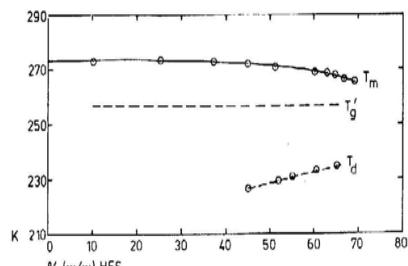
[Franks et al. (1977)]



**Fig. 1.** (a) DSC heating scan for quench cooled 50% PVP solution, showing the thermal transitions mentioned in the text; (b) DSC heating scan for a slow frozen 50% PVP solution; (c) DSC cooling scan for a 50% PVP solution which had previously been heated to 360 K in the calorimeter. Scanning directions are shown by horizontal arrows; scanning rate: 10 K min<sup>-1</sup>.



**Fig. 2.** Solid-liquid state diagram for water-PVP. Drawn out lines and  $\circ$  refer to  $M_n = 44,000$ ; broken lines and  $\diamond$  refer to  $M_n = 700,000$ ; the data of MacKenzie & Rasmussen (1972) are shown as filled-in circles, and their lower limit of vitrification at 40% is shown on the  $T_g$  curve.



**Fig. 6.** Solid-liquid state diagram for water-HES showing melting points,  $T_m$ , and tentative values for the devitrification,  $T_d$ , of quenched samples.  $T_g'$  is the glass transition of the concentrated solution (~70%) which remains after slow freezing and the separation of ice.

Figure 3

Figure 3 A compilation illustrating results from the work of Felix Franks et al. in the 1970s, who were the first to explicitly recognize and study the particular  $T_g'$  of frozen aqueous systems (Slade and Levine, 2009).

## T<sub>g</sub>, Glass Curve and State Diagram for Starch

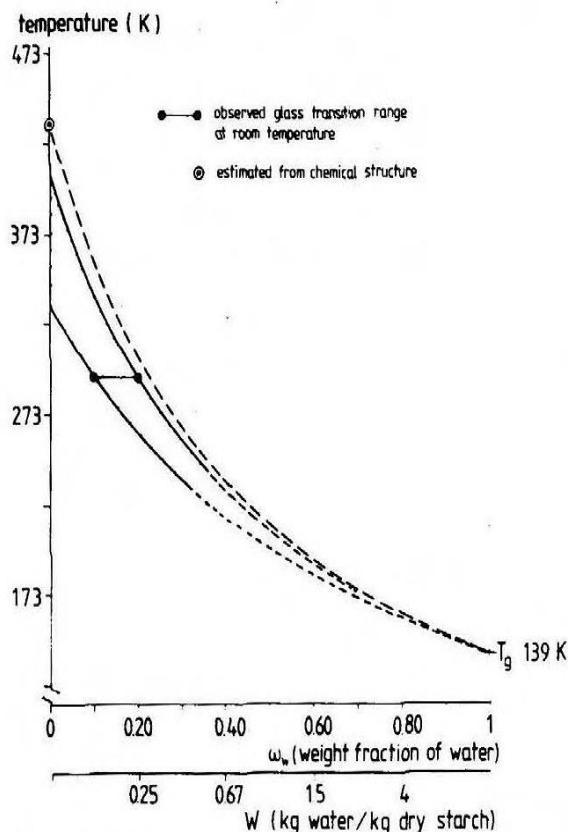
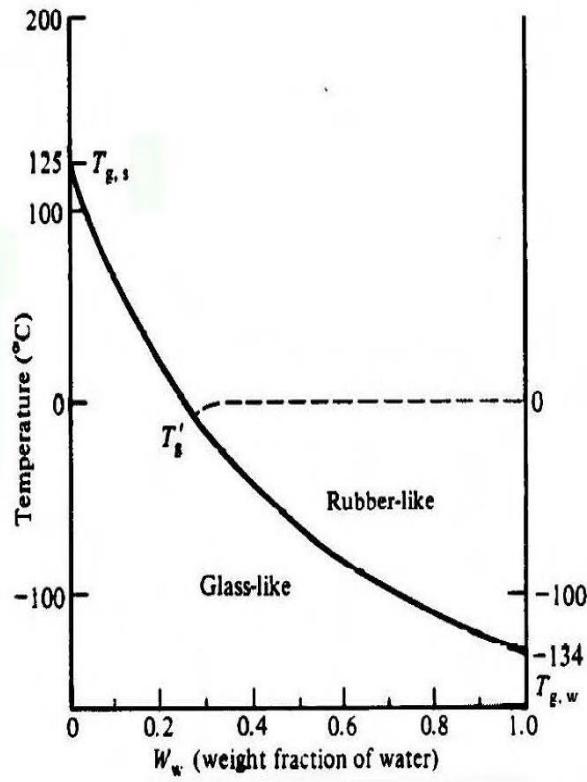


Figure 3.3.  
Estimated glass-rubber transition temperature range  
for starch-water mixtures as a function of  
mass fraction of water on total basis.  
[from 1981 van den Berg PhD thesis]



[van den Berg, 1986]

Figure 4

Figure 4 A compilation illustrating results from the doctoral thesis work of Cornelius van den Berg, in which the amorphous regions of native granular starches, their  $T_g$  value as a function of moisture content, and the resulting glass curve and state diagram for starch, were first explicitly discussed in 1981 (Slade and Levine, 2009).

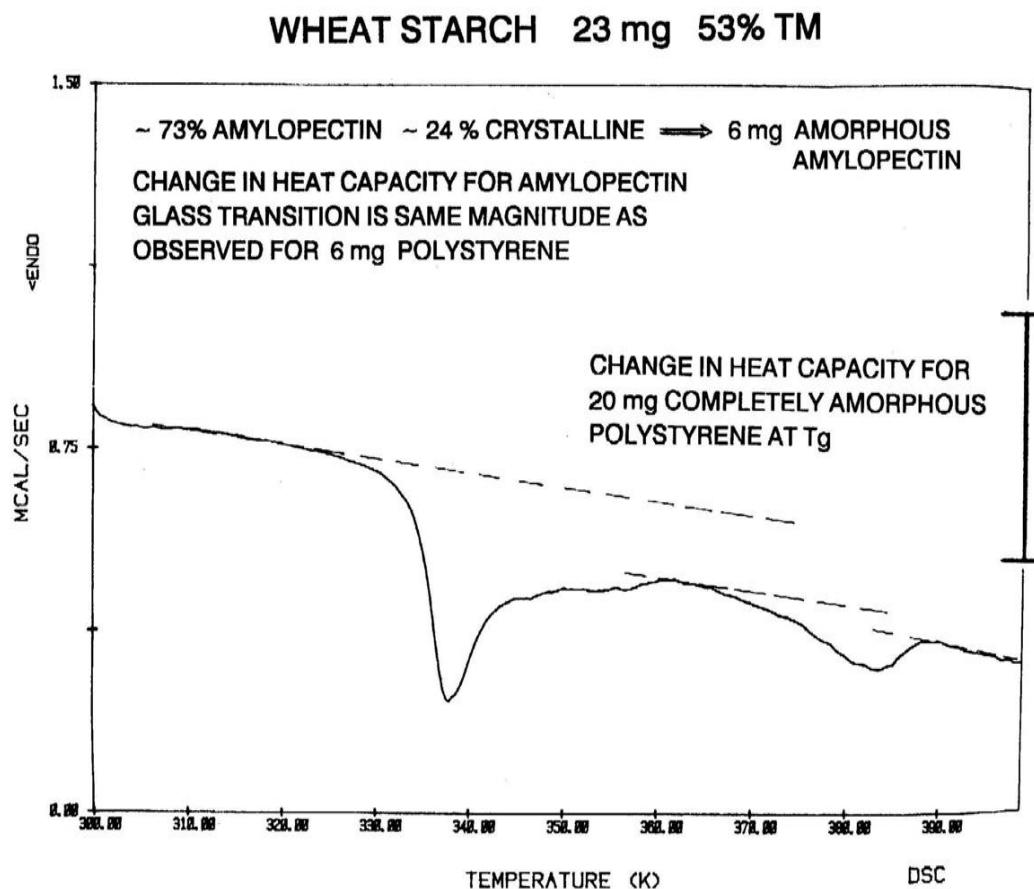


Figure 5

Figure 5 Definitive evidence, from DSC analysis, of the characteristic change in heat capacity at the glass transition of native granular wheat starch in excess water was first presented in 1984 (Slade, 1984; Slade and Levine, 1988).

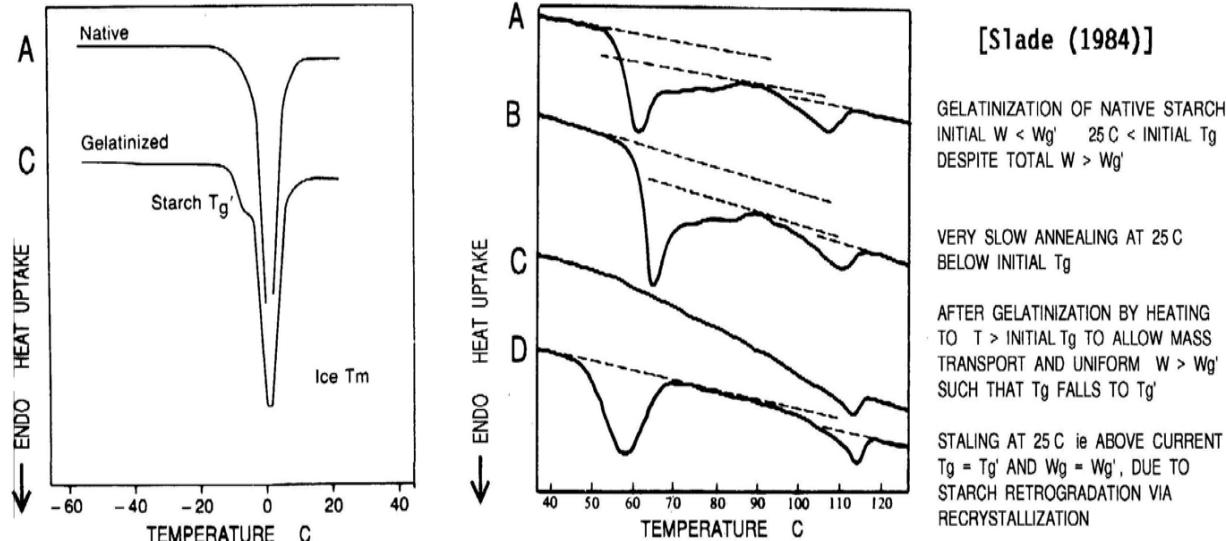
**LOCATION OF  $T_g$  : OPERATIONAL  $T_g$  DEPENDS ON TIME / TEMPERATURE / MOISTURE HISTORY**

**KEY DIAGNOSTIC CRITERIA OF PRACTICAL IMPORTANCE TO STARCH FUNCTIONALITY**

COMPARE RELATIVE  $\Delta C_p$  WHEN  $T_{expt}$  BEGINS BELOW INITIAL  $T_g$  eg BEGIN 25 C FOR NATIVE STARCH vs.  
ABOVE INITIAL  $T_g$  GELATINIZED OR STALED STARCH ie  $T_g'$

TEST TIMESCALE / EXTENT OF ANNEALING INITIAL  $T_g$  < Tanneal < INITIAL  $T_m$   
RECRYSTALLIZATION  $T_g' = \text{CURRENT } T_g < T_{ex} < \text{POTENTIAL } T_m$

EXAMINE ABSOLUTE MAGNITUDE  $\Delta C_p$   $\Delta C_p$  DUE TO  $\Delta$  EXPANSION COEFFICIENT OF FREE VOLUME AT  $T_g >$  MELT AT  $T_m$   
COMPARE ABSOLUTE MAGNITUDE TO VALUE FOR SYNTHETIC POLYMER



DuPont 990 DSC heat flow curves of wheat starch:water mixtures (45:55 w/w): (A) native granular; (C) rescan immediately after gelatinization of sample in A, which reveals a prominent  $T_g'$  at -10 C, preceding the  $T_m$  of ice. (Slade & Levine, 1988, Carbohydr. Polym., 8:183)

Perkin - Elmer DSC-2C heat flow curves of wheat starch: water mixtures (45:55 w/w): (A) native granular; (B) after 55 d annealing at 25 C of sample in A; (C) immediate rescan after gelatinization of sample in A; (D) after 55 d recrystallization at 25 C of sample in C. Dashed lines are extrapolated baselines. (Slade & Levine, 1987, Industrial Polysaccharides)

Figure 6

Figure 6 From DSC results, the temperature location of the  $T_g$  of starch was shown to coincide with the onset of the non-equilibrium melting temperature,  $T_m$ , which coincided in turn with the onset temperature of the so-called gelatinization endotherm for native starch in water (Slade, 1984; Slade and Levine, 1987a; Slade and Levine, 1988).

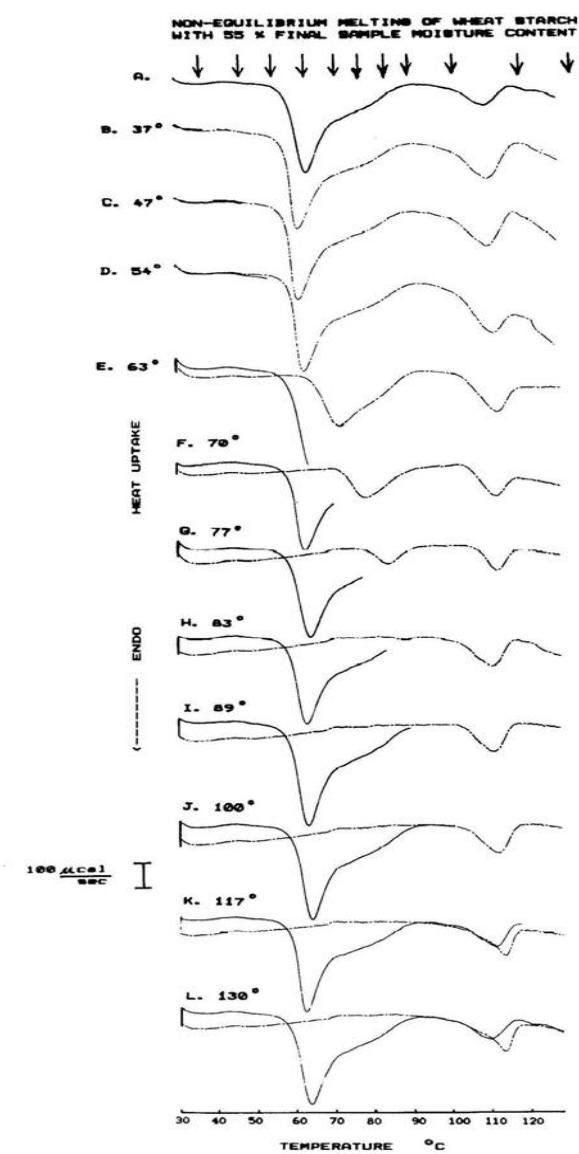


Figure 7

Figure 7 From DSC results, the Tg for normal wheat starch was as described in the caption for Fig. 6 (Slade and Levine, 1988).

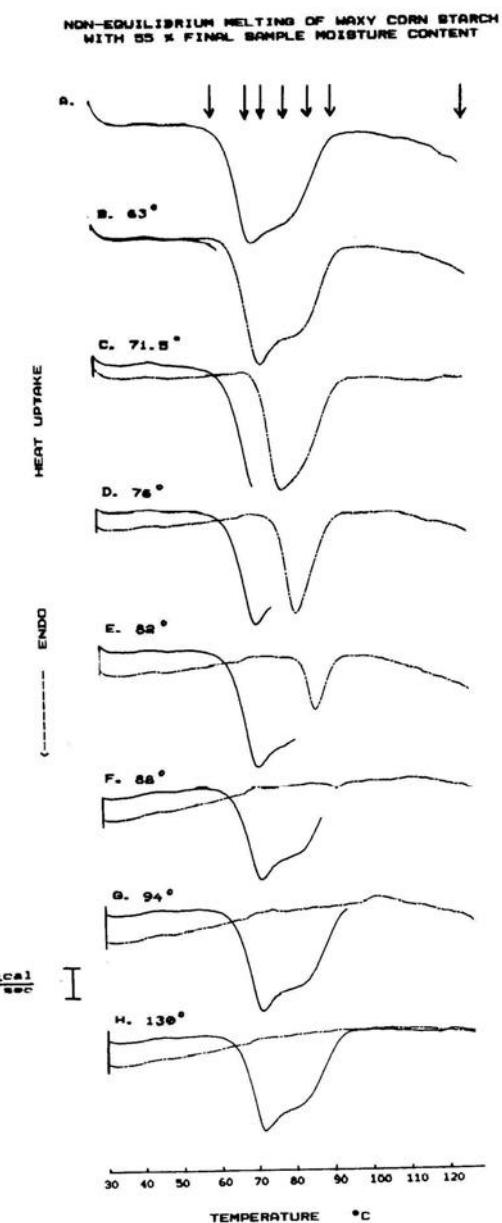


Figure 8

Figure 8 From DSC results, the Tg for waxy (i.e. all-amylopectin) corn starch was, likewise, as described in the caption for Fig. 6 (Slade and Levine, 1988).

## WHOLE GRAIN PROCESSING

- 1 RAW WHOLE GRAIN  
10 - 14 % TOTAL MOISTURE  
e.g., 34 LB WHEAT BERRIES AT 12 % MOISTURE
- 2 FIRST STAGE SWELLING  
SOAK WITH WATER OR  
COOK WITH WATER + ATMOSPHERIC STEAM TO ~ 27 % MOISTURE  
NOW 41 LB  
ALLOWS GELATINIZATION IF CONTINUE TO 3  
ALLOWS STABILIZATION BY PARBOILING IF CONTINUE TO 5
- 3 BEGIN SECOND STAGE SWELLING  
CONTINUE COOK WITH WATER + ATMOSPHERIC STEAM TO ~ 45 % MOISTURE  
NOW 55 LB  
THIS IS SHREDDING STAGE
- 4 COMPLETE SECOND STAGE SWELLING  
CONTINUE COOK WITH WATER + ATMOSPHERIC STEAM TO ~ 70 % MOISTURE  
NOW 100 LB  
THIS IS RTE BULGAR OR PILAF
- 5 PARBOILING = STABILIZATION BY ANNEALING / RECRYSTALLIZATION  
START FROM 2; ALTERNATIVE TO 3  
USE PRESSURIZED STEAM (15 PSI) TO STABILIZE WITHOUT VOLUME INCREASE  
STILL - 41 LB AND ~ 27 % MOISTURE, BUT DEVELOP RUBBERY TEXTURE  
REDUCED SOLIDS LOSS AND STICKINESS IF CONTINUE TO 3
- 6 PUFFING OR POPPING  
RAISE TEMPERATURE TO ABOUT 185 °C, DIRECTLY FROM 1  
GUN PUFF, HOT AIR POP, HOT OIL POP, MICROWAVE POP  
NOW < 30 LB, < 10 % MOISTURE  
THIS IS PUFFED WHEAT

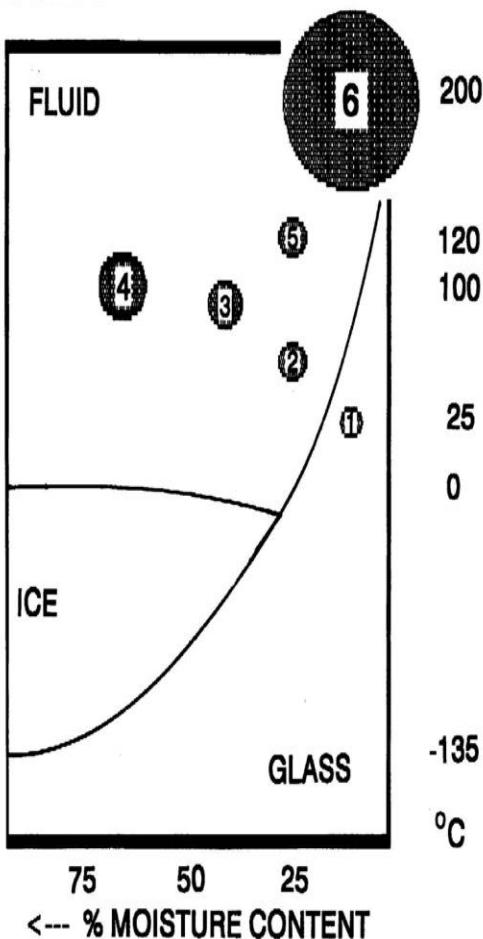


Figure 9

Figure 9 A schematic state diagram, incorporating the glass curve for starch, viewed as a conceptual representation of whole-grain processing (Slade and Levine, 1991).

# Cryotechnology of Frozen Foods

## Optimum freezer temperature

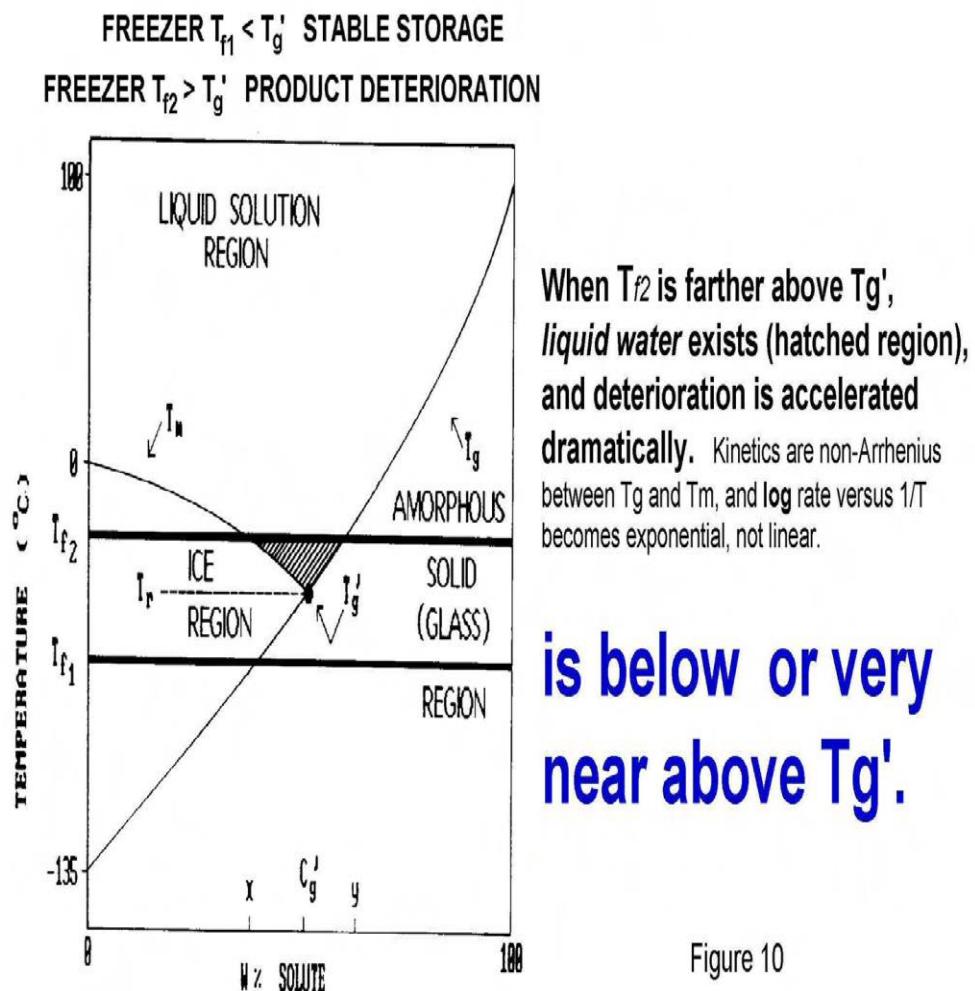
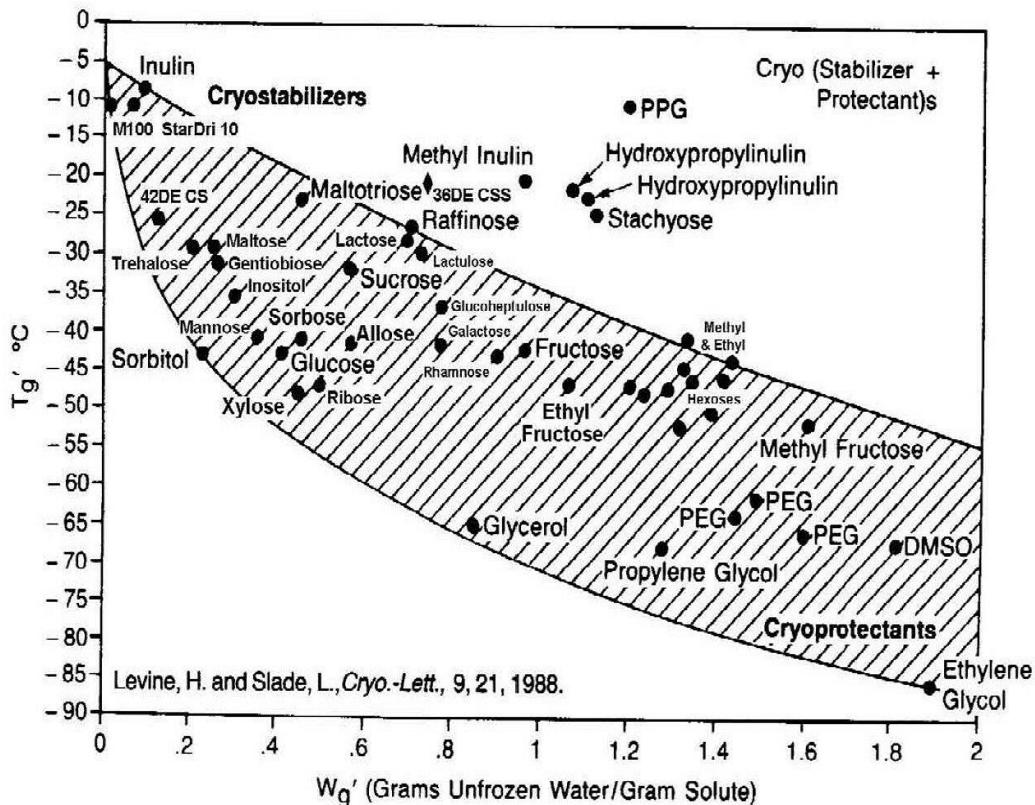


Figure 10

Figure 10 A schematic state diagram illustrating the basis of ‘cryostabilization technology’ for the freezer-storage stability of frozen food systems (Levine and Slade, 1988b).



Variation of the glass transition temperature,  $T_g'$ , for maximally frozen 20 w% solutions against  $W_g'$ , the composition of the glass at  $T_g'$ , in g unfrozen water/g solute, for a series of water-compatible carbohydrates, illustrating the cryostabilization "spectrum" from monomeric cryoprotectants to polymeric cryostabilizers. Solutes lying outside the hatched area of the "spectrum" [toward the upper right corner] exhibit properties of both cryoprotectants and cryostabilizers.

Figure 11

Figure 11 A plot of  $T_g'$  vs.  $W_g'$ , illustrating the 'cryostabilization technology' spectrum of ingredients in fabricated frozen foods, which can range from 'polymeric cryostabilizers' (at the upper left) to 'monomeric cryoprotectants' (at the lower right) (Levine and Slade, 1988b).

## LOW TEMPERATURE WATER CONTROL BY SUGARS

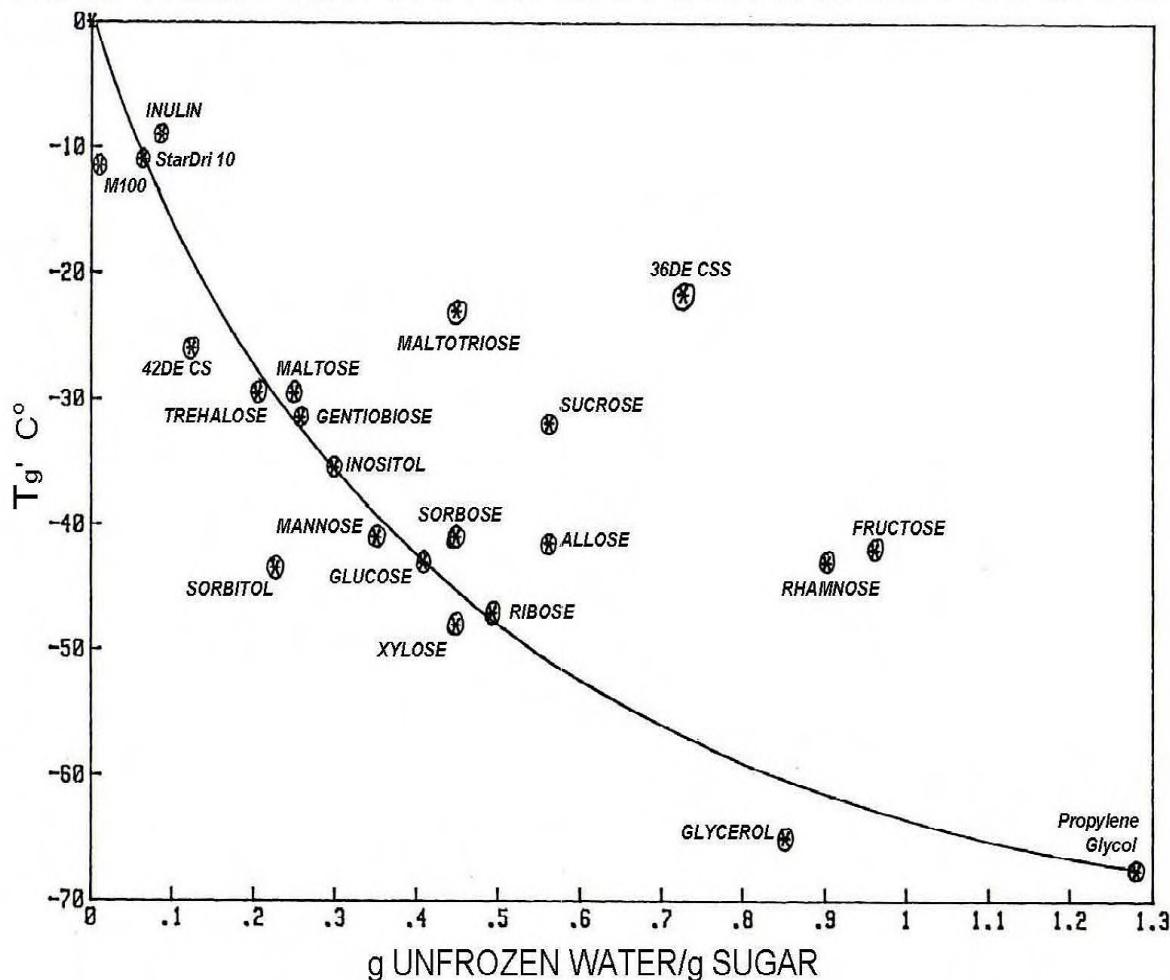


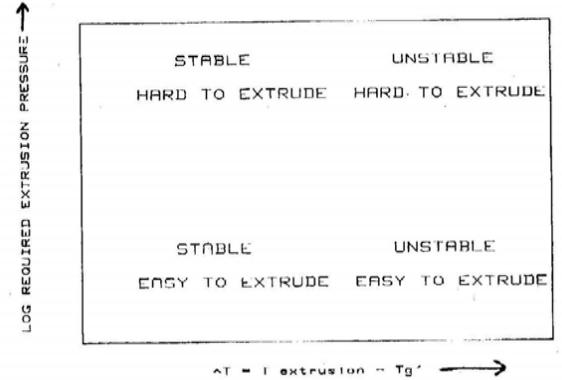
Figure 12

Figure 12 A simplified version of Fig. 11, showing the  $T_g^{\circ}/W_g^{\circ}$  locations for a spectrum of commercial SHPs, other carbohydrate sugars, and polyols, again ranging from higher  $T_g^{\circ}$ /lower  $W_g^{\circ}$  cryostabilizers at the upper left to lower  $T_g^{\circ}$ /higher  $W_g^{\circ}$  cryoprotectants at the lower right (Levine and Slade, 1988b).

**STABILITY AND EASE OF EXTRUSION OF A PATENTED  
SOFT-FROM-THE-FREEZER ICE CREAM**

---

- \* A principle of cryotechnology (revealed by "cryotechnology map"): INTRINSIC CORRELATIONS of stability (high  $T_g'$ ) with "hard-frozen" (low  $W_g'$ ) and instability (low  $T_g'$ ) with "soft-frozen" (high  $W_g'$ ) nature of products
- \* Extrusion of soft-serve ice cream (SSIC), at  $T_g' < T_{ext} < T_m$ : WLF-governed relaxation process in "rubbery" ice cream
- \* Plot log [required extrusion pressure] vs.  $\Delta T = T_{ext} - T_g'$  --> 4 quadrants of functionality
- \* TARGET for successful formulation of SSIC with good freezer-storage stability against ice crystal growth --> products in "stable/easy to extrude" quadrant



**STABILITY AND EHSE OF EXTRUSION OF SOFT SERVE ICE CREAM:  
PATENT APPLICATION - CONTENTS**

- \* Plot log extrusion pressure vs.  $\Delta T$  for experimental prototypes and competitive products --> patentable formulations
- \* Typical ice creams:  $T_g'$  range of -28 to -42°C, due to preponderance of mono- and disaccharide sweeteners
- \* DELIBERATE formulation with optimized combination of lower-Mw CHO sweeteners and polymeric SHP cryostabilizers --> optimum combination of stability and extrudability --> new proprietary formulas in patentable quadrant, separated from LESS stable competitive products

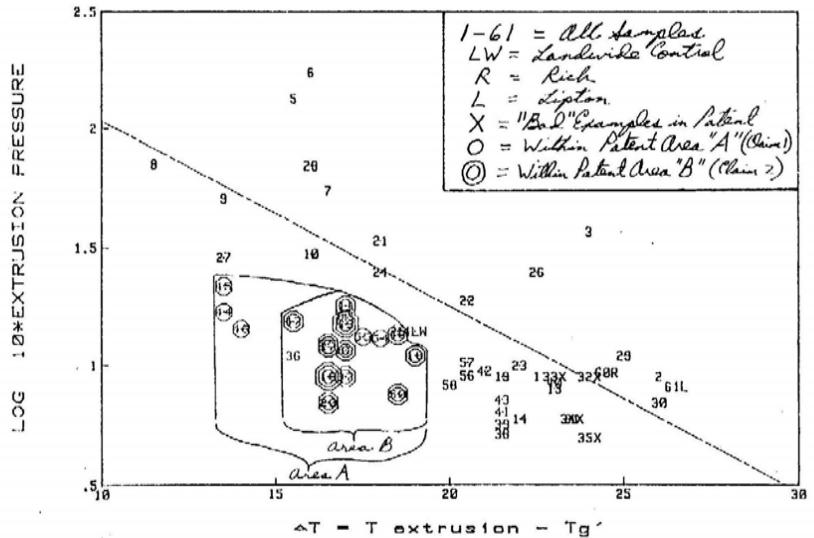


Figure 13

Figure 13 A compilation illustrating results from a Product Development program, in which an unusual 36-DE CSS, with unique high  $T_g'/W_g'$  functionality, was a key commercial SHP ingredient used to formulate a novel soft-from-the-freezer, extrudable ice cream product with good freezer-storage stability against ice crystal growth (Slade and Levine, 2009).

REAL FOOD SYSTEMS: CRYOSTABILIZATION OF FROZEN BREAD DOUGH -  
GF's PATENTED FREEZER-TO-OVEN, PROOFED-BEFORE-FROZEN BREAD DOUGH PRODUCTS  
\*\*\*\*\*

Storage Study Results: -20°F Freezer, 10-DE Maltodextrin Cryostabilizer

Ovenspring (cc)	Control (Pilla. HG)	Control + Maltodextrin	* Freezer-storage instability of control dough (1 lb loaf) --> steadily-decreasing ovenspring and baked loaf volume (plus increasing shrinkage of proofed, frozen dough blank) with increasing frozen-storage time
1 week	850	887	
3 weeks	650	600	
5 weeks	537	662	
8 weeks	475	750	

Baked Volume (cc)	* Cryostabilization with 10-DE maltodextrin --> elevated Tg' of aqueous phase --> greatly improved storage stability, after 8 weeks at -20°F, in terms of more stable BLV	
1 week	1900	1850
3 weeks	1775	1737
5 weeks	1678	1762
8 weeks	1582	1762

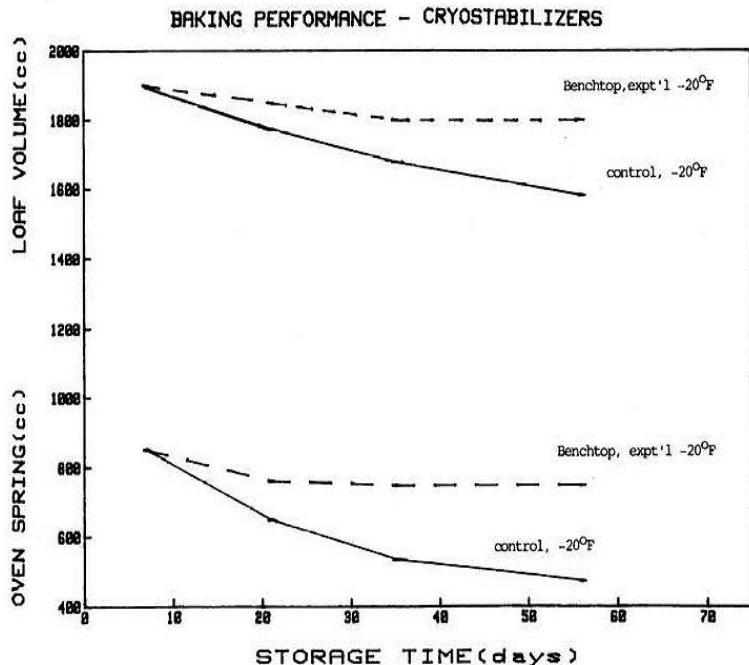


Figure 14

Figure 14 Cryostabilization technology was shown to be applicable, through the use of a 10-DE maltodextrin commercial SHP as an effective polymeric cryostabilizer, for a novel frozen bread dough product (Levine and Slade, 1990a).

# STRUCTURE - FUNCTION RELATIONSHIPS FOR COMMERCIAL STARCH HYDROLYSIS PRODUCTS

Plateau limit for entanglement of SHP ( $M_n > 3000$ ) agrees with literature range for Entanglement  $> 1250$  for synthetic linear high polymers.

Entanglement networks may function as transient or permanent networks, depending on time scale and chemical or mechanical conditions.

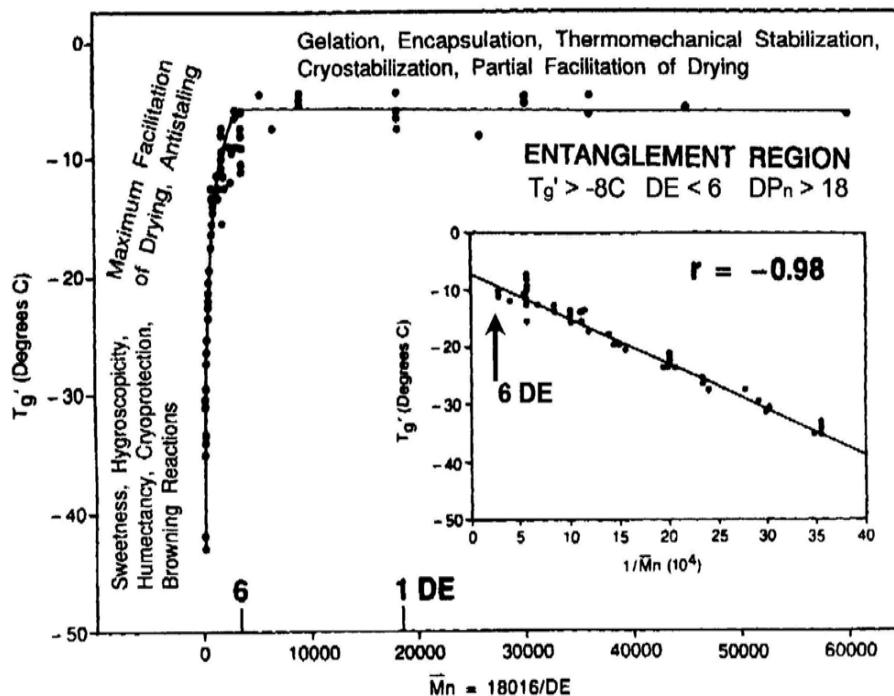


Figure 15

Figure 15 A plot of  $T_g'$  vs. MW/DE, utilized as a basis for the construction of a conceptual ‘map’ of the structure-function relationships for a large family of commercial SHPs (Levine and Slade, 1986).

# LINK FUNCTIONAL COMPONENTS TO FLOUR SPECIFICATIONS?

[ WHC ~ SRC water  
g H<sub>2</sub>O / g dry  
Component ]

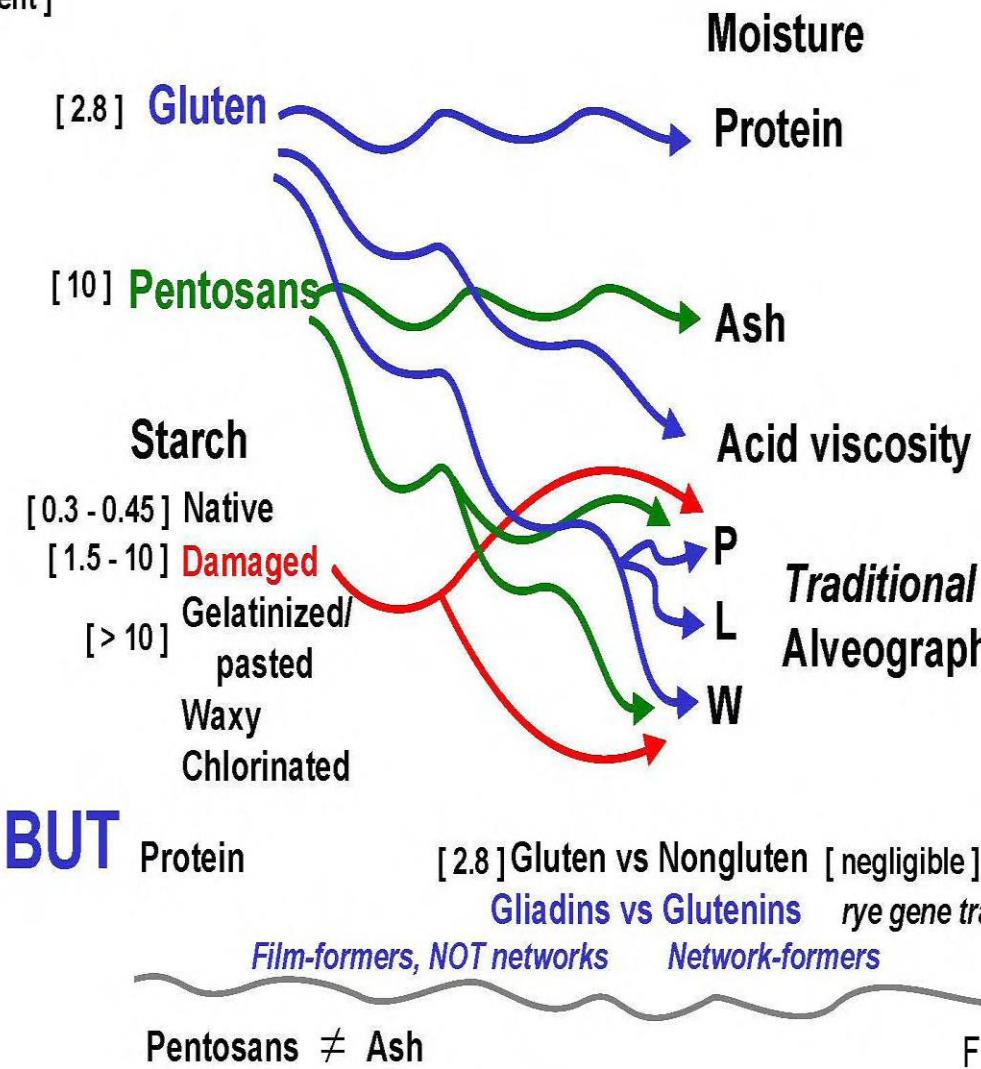


Figure 16 Conceptual illustration of the linkages between flour functional components and flour specifications (Slade and Levine, 1993).

## WHAT DO WE LOOK FOR IN THE ALVEOGRAM ?

LOCATE CONTRIBUTIONS BY FLOUR FUNCTIONAL COMPONENTS DURING BUBBLE EXPANSION  
RELATE ALVEOGRAM RESULTS TO SRC VALUES USING 4 SOLVENT AACC 56-11

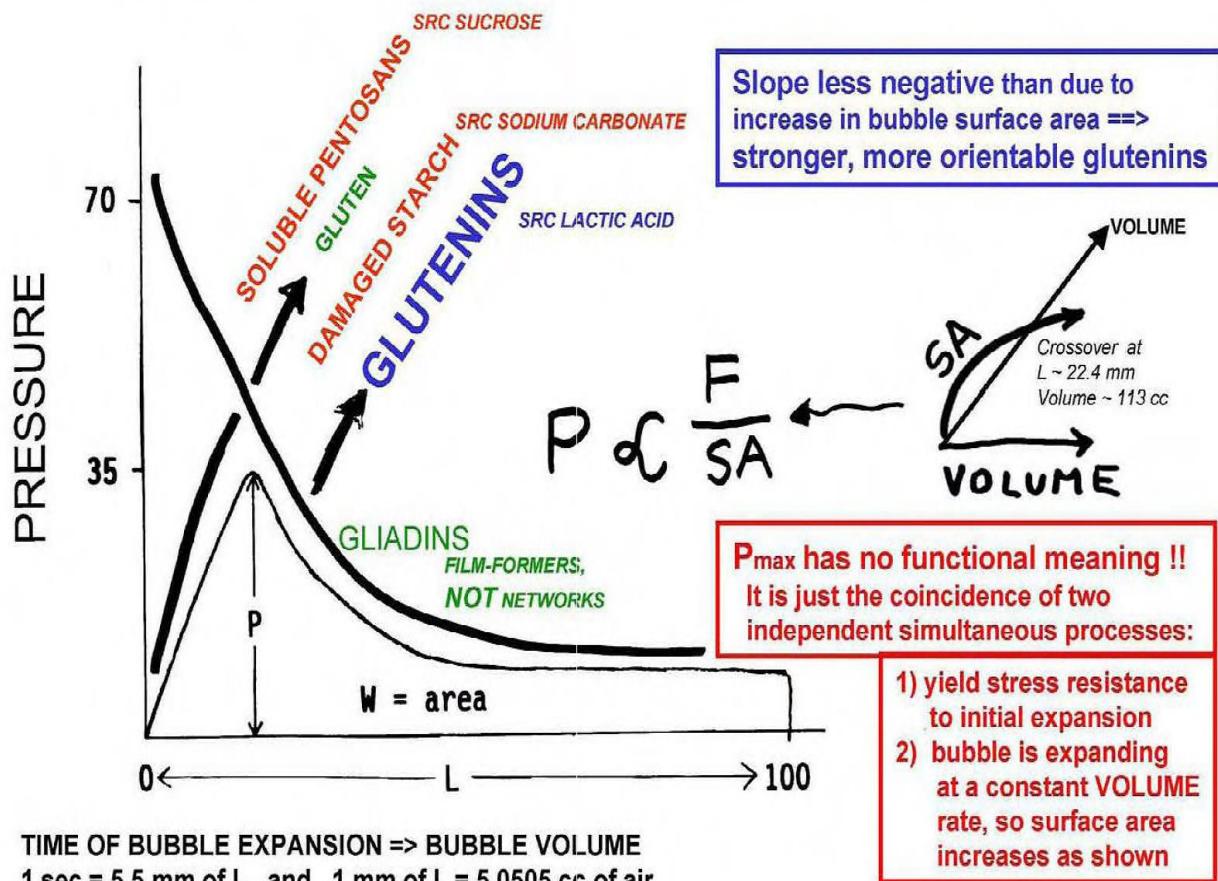


Figure 17

Figure 17 An idealized flour alveograph profile, annotated with additional underlying information available from such an alveogram (Kweon et al., 2011).

## ROLES OF SOLUBILITY PARAMETER (ENERGETICS) AND $T_g$ (KINETICS) IN FLOUR POLYMER PERFORMANCE

### The Technology of Plasticizers

J. KERN SEARS and JOSEPH R. DARBY (Retired)  
 A Wiley-Interscience Publication 1982  
 JOHN WILEY & SONS New York  
 Modified by Slade (Nov 1991)

SRC is the standard method to measure the Solubility Parameter of polymers.

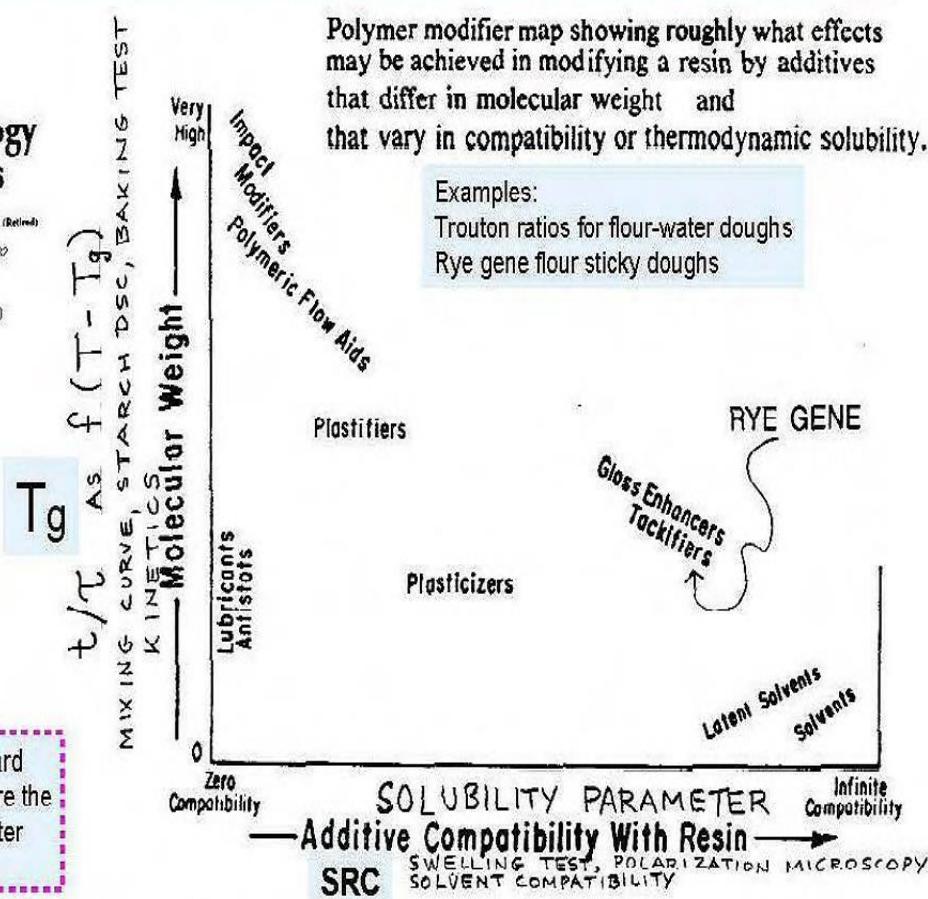


Figure 18

Figure 18 The nature of flour polymer-solvent interactions -- involving solvation and swelling, but not dissolution -- has been characterized in terms of a 'Solubility Parameter' approach adopted from synthetic polymer science, wherein solvent retention capacity is the standard method used to measure the Solubility Parameter of polymers (Sears and Darby, 1982; Slade and Levine, 2009).



Figure 19

Figure 19 SRC technology led to the development and commercialization in 2004 of a new cultivar of Washington soft white spring wheat, named ‘Louise’ wheat by its breeder (Slade and Levine, 2009).

## COMPARISON OF COOKIE FORMULATIONS

INGREDIENT	AACC METHOD 10-52 SUGAR-SNAP	AACC METHOD 10-53 MODEL WIRE-CUT (APPROVED 9/92)
FLOUR	100      14% m	100      13% m
SUGAR BROWN SUGAR	60      Bakers' Special	42      32 Fine Granulated 10
SHORTENING	30	40
HFCS		1.5
NFDM	3	1
SALT	0.45	1.25
SODIUM BICARBONATE	1.8	1
AMMONIUM BICARBONATE		0.5
AMMONIUM CHLORIDE	0.5	
WATER	15      vary to adjust rheology	22      constant
TOTAL SUGAR + WATER	75	64
RATIO SUGAR / WATER	4	1.9
SUGAR PARTICLE SIZE	177 $\mu$	297 $\mu$

Figure 20

Figure 20 A new wire-cut cookie test-baking formula/method was created and developed, becoming AACC Method 10-53, for the practical evaluation of flour quality and functional performance for commercial cookie and cracker baking (AACC International, 2009).

## ROLE OF PEN ENZYME IN FLOUR FUNCTIONALITY

EFFECT OF PEN WATER COMPENSATION

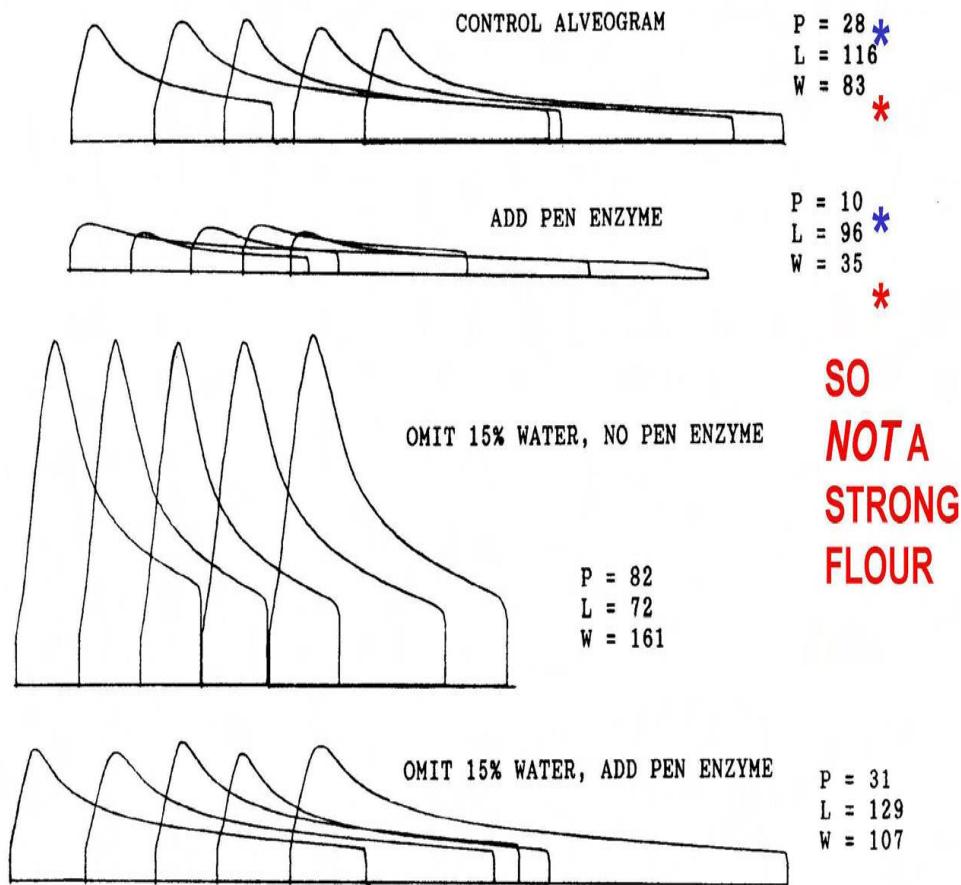
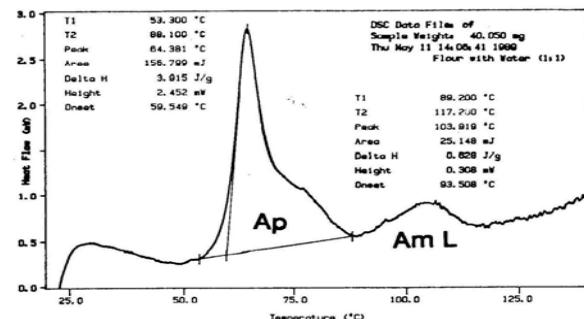
[Slade and Levine (1993h)]  
OHIO SRW-BASED FLOUR

Figure 21

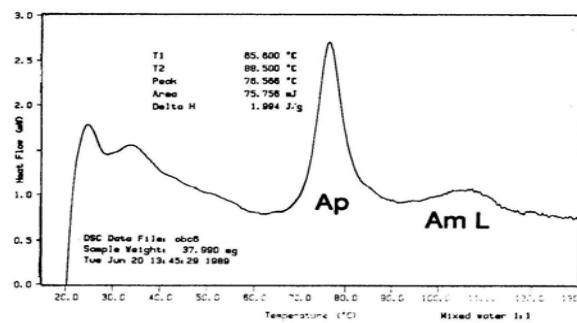
Figure 21 Alveograph profiles illustrating the role of pentosanase enzyme in flour functionality (Slade and Levine, 1993; Levine and Slade, 2004).

**DIAGNOSTIC DSC****COOKIE / CRACKER FLOUR**

**100% NATIVE Ap**  
**100% NATIVE Am L**

**COOKIE**

**100% NATIVE Ap**  
**HIGH SUGAR**  
**100% NATIVE Am L**

**LEAN CRACKER**

**40% NATIVE Ap**  
**120% NATIVE Am L**

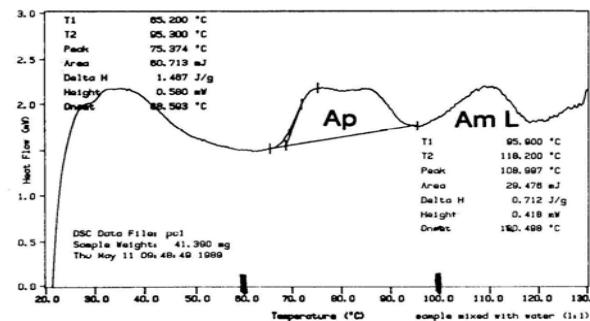
**Figure 22****140 F 212 F**

Figure 22 DSC thermograms for samples, each mixed 1:1 by weight with water, of Nabisco's typical soft wheat-based flour for cookies and crackers, a baked wire-cut cookie, and a baked lean cracker, both products made with that same flour (Levine and Slade, 1990b).

## DIAGNOSTIC DSC OF CRACKERS

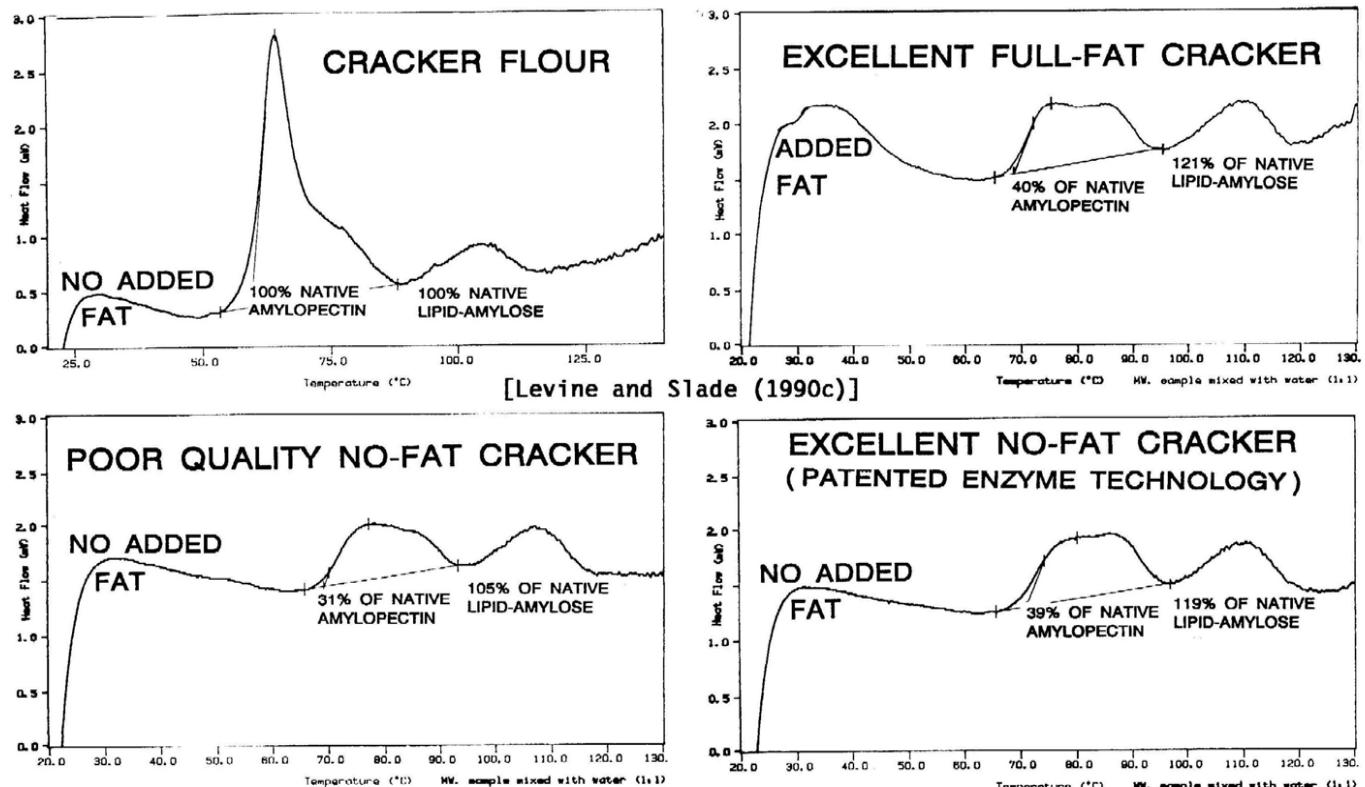


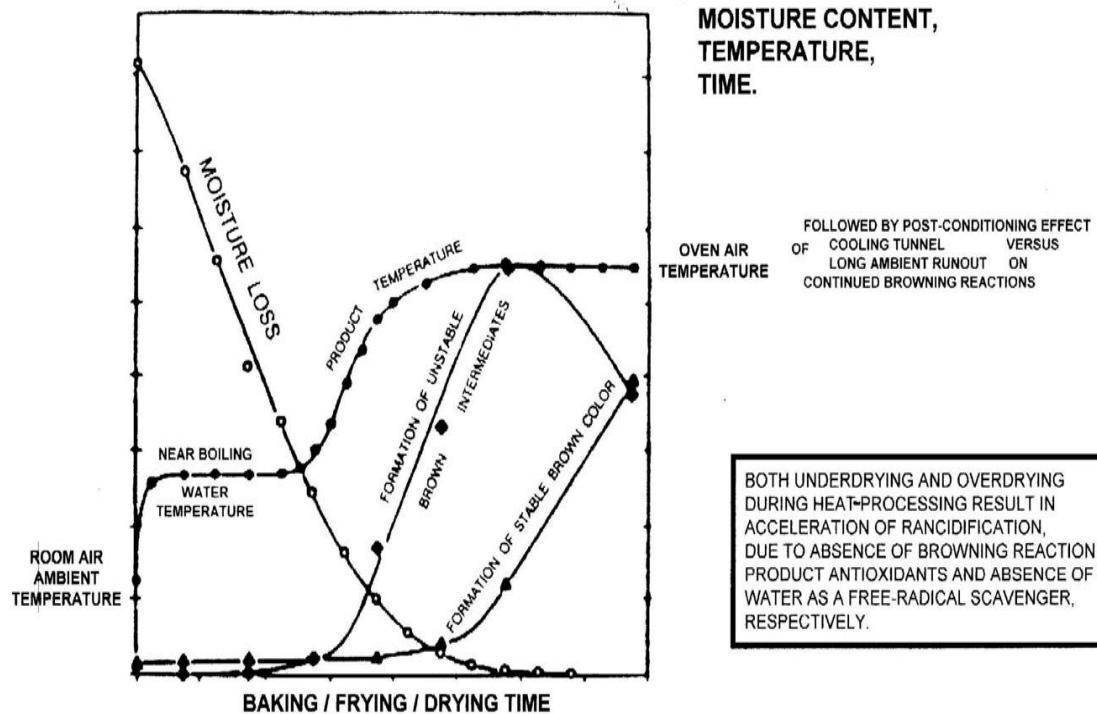
Figure 23

Figure 23 DSC thermograms from a study on crackers. The top two thermograms were for the same cracker flour and excellent-quality full-fat saltine cracker as in Fig. 27. The bottom-left thermogram was for a poor-quality no-fat saltine cracker prototype. In contrast, the bottom-right thermogram was for an excellent-quality no-fat saltine cracker, commercially produced through the application of Nabisco's patented (Craig et al., 1992) pentosanase enzyme technology (Levine and Slade, 1990b).

## BROWN COLOR DEVELOPMENT AND STABILITY

FOR A GIVEN COMPOSITION OF BROWNING REACTANTS, COLOR DEVELOPMENT DEPENDS ON

MOISTURE CONTENT,  
TEMPERATURE,  
TIME.



UNSTABLE BROWN INTERMEDIATES FADE SOON AFTER HEAT-PROCESSING (BAKING / FRYING / DRYING).

FINAL STABLE BROWN COLOR PERSISTS DURING STORAGE, IF LOW MOISTURE CONTENT IS MAINTAINED.

BUT, FADING EVEN OF STABLE BROWN COLOR IS ACCELERATED BY MOISTURE MIGRATION FROM "BONED" WET CENTER TO DRIER SURFACE, OR BY MOISTURE UPTAKE FROM ENVIRONMENT (WITH ADDITIONAL INCREASED RISK OF CHECKING-INDUCED BREAKAGE).

Figure 24

Figure 24 An illustration of the principles of 'brown color development and stability', as applicable to color formation during cookie baking, and baked-color stability and the resulting absence of color fading during product shelf-life (Slade and Levine, 1991).

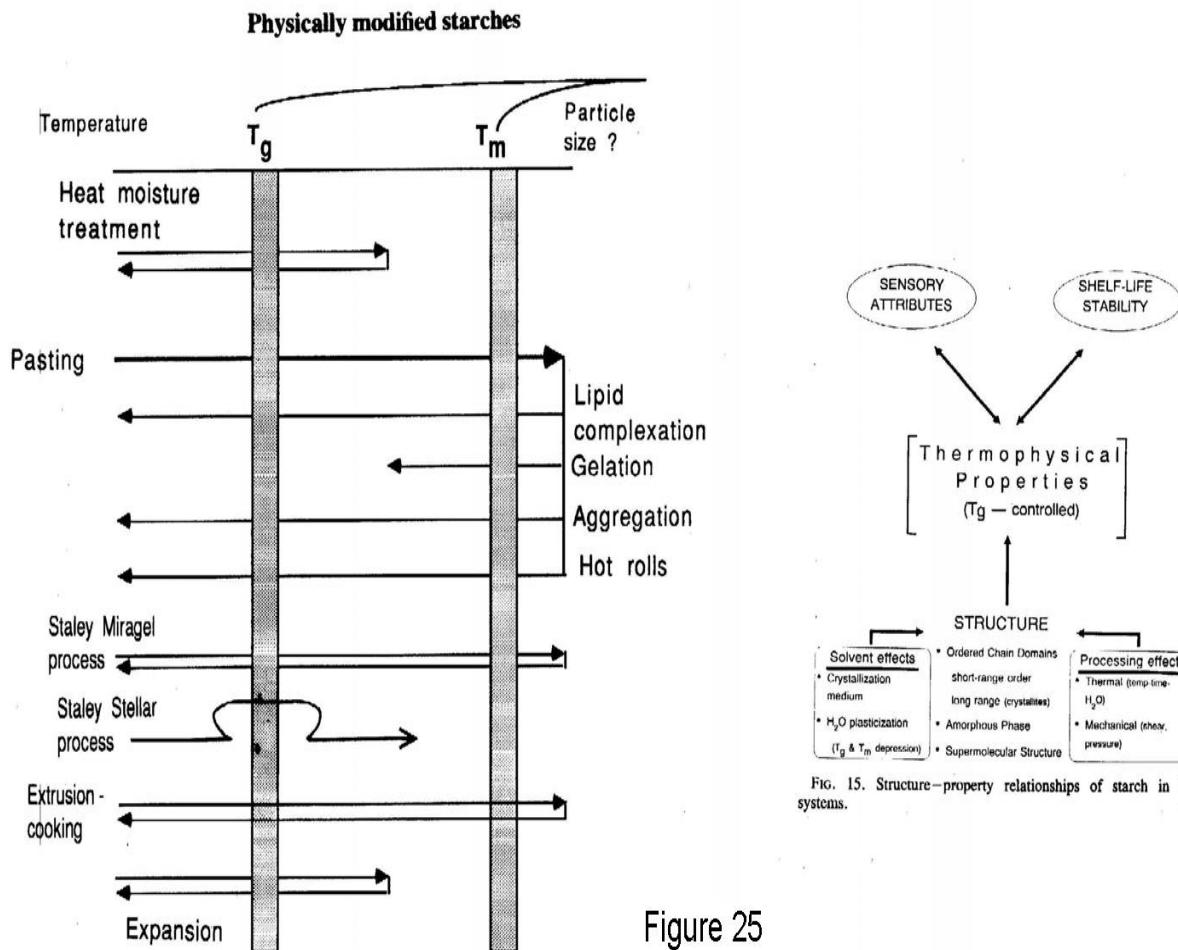


Figure 25

Figure 25 An illustration of two 'Food Polymer Science'-based treatments (on the left, from Colonna and Bulean (1992); on the right, from Biliaderis (1991)) of structure-property relationships of starch (Slade and Levine, 2009).

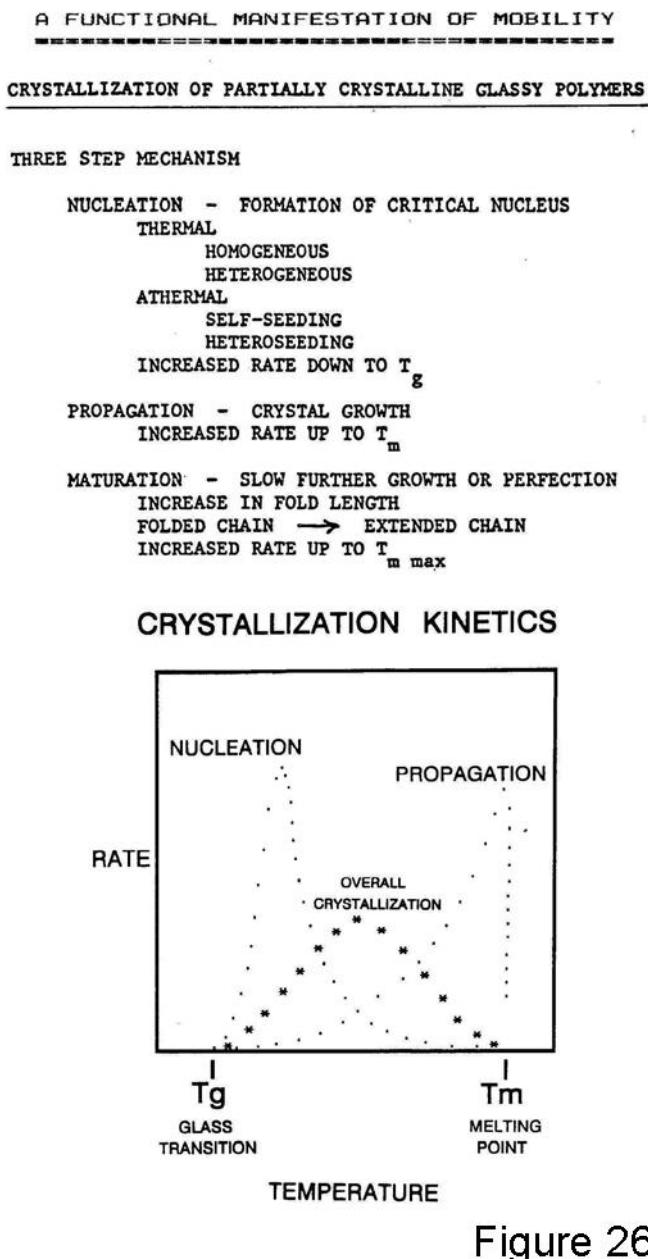


Figure 26

Figure 26 A generalized description of the crystallization kinetics theory and mechanism for partially crystalline glassy polymers, adopted from synthetic polymer science by the FPS approach (Levine and Slade, 1990a).

## KINETICS OF STARCH RETROGRADATION

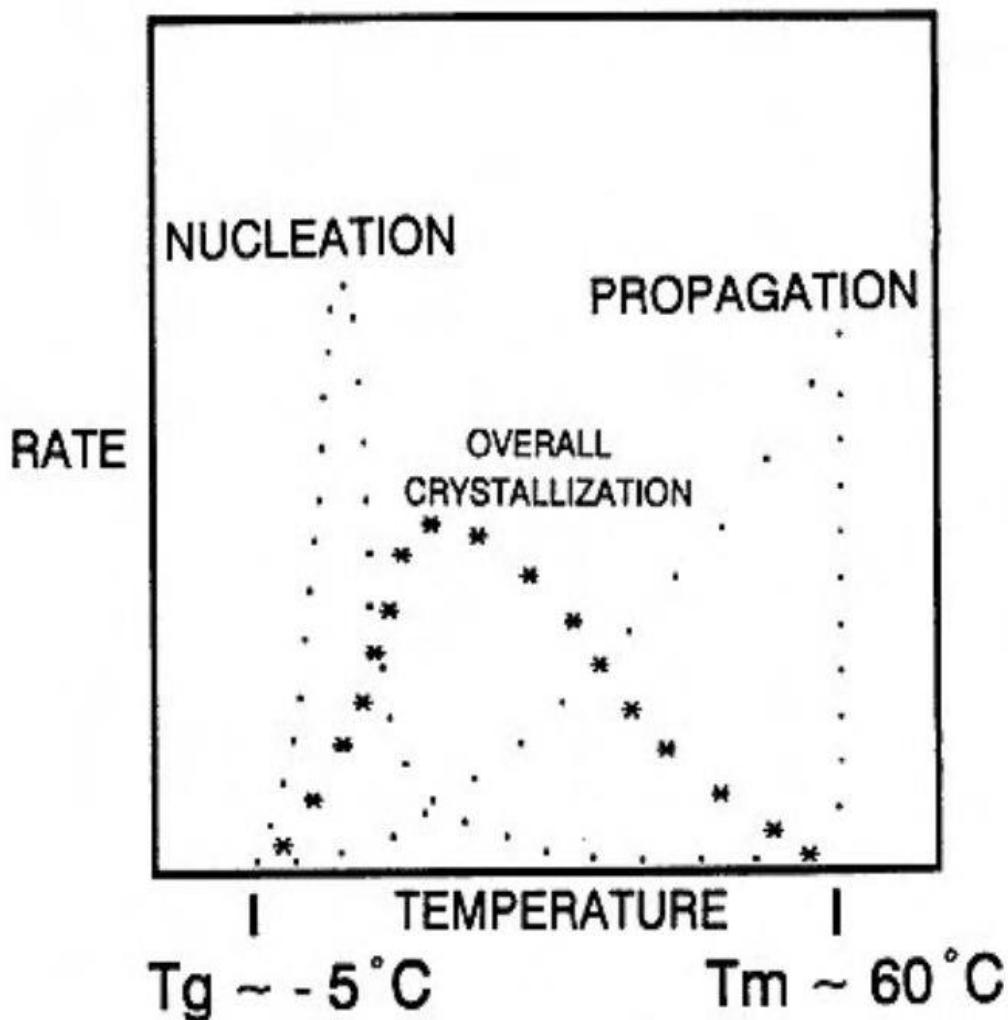
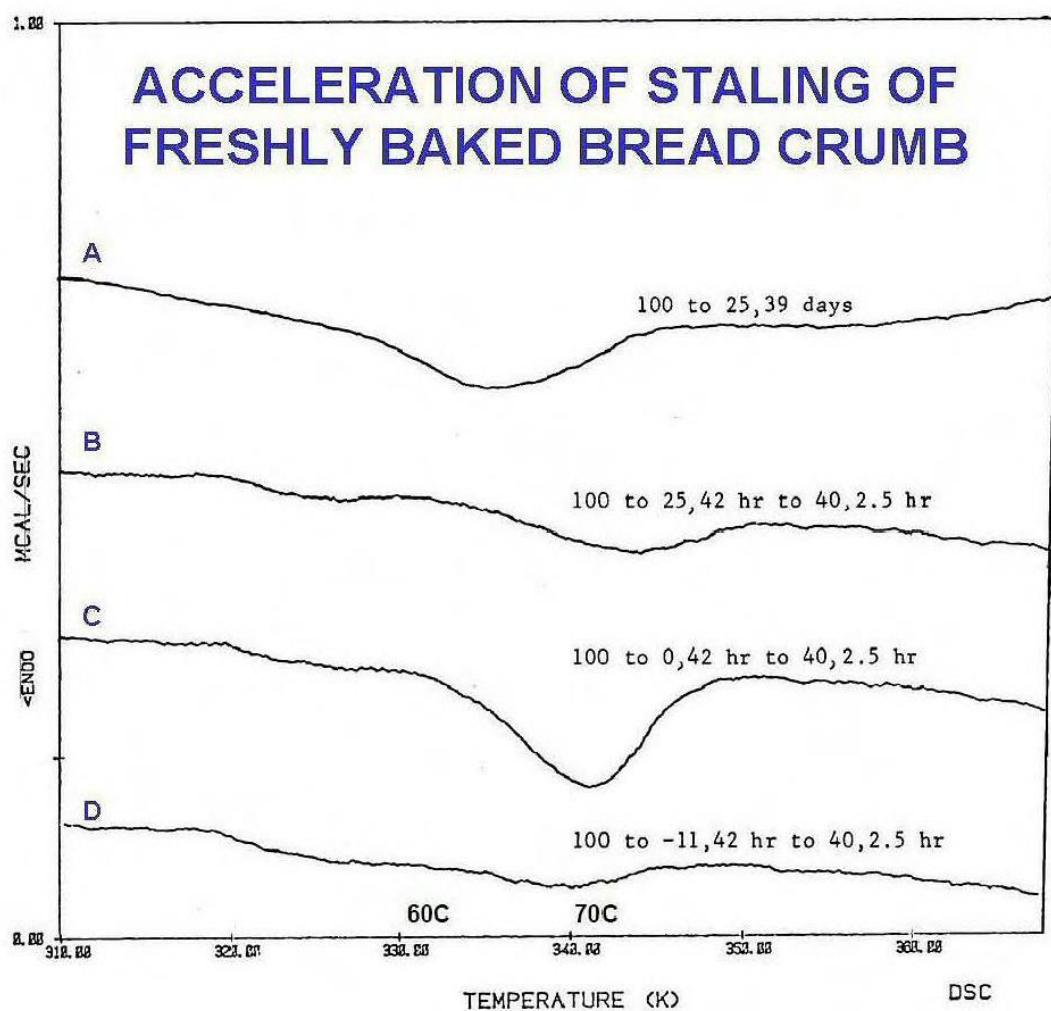


Figure 27

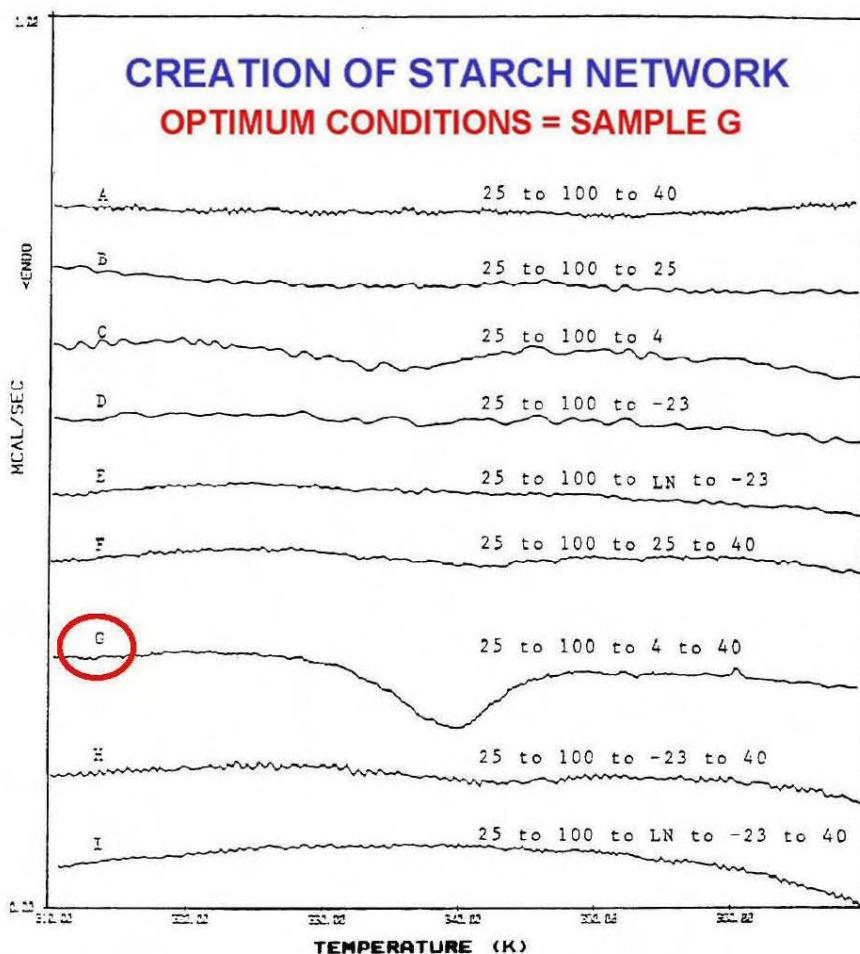
Figure 27 A plot of the crystallization kinetics mechanism for partially crystalline glassy polymers -- modified from the plot in Fig. 33 -- specifically applied to describe the kinetics of the crystallization process underlying starch retrogradation in, e.g., as-is moisture baked bread (Levine and Slade, 1990a).



DSC heat flow curves of freshly baked white bread crumb staled at different storage temperatures and times: A) 25C for 39 days; B) 25C for 42 hours, then 40C for 2.5 hours; C) 0C for 42 hours, then 40C for 2.5 hours; D) -11C for 42 hours, then 40C for 2.5 hours.

Figure 28

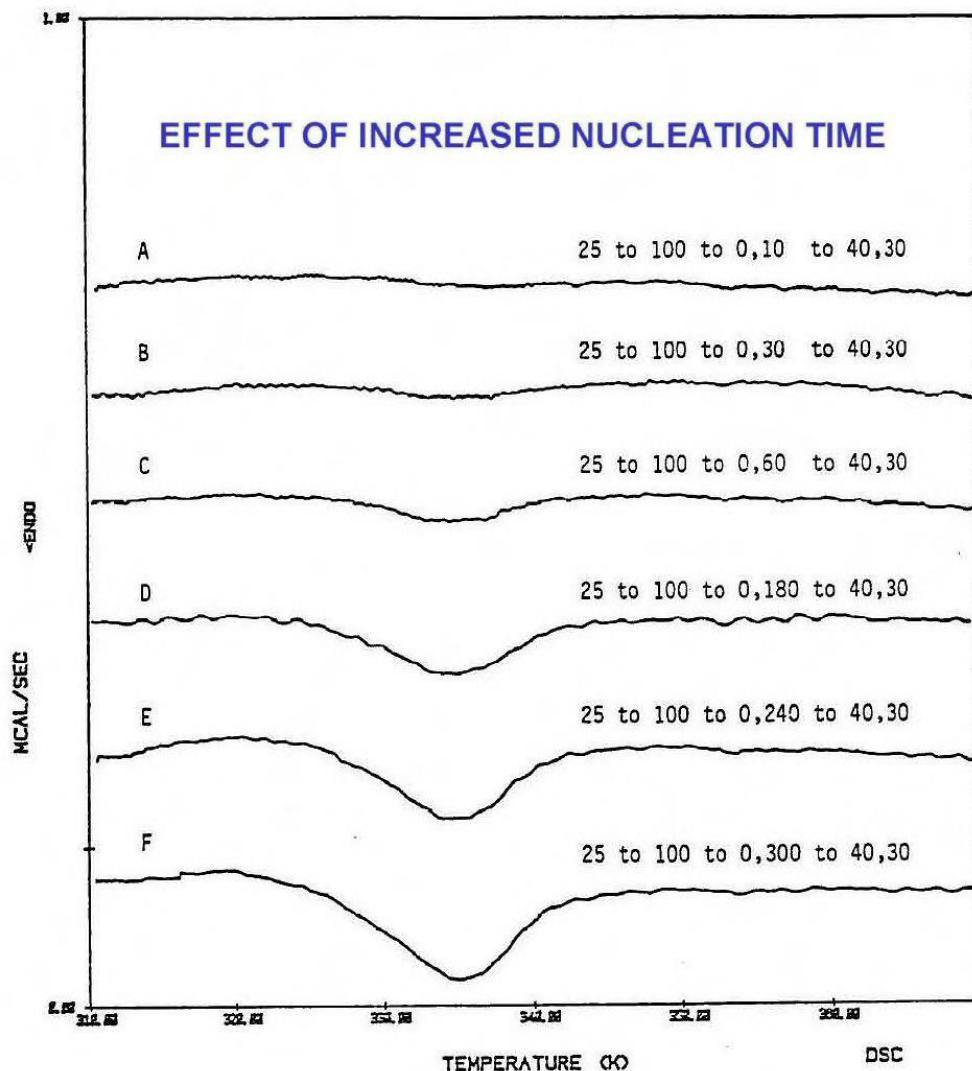
Figure 28 DSC thermograms -- for samples of freshly baked white bread crumb staled at the different storage temperatures and times indicated -- illustrating the specific temperature/time conditions under which staling could be greatly accelerated (Slade and Levine, 1987a).



DSC heat flow curves of wheat starch:water 1:1 mixtures, stored under different T/time conditions immediately following gelatinization: **A**) 40C for 4.5 hr; **B**) 25C for 3.5 hr; **C**) 4C for 3 hr; **D**) -23C for 2.5 hours; **E**) -196C for 1 min, then -23C for 2 hr; **F**) 25C for 2 hr, then 40C for 5 hr; **G**) 4C for 2 hr, then 40C for 6.5 hr; **H**) -23C for 2 hr, then 40C for 6 hr; **I**) -196C for 1 min, then -23C for 2 hr, then 40C for 5.5 hr.

Figure 29

Figure 29 DSC thermograms -- for samples of 1:1 wheat starch:water mixtures, stored under different temperature/time conditions immediately following gelatinization -- illustrating the specific, optimum temperature/time conditions identified for the creation of a staled starch network (Slade and Levine, 1987a).



**DSC heat flow curves of wheat starch:water 1:1 mixtures, nucleated for different times at 0°C, then propagated for 30 min at 40°C, immediately following gelatinization:**  
**A) 10 min; B) 30 min; C) 60 min; D) 180 min; E) 240 min; F) 300 min.**

**Figure 30**

Figure 30 DSC thermograms -- for samples of gelatinized 1:1 wheat starch:water mixtures, nucleated for different times at 0°C, then propagated for 30 min at 40°C -- illustrating the predominant effect of increased nucleation time at 0°C on the accelerated extent of starch staling (Slade and Levine, 1987a).

## CASE STUDY

THEORY → PRACTICE

### GOAL TO CREATE A UNIQUE RESISTANT STARCH WITH THERMOMECHANICAL STABILITY IN BAKING AND EXTRUSION PROCESSES

- NEED CRYSTAL MELTING ABOVE 140C AT HIGH WATER CONTENT
- NEED TO AVOID RECRYSTALLIZATION OF TYPICAL STALED STARCH ( $T_m \sim 60C$ ) AND AMYLOSE-LIPID CRYSTALS ( $T_m \sim 110C$ )

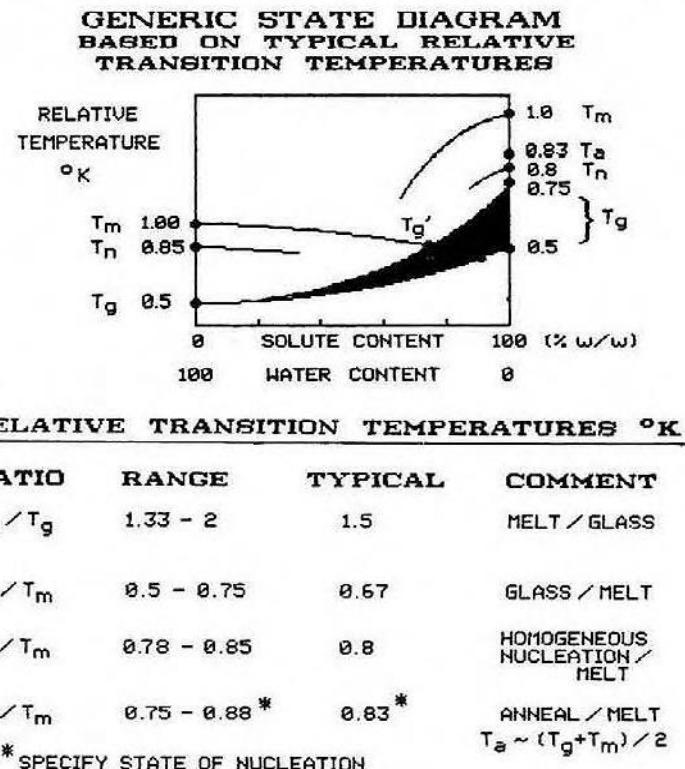


Figure 31

Figure 31 A case study of a Nabisco R&D program that put theory into practice, with the goal to create a unique enzyme-resistant starch (RS), a food ingredient with enhanced thermomechanical stability in commercial baking and extrusion processes (Slade and Levine, 1987a, 2009).

## X-150 was a Unique RS 3

- Heat-stable with a melting point of 150°C
- Superior baking characteristics
  - Low water-holding capacity
  - Browning
  - Crisp texture
- 50% insoluble fiber by AOAC Method 991.43; therefore was calorie-reduced
- Functioned as a flour-replacer ingredient in a wide range of grain-based products

Figure 32

Figure 32 A description of the properties of the RS alluded to in Fig. 39, Nabisco's so-called X-150 enzyme-resistant starch, which was a unique Type-3 RS comprised of retrograded amylose (Slade and Levine, 2009).

## X - 150 Process Flow Chart

Stage One & Stage Two

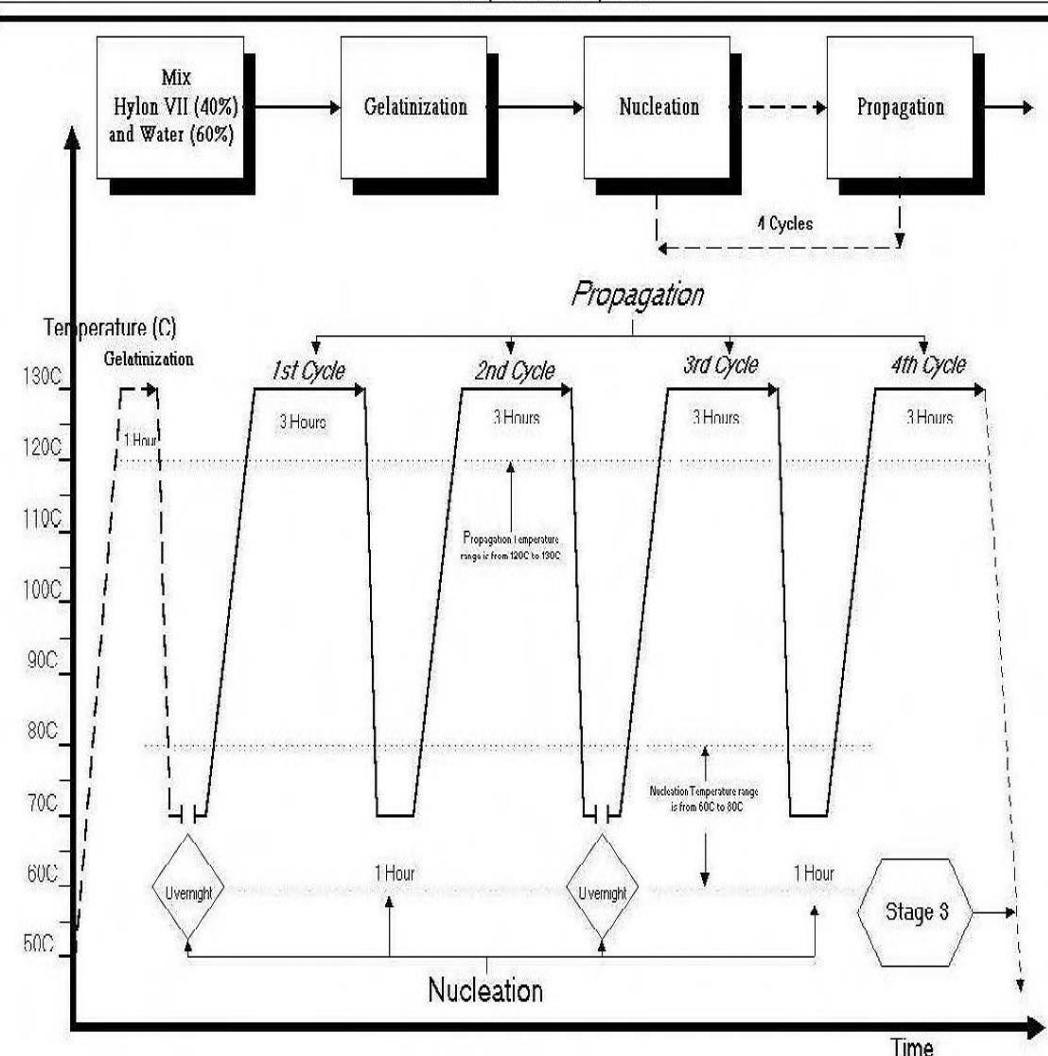


Figure 33

Figure 33 A detailed illustration of the three-stage Process Flow Chart for the pilot-plant manufacture of X-150 (Slade and Levine, 2009).

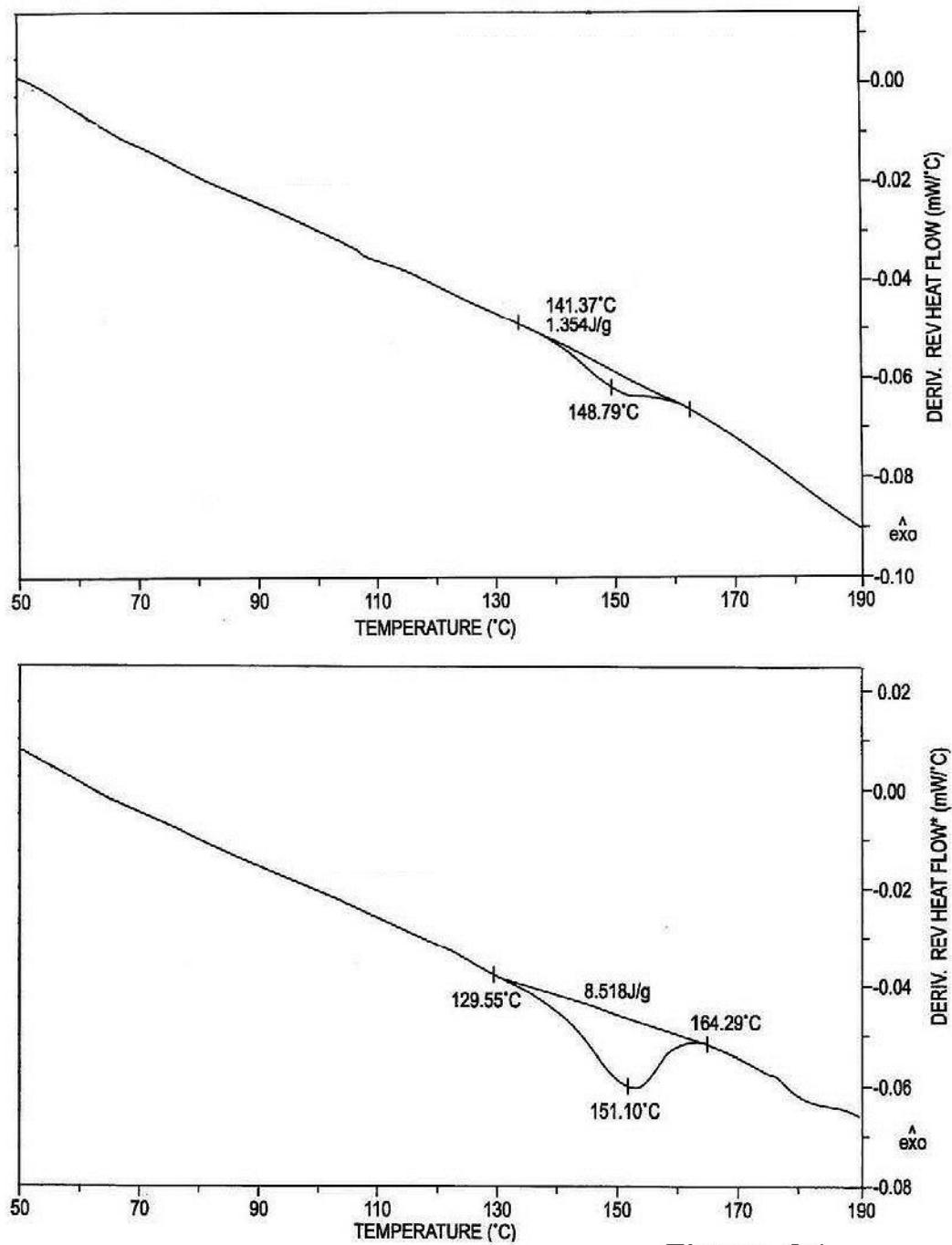


Figure 34

Figure 34 Modulated DSC thermograms for two X-150 samples, which show the characterizing melting endotherm at  $T_m \sim 150^\circ\text{C}$ , most clearly in the bottom curve for an isolated RS

# ACCEPTED MANUSCRIPT

crystalline component of the stage-3 X-150 product (Haynes et al., 2000; Slade and Levine, 2009).

**AACC 10-53 Wire-Cut Cookie Test Baking**  
with High Quality Biscuit Flour and 50% Replacement of Flour  
by Nabisco Patented X-150 and National Starch Commercial RS Ingredients

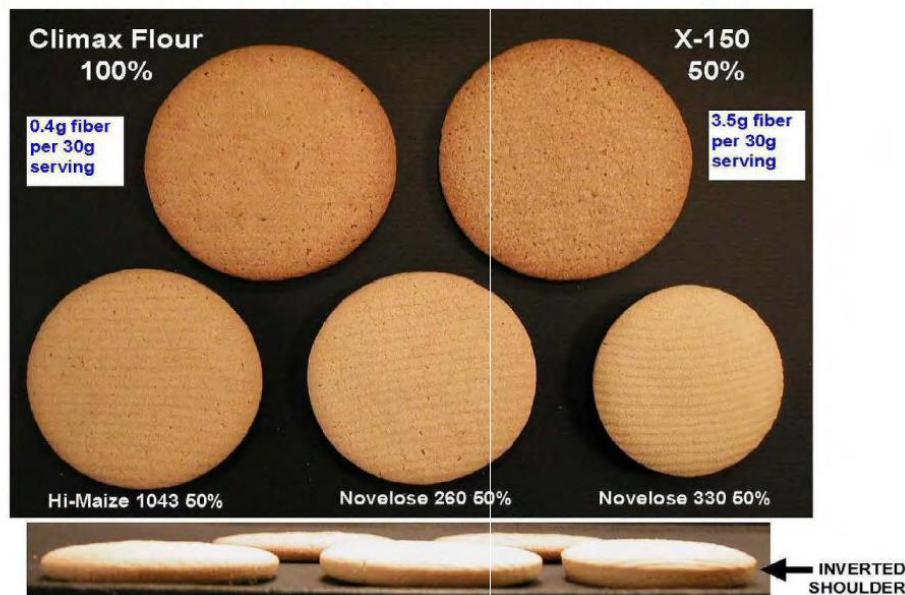


Figure 35

Figure 35 Cookie photographs illustrating the superior cookie-baking functionality of X-150, as a 50% flour-replacer ingredient, which was demonstrated using the standard AACC 10-53 wire-cut cookie test-baking method (Slade and Levine, 2009).