

# Glass Transitions of Extrudates: Relationship with Processing-Induced Fragmentation and End-Product Attributes

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ABSTRACT

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We used differential scanning calorimetry to measure glass transition temperatures ( $T_g$ ) for two types of corn-flour extrudates that differed primarily in their amylose-to-amylopectin ratios. Our experiments were designed so that extrusion-induced fragmentation represented the primary cause of changes in  $T_g$ . We found that the extent of fragmentation, as monitored by reductions in the  $T_g$  of the extrudates, increased with the specific mechanical energy generated in the extruder. Further, the  $T_g$  of the extrudate decreased rapidly with increases in moisture content,

thereby demonstrating that the glass phase of the extrudate is sensitive to the relative humidity of the storage environment. The  $T_g$  values of the extrudates also related to crispness and denseness, two important sensory-textural properties. Based on these results, we propose the use of  $T_g$  measurements on extrudates as a criterion for adjusting extruder operating conditions to produce extrudates with optimal textural properties, as well as to select optimum storage conditions (temperature and relative humidity) to improve stability and shelf life of extruded products.

Extrusion is a high-temperature, short-time cooking process that finds wide application in the food industry. Starch- and protein-based flours represent two frequently encountered raw materials for extrusion. In the extruder, these biopolymer mixtures are subjected to thermomechanical stress that can produce extrudates with lower molecular weights than the original feed material. A comparison of the weight average molecular weights of amylose and amylopectin before and after drum drying and extrusion reveals a considerable decrease in the molecular weight of the extruded samples (Colonna et al 1989). This breakdown of biopolymers during extrusion is considered to be the result of mechanical rather than thermal degradation, although thermal degradation is known to occur during prolonged heating processes. With regard to the influence of temperature, in a review of thermal decomposition of carbohydrates, Tomasik (1989) noted that depolymerization occurs in dry starch below 300°C, forming dextrins. However, the time required for such thermal dextrinization is longer (minutes or hours, depending on the use of catalyst) than that required for processing in extruders (typically seconds).

Gel-permeation chromatography, enzymatic digestion, and dilute solution viscometry have been used to demonstrate the depolymerization of starch polymers during extrusion and to characterize processing-induced changes in their functional properties (Colonna et al 1989, Chinnaswamy and Hanna 1990, Wen et al 1990). Schweiser and Reimann (1986) demonstrated that the extent of extrusion-induced starch breakdown is the same for whole, natural wheat flour as it is for the pure, isolated starch component. This result suggests that the proteinaceous and fibrous matrix offers no significant protection to the starch against extrusion-induced fragmentation. More importantly, this result demonstrates that fragmentation studies on the purified starch samples can provide information relevant to the whole, natural flour.

Processing-induced degradation of starches and flours into smaller size macromolecules has been investigated by various groups (Gomez and Aquilera 1983, 1984; Kim and Hamdy 1987; Colonna et al 1989). Porter and Casale (1985) extensively reviewed the stress-induced reactions that occur during processing. They noted that, as the polymer molecular weight increases, the mechanical energy applied to the polymer can be converted to stored molecular energy rather than dissipated as heat. This stored molecular energy can result in polymer deformation, followed by elongation, and, ultimately, bond rupture. Bond rupture causes a change in the polymer molecular weight and its distribution;

the breakdown of the polymer molecules appears to result from random chain scission. Conley (1970) also noted that the large shear rates of operations such as extrusion and milling cause degradation of polymers by purely mechanical forces. Davidson et al (1984) investigated the effect of various extruder operating conditions on the extent of molecular degradation. Studies on synthetic polymers suggest that degradation of polymers results from the concentration of mechanical energy into a small number of polymer bonds, caused by extensive chain entanglement (Basedow et al 1979). Wen et al (1990) studied the extrusion of corn meal under various moisture content, screw speed, and temperature conditions. These investigators concluded that maximal fragmentation generally occurred when mechanical energy was at its peak. Harper (1989) also reported that specific mechanical energy (SME) provides a good characterization of the extrusion process. Further, Bagley and Christianson (1989) found SME to be an important factor for design engineering.

In this report, we use the glass transition temperature ( $T_g$ ), as detected by differential scanning calorimetry (DSC), to characterize extrudates as a function of the SME of processing. Glass transitions previously were observed in noncrystalline regions of partially crystalline polymers such as starches and proteins (Kakivaya and Hoeve 1975, Eisenberg 1984, Hosney et al 1986, Zelezna and Hosney 1987).  $T_g$  defines a transition from a brittle, metastable, amorphous solid to a rubbery, unstable, amorphous liquid. It is reasonably well-established that the  $T_g$  of a polymer is related to the molecular weight of the polymer. Consequently, a process such as extrusion, which can reduce molecular weight by processing-induced fragmentation of the component polymer, should produce a product with a  $T_g$  value lower than that of the unprocessed feed material.

Figure 1 shows an idealized schematic diagram of the variation of enthalpy and heat capacity with temperature for amorphous polymers near  $T_g$ . The discontinuity in the apparent heat capacity at  $T_g$  is the basis of its determination by DSC.

One of the primary objectives of this study was to measure extrudate  $T_g$  to characterize the extent of processing-induced fragmentation in corn flour as a function of SME and relate our data to sensory attributes. To this end, we measured the influence of SME on the  $T_g$  of extrudates for two types of corn flour. We related our DSC-derived  $T_g$  data to processing-induced starch fragmentation, as well as to sensory-textural attributes of the extrudates. In addition to changes in the polymer molecular weight, the  $T_g$  can also be altered significantly by the presence of water as a diluent (Eisenberg 1984, Levine and Slade 1988, Orford et al 1990). Consequently, we measured how moisture alters the  $T_g$  of our extrudates. It should be emphasized that our data reveal general trends rather than rigorous mathematical correlations. Based on these trends, we suggest that the relationships we observed between processing conditions (SME), moisture-dependent extrudate physical properties ( $T_g$ ), and extrudate

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sensory attributes (crispness), can be used to define processing conditions designed to yield extrudates with desired sensory attributes and to define storage conditions (temperature, relative humidity) that enhance the stability and, therefore, the shelf life of extruded products.

## MATERIALS AND METHODS

### Materials

Two types of corn flour with different amylose-to-amylopectin ratios were obtained from National Starch and Chemical Co. (Bridgewater, NJ). High-amylopectin corn flour contains 60% starch (100% amylopectin), 11% protein, 3% fat, and 10–12% water. High-amylose corn flour contains 60% starch (30% amylopectin, 70% amylose), 10% protein, 4–5% fat, and 10–12% water.

### Extrusion

Each corn flour was extruded in a corotated twin-screw extruder (Werner & Pfleiderer, model ZSK-30). For all extrusion runs, the moisture content of the feed was kept constant at 20% (db). Mass flow rate and screw speed were adjusted to yield different SME values, which were calculated using the following equation:

$$\text{SME} = \text{Torque} \times \text{screw speed} / \text{mass flow rate}$$

Four test runs were performed for each type of corn flour. SME values for the four test runs on high-amylopectin corn flour were 452, 519, 827, and 1,386 kJ/kg. For high-amylose corn, the corresponding values were 303, 525, 531, and 630 kJ/kg.

### DSC Experiments

Thermograms of each extrudate were determined using a computer-controlled, pressure-variable, temperature scanning calorimeter (model DSC 111, Setaram, France). This instrument allowed us to run samples adiabatically at a predetermined, controlled pressure over a selected temperature range. The capability to conduct runs at a defined and controlled pressure is important. This is in contrast to conventional DSC instruments (e.g., Perkin Elmer DSC 7) in which the sample is sealed in a cell and ex-

periences an undefined increase in pressure with increasing temperature (a pressure-cooker effect). Before the DSC cell was loaded, all extruded samples were ground to 20-mesh size (Wiley mill, Arthur H. Thomas Co.). Some of the extrudates were freeze-dried before the DSC experiments. Freeze-dried samples were run at a pressure of 1 atm.

Extrudate samples of various moisture contents were prepared by equilibrating the extrudate over saturated salt solutions under vacuum for 48 hr. Various saturated salt solutions were used to achieve different environments of 6–92% rh. The actual moisture content of each sample was determined from the weight difference before and after equilibration. DSC runs of moist samples were carried out at 25 atm, thereby shifting the water peak outside the  $T_g$  range. All DSC measurements were conducted using fluid-tight stainless steel crucibles with controlled-pressure environments. The crucibles were completely filled with sample, sealed, and weighed. An empty crucible of the same properties was used for reference. The upper temperature limit of the runs was dictated by the thermal decomposition of the samples. All DSC measurements employed a scanning rate of 5°C/min. The resulting data were analyzed using well-established procedures to construct heat capacity curves and to calculate  $T_g$  values. The onset temperature is designated in Figure 1 as  $T_g$ .

### X-Ray Powder Diffraction

Powder diffraction patterns of pre- and postextruded corn flours were recorded with an x-ray diffractometer (PAD V, Scintag Inc., Santa Clara, CA) over the  $2\theta$  range of  $5^\circ \leq 2\theta \leq 45^\circ$  at a scanning rate of 3°/min. Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) was used as the x-ray source.

## RESULTS AND DISCUSSION

According to Eisenberg (1984) and Levine and Slade (1988),  $T_g$  can be influenced by factors such as pressure, diluents (e.g., water), the degree of cross-linking, crystallinity, and molecular weight. To eliminate the effect of the changes in pressure, we conducted all our DSC measurements in a special cell that maintained a constant pressure over the entire temperature range studied. To minimize the effect of the diluent water, extrudates were freeze-dried before calorimetric measurement. Corn flour does not undergo processing-induced cross-linking (B. P. Wasserman, *private communication*). This precludes this variable as an influence on our  $T_g$  data. Our x-ray diffraction results revealed that all the extrudates exhibited amorphous structures after processing. Thus, our  $T_g$  data were not influenced by differences in crystallinity. For these reasons, the differences in our  $T_g$  measurements for corn flour extrudates can be related to differences in extrudate molecular weight produced by processing-induced fragmentation at various SME values.

We used DSC to measure  $T_g$  of pre- and postextruded corn flour and to relate changes in  $T_g$  to processing-induced polymer fragmentation as a function of SME. We consider this experimental approach to be superior to other methods because  $T_g$  more directly reflects processing-induced fragmentation than does gel-permeation chromatography or dilute solution viscometry. The latter two techniques both require that the material be dissolved and in the liquid state. By contrast, DSC measurements can be performed on solid samples as well as liquids. Furthermore, Colonna et al (1989) emphasized that molecular weight resolution by gel-permeation chromatography increases when the elution volume is shifted toward high values. Hence, this technique will not be sensitive to very large or very small molecules. In addition, Finegold et al (1989) noted that changes in the constant-pressure heat capacity, as a function of temperature, provided a better measure of the  $T_g$  than viscosity data. Thus, we have used DSC to measure the  $T_g$  of pre- and postextruded corn flour as a function of the SME of the processing conditions.

### Decreased $T_g$ with Increased SME

SME is an extrusion parameter combining the effects of mass flow rate and screw speed (see equation above). Therefore, the

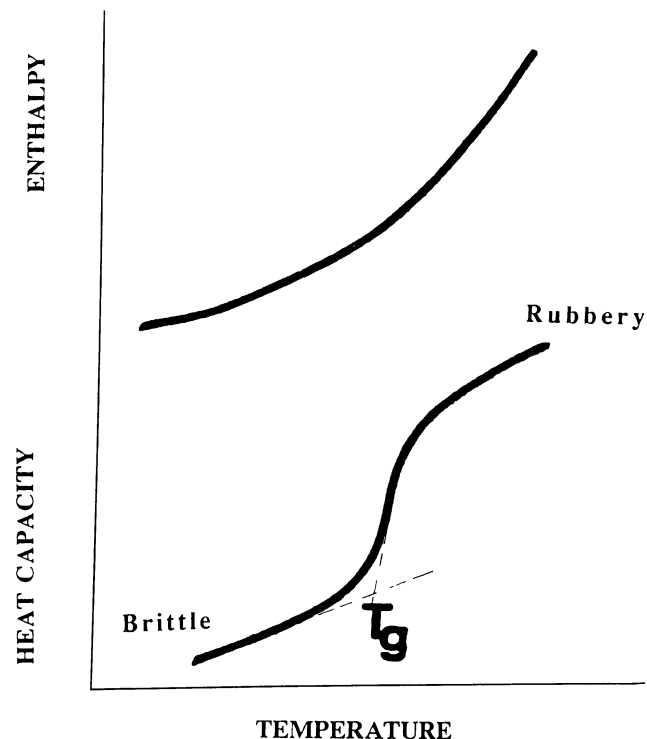


Fig. 1. Idealized schematic of the variation of enthalpy and heat capacity with temperature for amorphous polymers near glass transition temperatures ( $T_g$ ).

SME can be considered a measure of the extent of stress applied to a polymer.  $T_g$  is sensitive to molecular weight changes. In fact, Eisenberg's (1984) plots of  $T_g$  versus molecular weight were linear with negative slopes. In other words, high molecular weight polymers generally exhibit high  $T_g$  values. Consequently, a process, such as extrusion, that causes a reduction in molecular weight by processing-induced fragmentation of the component polymer should produce a product with a  $T_g$  value lower than that of the unprocessed feed material. Thus, a decrease in  $T_g$  of a feed

material, such as corn flour, with an increase in SME of processing provides a good indication of processing-induced fragmentation into smaller macromolecules. Our data are consistent with these expectations.

Figures 2 and 3 plot  $T_g$  as a function of SME for extrudates of high-amylopectin and high-amylose corn flour, respectively. Note that, for both corn flours, the  $T_g$  of the extrudate decreases when the SME of processing increases. To be specific, for high-amylopectin corn flour, we observe a  $\sim 50^\circ\text{C}$  reduction in  $T_g$  over a 934 kJ/kg SME range (452–1,386 kJ/kg) or a  $\Delta T_g/\Delta\text{SME}$  value of  $0.0535^\circ\text{C}/(\text{kJ}/\text{kg})$ . For high-amylose corn flour, we observe approximately a  $30^\circ\text{C}$  reduction in  $T_g$  over an SME range of 327 kJ/kg (303–630 kJ/kg) or a  $\Delta T_g/\Delta\text{SME}$  value of  $0.0917^\circ\text{C}/(\text{kJ}/\text{kg})$ . Thus, for both extrudates, as the SME of processing increases, the  $T_g$  decreases. Interestingly, however, the quantitative impact of this  $\Delta T_g/\Delta\text{SME}$  effect is quite different for the two types of corn flour we studied, which may be related to their different amylose-amylopectin ratios. Clearly, further studies are required to assess this possibility.

#### Destruction of the Crystalline Structure

Charbonniere et al (1973) investigated the effect of extrusion on the crystallinity of waxy corn starch. They reported that extrusion cooking destroys the crystalline structure partially or

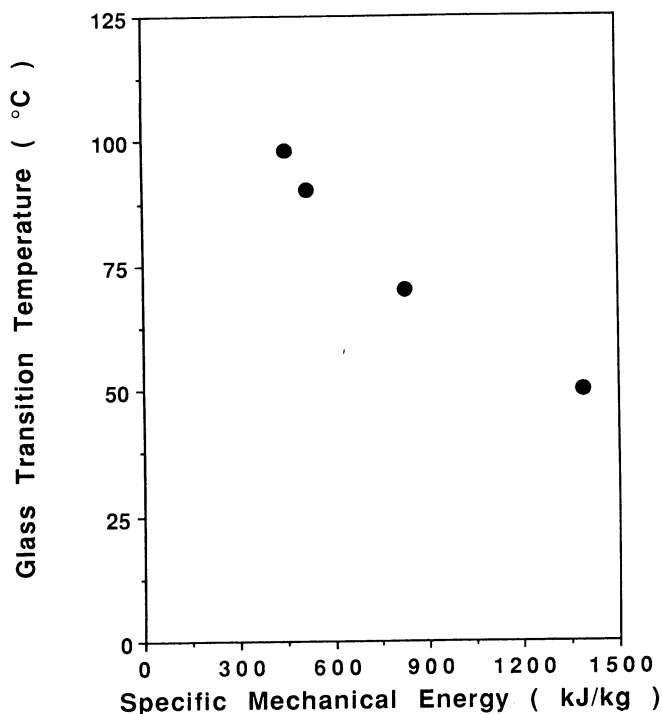


Fig. 2. Influence of specific mechanical energy on the glass transition temperatures of extrudates produced from high-amylopectin corn flour.

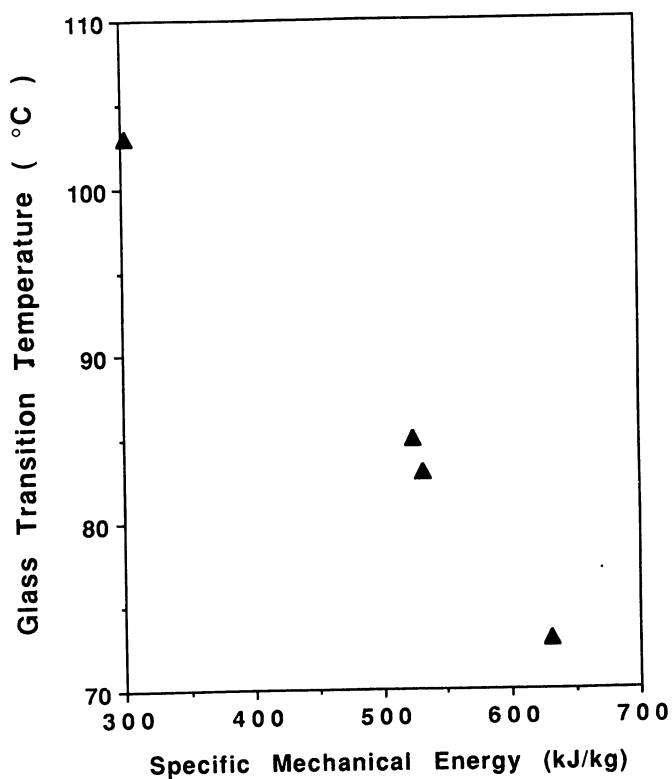


Fig. 3. Influence of specific mechanical energy on the glass transition temperatures of extrudates produced from high-amylose corn flour.

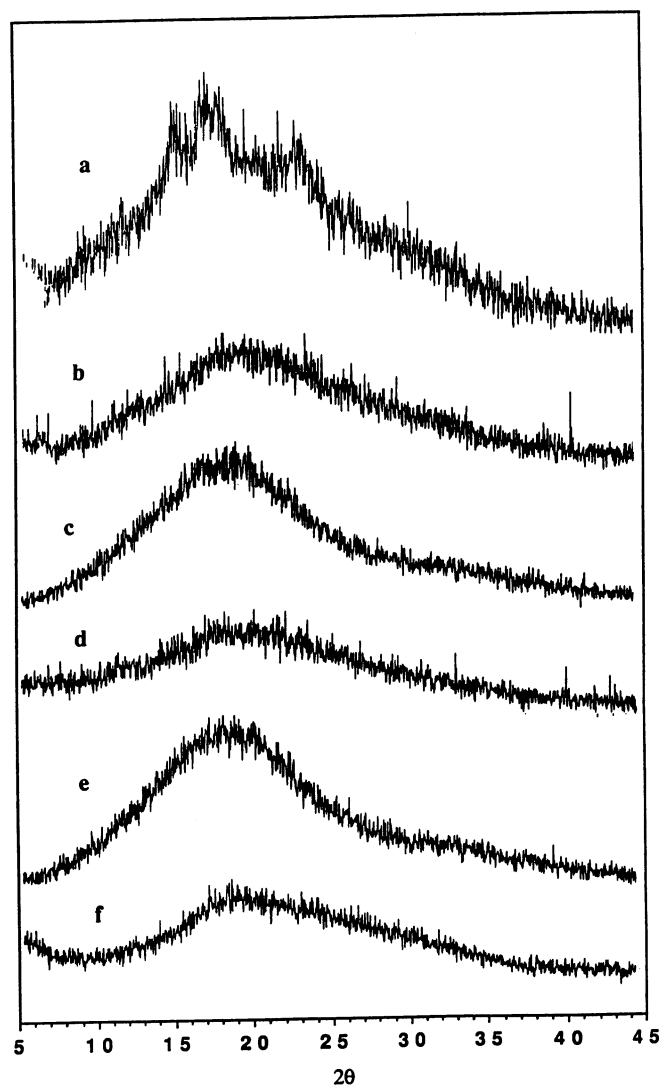


Fig. 4. X-ray powder diffraction patterns, produced under various specific mechanical energy conditions for high-amylopectin corn flour. a: original, unprocessed, high-amylopectin corn flour pattern showing crystalline structure. b–e: specific mechanical energy of 452, 519, 827, and 1,386 kJ/kg, respectively. f: grease pattern showing amorphous (noncrystalline) structure.

completely, depending on the amylose-amylopectin ratio and on the extrusion variables. At extrusion temperatures above 100°C, the structure is completely destroyed, leading to an x-ray diffraction pattern typical of an amorphous state. The x-ray results reported here on corn flour extrudates are consistent with the observations of Charbonniere et al (1973).

Figure 4 shows the X-ray powder diffraction patterns, produced under various SME conditions, that we obtained for high-amylopectin corn flour and a number of its extrudates. We used the powder diffraction pattern of grease (Fig. 4f) for comparison because it possesses an amorphous (noncrystalline) structure. The oscillating or periodic saw-tooth fine structure observed for the preextruded, high-amylopectin corn flour (Fig. 4a) is characteristic of crystalline structures. The smooth curvatures of the four extruded samples (Fig. 4b-e) are similar to that of grease, which is characteristic of amorphous (noncrystalline) structures. Note that, in these patterns, the intensity of the broad peak is related to the thickness of the material but not to the presence of any crystallinity. Thus, these diffraction patterns reveal that the original, unprocessed, high-amylopectin corn flour possessed some crystalline structure that was destroyed by the extrusion process.

### $T_g$ and Sensory-Textural Attributes

Levine and Slade (1988) and Noel et al (1990) noted that  $T_g$  is relevant to food processing operations (e.g., freezing, drying, extrusion) and correlates well with quality attributes (e.g., texture, stability, and flavor release in low-moisture systems). They also found that such product quality attributes can be maintained by adjusting the formulation of product and the operating and storage conditions relevant to the  $T_g$  of the end product. We also observed this relationship between  $T_g$  and end-product attributes for corn flour extrudates.

The  $T_g$  values of our corn flour extrudates exhibited trends related to sensory attributes (crispness and denseness) already evaluated. Chen et al (1991) used quantitative descriptive analysis, adapted for extruded products, to evaluate the relevant sensory attributes. In our study, an increase in crispness is qualitatively

related to an increase in  $T_g$  (Fig. 5). It should be noted that, in the sensory evaluation studies of extrudates by Chen et al (1991), brittle materials are described as *crisp*. As  $T_g$  is defined as the temperature at which a material changes from a glassy, brittle (*crisp*) state to a rubberlike, liquid (*chewy*) state, the relationship between  $T_g$  and crispness may provide a criterion for adjusting extruder operating conditions to produce extrudates with optimal crispness. The data plotted in Figure 5 suggest that a threshold  $T_g$  value may have to be reached before crispness increases with  $T_g$ . By contrast, in Figure 6 we find that the denseness decreases as  $T_g$  increases.

### Moisture Dependence of $T_g$

Figure 7 shows the effect of moisture content on  $T_g$  for an extrudate of high-amylopectin corn flour produced at an SME of 452 kJ/kg. Note that, upon increasing the water content, the value of  $T_g$  drops rapidly over the moisture content range studied. This typical behavior is observed in all synthetic and natural amorphous polymers upon addition of a diluent. The inset of Figure 7 shows the experimental adsorption isotherm for the same extrudate, which was determined by equilibrating the extrudate over various saturated salt solutions at 27°C.

In amorphous dry foods such as extrudates, when the  $T_g$  is close to room temperature at a given moisture content, the extrudate, in a plasticized, rubbery state, loses the desired textural attributes. The plasticizing effect of increasing moisture content at constant temperature is identical to the effect of increasing temperature at constant moisture content as reported by Levine and Slade (1988). Therefore, the  $T_g$  of extrudates can be useful in determining the proper temperature and relative humidity for storage conditions. Knowledge of adsorption isotherms at various temperatures is needed to calculate equilibrium moisture content, which, in turn, is an important factor affecting  $T_g$ . The relationship between  $T_g$  and sensory properties that we observed may provide a basis for evaluating the textural acceptability of food material by measuring  $T_g$ .

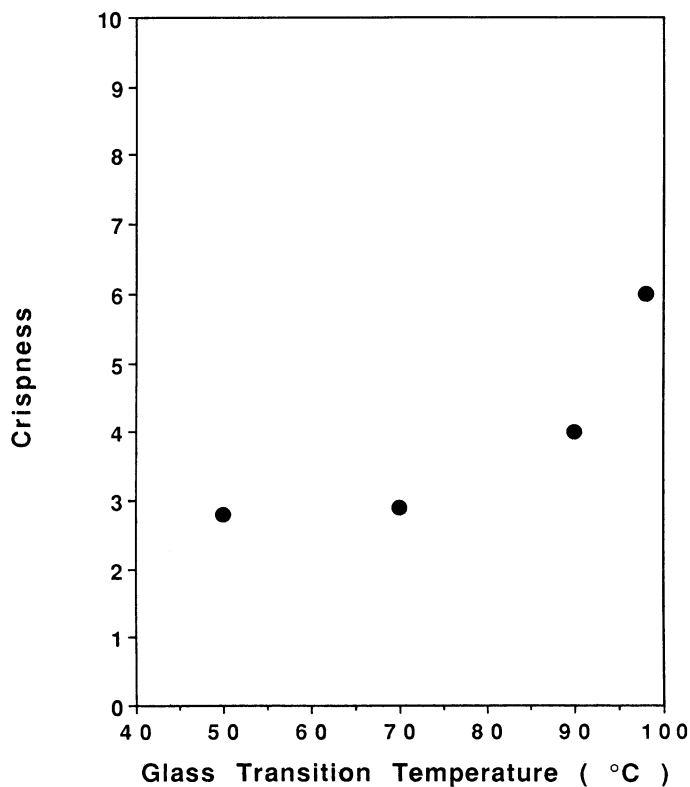


Fig. 5. Relationship between crispness (Chen et al 1991) and glass transition temperature for the extrudates from high-amylopectin corn flour.

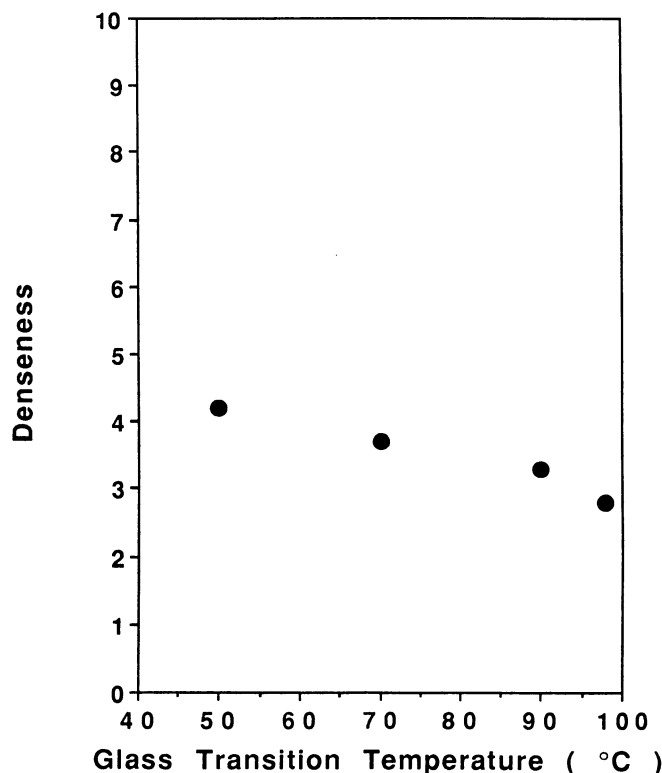


Fig. 6. Relationship between denseness (Chen et al 1991) and glass transition temperature for the extrudates from high-amylopectin corn flour.

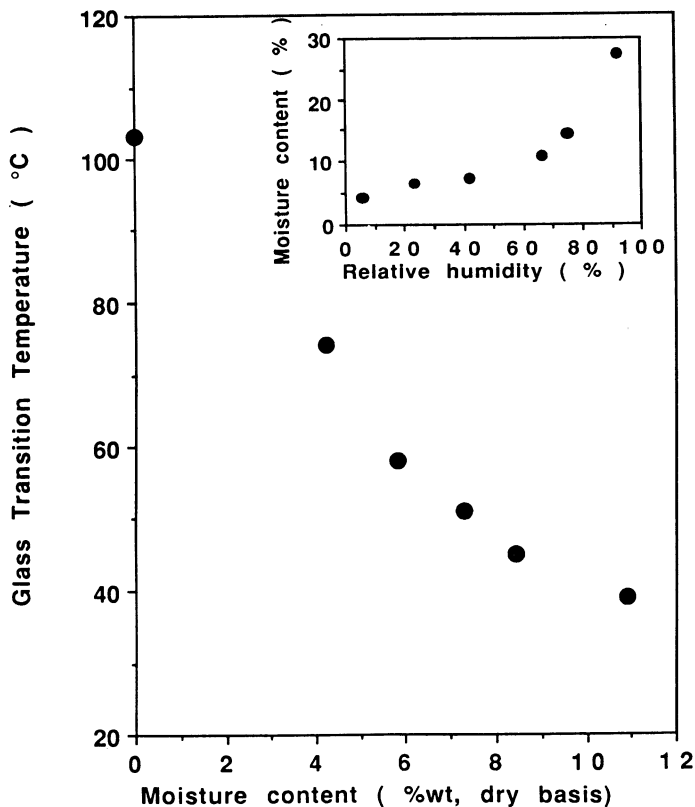


Fig. 7. Effect of moisture content on glass transition temperature for an extrudate of high-amylopectin corn flour produced at a specific mechanical energy of 452 kJ/kg. Inset: adsorption isotherm of extrudate at 27°C.

### CONCLUSIONS

We used DSC to measure  $T_g$  of two types of corn flour extrudates differing primarily in amylose-to-amylopectin ratios. Our experiments were designed so that extrusion-induced fragmentation represented the primary cause of changes in  $T_g$ . We found that the extent of fragmentation, as monitored by reductions in the  $T_g$  of the extrudates, was related to the SME of processing. We showed that the  $T_g$  of the extrudate decreased rapidly with increases in the moisture content. This observation showed that the  $T_g$  is very sensitive to the relative humidity of the storage environment. We also showed that the extrudate  $T_g$  values were related to crispness and denseness, two sensory-textural properties. These results suggest that  $T_g$  measurements on extrudates may provide a useful criterion for adjustment of extruder operating conditions for desired textural properties, as well as for the selection of optimum storage conditions of temperature and relative humidity for enhancing the stability and shelf life of extruded products.

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### LITERATURE CITED

- BAGLEY, E. B., and CHRISTIANSON, D. D. 1989. Some recent developments in food rheology. In: *Engineering and Food*, Vol. 1. W. E. L. Spiess and H. Schubert, eds. Elsevier, London.
- BASEDOW, A. M., EBERT, K. H., and HUNGER, H. 1979. Effect of mechanical stress on the reactivity of polymers: Shear degradation of polyacrylamide and dextran. *Makromol. Chem.* 180:411-427.
- CHARBONNIERE, R., DUPRAT, P., and GUILBOT, A. 1973. Changes in various starches by cooking-extrusion processing. II. Physical structure of extruded products. (Abstr.) *Cereal Sci. Today* 18:286.
- CHEN, J., SERAFIN, F. L., PANDYA, R. N., and DAUN, H. 1991. Effects of extrusion conditions on sensory properties of corn meal extrudates. *J. Food Sci.* 56:84.
- CHINNASWAMY, R., and HANNA, M. A. 1990. Macromolecular and functional properties of native and extrusion-cooked corn starch. *Cereal Chem.* 67:490-499.
- COLONNA, P., TAYEB, J., and MERCIER, C. 1989. Extrusion cooking of starch and starchy products. Pages 247-319 in: *Extrusion Cooking*. C. Mercier, P. Linko, and J. M. Harper, eds. Am. Assoc. Cereal Chem.: St. Paul, MN.
- CONLEY, R. T. 1970. *Thermal Stability of Polymers*. Vol. 1. R. T. Conley, ed. Marcel Dekker: New York.
- DAVIDSON, V. J., PATON, D., DIOSADY, L. L., and RUBIN, L. J. 1984. A model for mechanical degradation of wheat starch in a single-screw extruder. *J. Food Sci.* 49:1154-1157.
- EISENBERG, A. 1984. The glassy state and the glass transition. Pages 55-95 in: *Physical Properties of Polymers*. Am. Chem. Soc.: Washington, DC.
- FINEGOLD, L., FRANKS, F., and HATLEY, R. H. M. 1989. Glass/rubber transitions and heat capacities of binary sugar blends. *J. Chem. Soc. Faraday Trans.* 85:2945-2951.
- GOMEZ, M. H., and AQUILERA, J. M. 1983. Changes in the starch fraction during extrusion-cooking of corn. *J. Food Sci.* 48:378.
- GOMEZ, M. H., and AQUILERA, J. M. 1984. A physicochemical model for extrusion of corn starch. *J. Food Sci.* 49:40-43, 63.
- HARPER, M. J. 1989. Food extruders and their applications. Pages 1-15 in: *Extrusion Cooking*. C. Mercier, P. Linko, and J. M. Harper, eds. Am. Assoc. Cereal Chem.: St. Paul, MN.
- HOSENEY, R. C., ZELEZNAK, K., and LAI, C. S. 1986. Wheat gluten: A glassy polymer. *Cereal Chem.* 63:285-286.
- KAKIVAYA, S. R., and HOEVE, C. A. J. 1975. The glass point of elastin. *Proc. Nat. Acad. Sci. USA* 72:3505-3507.
- KIM, K., and HAMDY, M. K. 1987. Depolymerization of starch by high pressure extrusion. *J. Food Sci.* 52:1387-1390.
- LEVINE, H., and SLADE, L. 1988. Collapse phenomena a unifying concept for interpreting the behaviour of low moisture foods. Pages 149-180 in: *Food Structure Its Creation and Evaluation*. J. M. V. Blanshard and J. R. Mitchell, eds. Butterworths: London.
- NOEL, T. R., RING, S. G., and WHITTAM, M. A. 1990. Glass transition in low moisture foods. *Trends Food Sci. Technol.* 1:62-67.
- ORFORD, P. D., PARKER, R., and RING, S. G. 1990. Aspects of the glass transition behaviour of mixtures of carbohydrates of low molecular weight. *Carbohydr. Res.* 196:11-18.
- PORTER, R. S., and CASALE, A. 1985. Recent studies of polymer reactions caused by stress. *Polym. Eng. Sci.* 25:129-156.
- SCHWEISER, T. F., and REIMANN, S. 1986. Influence of drum drying and twin-screw extrusion cooking on wheat carbohydrates. I. A comparison between wheat starch and flours of different extraction. *J. Cereal Sci.* 4:193-203.
- TOMASIK, P. 1989. The thermal decomposition of carbohydrates. *Adv. Carbohydr. Chem. Biochem.* 47:203.
- WEN, L., RODIS, P., and WASSERMAN, B. P. 1990. Starch fragmentation and protein insolubilization during twin-screw extrusion of corn meal. *Cereal Chem.* 67:268-275.
- ZELEZNAK, K. J., and HOSENEY, R. C. 1987. The glass transition in starch. *Cereal Chem.* 64:121-124.

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