

Effect of Specific Mechanical Energy on Properties of Extruded Protein-Starch Mixtures

Maoz Gropper,¹ Carmen I. Moraru,¹ and Jozef L. Kokini^{1,2}

ABSTRACT

Cereal Chem. 79(3):429–433

The effect of the specific mechanical energy (SME) during extrusion of a protein-starch mixture was studied by analyzing the glass transition temperature (T_g) and starch gelatinization. We found that the SME values of 344 to 2108 kJ/kg did not significantly change the T_g of the product. To explain the insensitivity of T_g to SME in spite of reported fragmentation taking place during extrusion, we studied the effect of the molecular weight (MW) on T_g in a model system consisting of dextrans of

varying molecular weights. We found that the effect of the molecular weight on the T_g reached a plateau at 6.7×10^4 . Because the reported size of the fragments created during the extrusion process is larger than this, we were able to explain the apparent insensitivity of T_g to SME in the protein-carbohydrate matrix studied. However, we found that starch gelatinization varied with SME, the degree of gelatinization being higher for systems exposed to higher SME.

Food extrusion is a process that involves applying thermal and mechanical energy to food ingredients in a process of mixing and cooking. The formulations commonly used for this process consist of food polymers: carbohydrates (most commonly starches) and proteins (gluten, soybean proteins, meat proteins, etc.) that contribute to the texture of the products.

The specific mechanical energy (SME) is responsible for fragmentation of starch molecules (Gomez and Aguilera 1983, 1984; Davidson 1984; Van Lengerich 1990; Wen et al 1990; Lai 1991; Politz et al 1994). As a result of the applied shear forces, amylopectin molecules are broken mainly at the α -1:6 bonds. This phenomenon was attributed to the decrease in the viscosity with the increase in water content that decreased the shear forces applied to the molecules (Gomez and Aguilera 1983, 1984; Davidson 1984). The degradation products are macromolecules in the range of 50,000–200,000 MW (Fennema 1985). Limits of 10^5 to 10^7 MW for the fragments were also reported by Van Lengerich (1990) and Politz et al (1994). According to Van Lengerich (1990), after maximum depolymerization of amylopectin occurs during extrusion cooking, no significant further molecular degradation of starch takes place. These studies also showed that over the water content range of 20–30%, the higher the water content, the lesser the degradation. In contrast to these observations on starch degradation, Wen et al (1990) found that corn proteins were more resistant to the shear forces and did not fragment during extrusion.

Kaletunc and Breslauer (1993 and 1996) and Barrett and Kaletunc (1998) used the model of starch fragmentation to explain their results that showed a decrease in the glass transition temperature (T_g) with the increase of SME.

An additional effect of SME on starch is the gelatinization process that takes place during extrusion (Gomez and Aguilera 1983, 1984; Van Lengerich 1990). The higher the SME, the higher the degree of gelatinization. In contrast to the effect of water on macromolecule fragmentation, gelatinization of starch is more intense at higher water content.

The objective of this research was to study the effect of SME on the glass transition, gelatinization, and microstructure of mixed protein-starch systems and to examine the validity of the degradation models in explaining the correlation between T_g and SME. To explain our results, which did not confirm observations in the literature, the relationship between molecular weight and T_g was studied for glucose polymers in the range of 345 to 2,000,000 MW.

These studies offered the needed T_g versus molecular weight relationships to explain our observations on the extruded system.

42/42 SK
42/42 SK
42/21 SKN
42/42
42/42
42/21
42/42 IGEL
28/28
28/28
28/28
42/42 IGEL
28/28
28/28
28/28
KB 45/5/20
28/14
28/14
28/14
20/20
20/20
20/20
20/20
20/20
KB 45/5/20
20/20
20/20
20/20
20/20
20/20
20/20
20/10
14/14
14/14
14/14
14/14
14/14
14/14

Fig. 1. Extruder screw configuration. Conveying elements (SK, SKN); mixing elements (IGEL, KB); pitch/screw length (42/21); staggering angle of discs/number of discs/element length (45/5/14).

¹ Food Science Department, Rutgers–The State University of New Jersey, 65 Dudley Road, New Brunswick, NJ 08901.

² Corresponding author. E-mail: kokini@aesop.rutgers.edu Phone: 732-932-9611 ext 201.

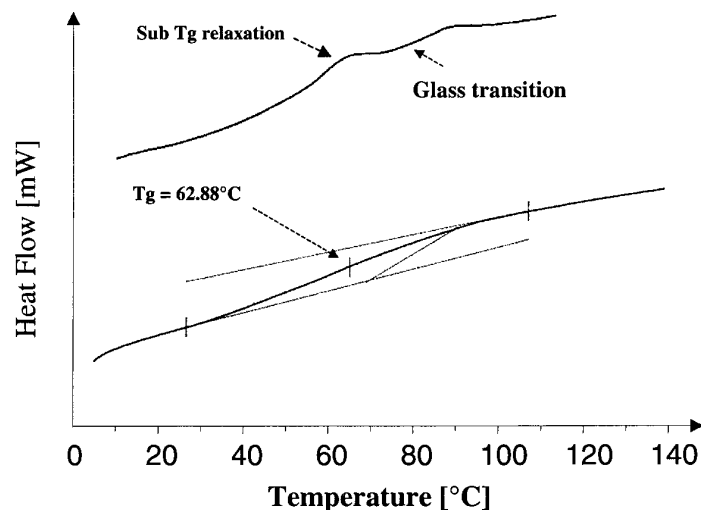


Fig. 2. Differential scanning calorimetry (DSC) scan (a) and rescan (b) of extruded wheat flour and meat formulation at a_w 0.546.

TABLE I
Extrusion Conditions Used for Sample Manufacturing

Sample No.	Die Temp. (°C)	Die Pressure (psi)	Max. Extrusion Temp. (°C)	Torque (%)	Screw Speed (rpm)	Feed Flow Rate (g/min)	Specific Mechanical Energy (kJ/kg)
1	70	920	124	29	200	133.2	344
2	71	900	124	28	200	114.4	381
3	73	880	123	27	200	95.6	434
4	75	890	124	26.5	200	76.8	512
5	85	850	126	26	200	57.2	687
6	95	740	129	15	200	30.0	1,092
7	95	800	130	15.5	150	19.7	1,288
8	95	740	129	15	200	24.9	1,315
9	96	720	130	14	200	19.7	1,552
10	97	620	128	12	250	19.7	1,662
11	95	580	127	11	300	19.7	1,829
12	95	730	130	14	200	14.5	2,108

TABLE II
Extrusion Conditions Used to Prepare Expanded Samples for Specific Mechanical Energy (SME) Analysis

Sample No.	Die Temp. (°C)	Die Pressure (psi)	Max. Extrusion Temp. (°C)	Torque (%)	Screw Speed (rpm)	Feed Flow Rate (g/min)	SME (kJ/kg)
1	101	150	131	10	100	76.8	142
2	101	160	131	8	150	76.8	170
3	101	140	131	7	200	76.8	199
4	101	130	131	6	250	76.8	213
5	101	130	131	7	300	76.8	298.6

MATERIALS AND METHODS

Materials

The formulation used for all the extrusion conditions was obtained from whole wheat flour, meat meal, and water. The composition was starch 32.8%, water 31%, meat proteins 12.6%, gluten protein 12.8%, ash 4.42%, fat 3.85%, and fibers 2.04%. Dextrins in the range of 10,500 to 2,000,000 MW and maltose at 345 MW were purchased from Sigma. Dextrins lot numbers were 69H1273 (MW 10,500), 109H0012 (MW 43,200), 69H1274 (MW 67,300), 69H1267 (MW 473,000), 125H10761 (MW 2,000,000).

Extruded Samples

All the extruded samples were manufactured using an intermeshing twin-screw extruder (model ZSK-30, Werner & Pfleiderer, Ramsey, NJ). The screw configuration used is presented in Fig. 1. Individual cooling and heating systems controlled the temperature in each of the five zones of the barrel. The samples prepared for differential scanning calorimetry (DSC) measurements were extruded using a

slit die, with the channel dimensions of 150 × 20 × 1 mm, without supplementary cooling at the die. The extrusion conditions used are presented in Table I.

The samples prepared for the microscopy analysis were extruded using an expansion die with a diameter of 3 mm, using the extrusion conditions presented in Table II. The SME was calculated as:

$$\text{SME} = \text{net torque} \times \text{screw speed} / \text{mass flow rate (kJ/kg)} \quad (1)$$

The ingredients were mixed with water before extrusion using a solids mixer (Hobart Mfg. Co., Troy, OH). To feed the mixture into the extruder from the hopper, a feeder with co-rotating twin screws (K-Tron Co., Pittman, NJ) was used. This allowed the control of the feeding rate into the extruder. The feeder was calibrated at the beginning of each extrusion experiment. After extrusion, the samples were cut in the appropriate shape for each type of analysis and placed in dessicators for seven days, over P₂O₅ ($a_w = 0$) to dry them. After dehydration, the samples were rehydrated to $a_w = 0.546$ and $a_w = 0.326$ by placing them in dessicators over saturated solutions of NaBr and MgCl₂, respectively.

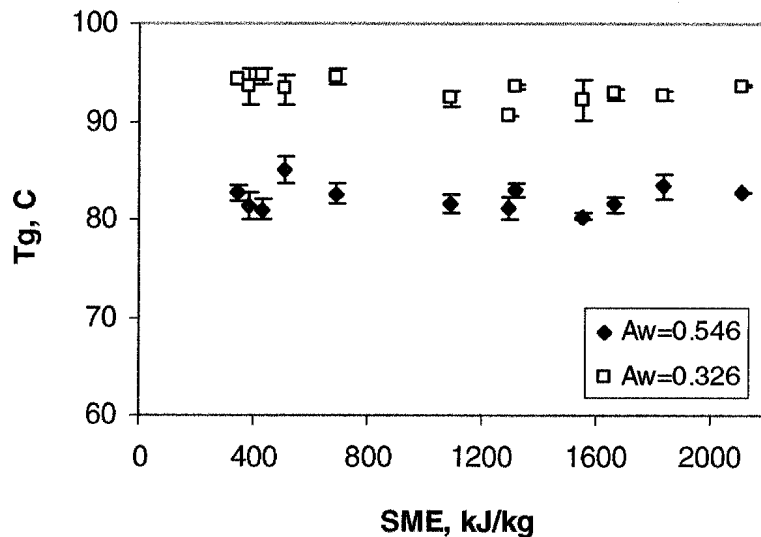


Fig. 3. Effect of specific mechanical energy (SME) on measured glass transition (T_g) in the first DSC scan at a_w 0.326 and 0.546.

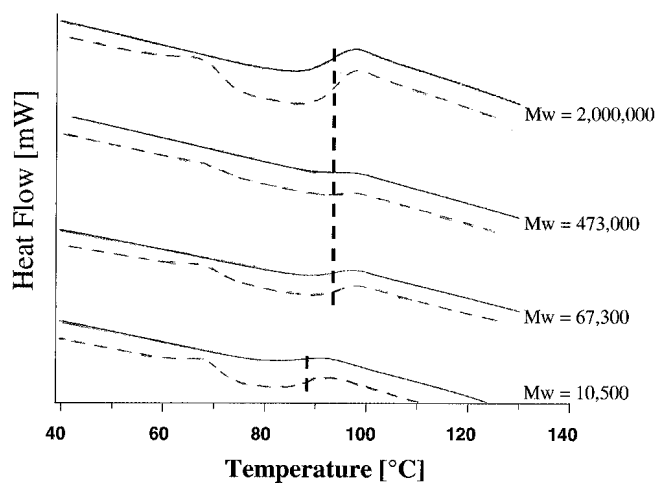


Fig. 4. Differential scanning calorimetry (DSC) thermograms of dextrans at a_w 0.326.

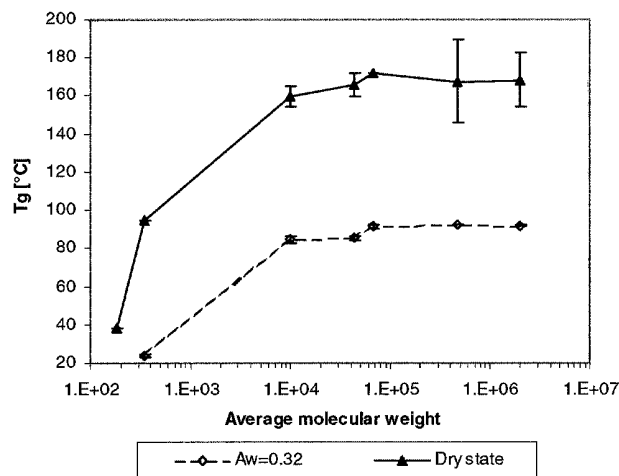


Fig. 5. Effect of dextran molecular weight on measured glass transition (T_g) and T_g of maltose in first differential scanning calorimetry (DSC) scans. Values for T_g of dry maltose and glucose taken from Noel et al (1993).

Solutions of 30% dextran and maltose were freeze-dried and equilibrated over saturated salt solution of a water activity of 0.326.

Dry dextran samples were prepared by freeze-drying the powders obtained from the manufacturer and then equilibrating them in a desiccator over P_2O_5 ($a_w = 0$) for three weeks.

Measurements were made using a DSC7 (Perkin Elmer, Norwalk, CT). Samples were placed in stainless steel capsules to avoid any moisture loss during measurement. A typical sample weighed 40 mg. The scanning rate was $10^\circ\text{C}/\text{min}$. The scanning temperature range was -10 to 110°C for the extrudates and -10 to 200°C for the dextran samples.

The dry expanded extrudates were cooled with liquid nitrogen and fractured with a knife to get specimens with a characteristic surface. The specimens were mounted with the fractured side up on copper stubs, and coated with a thin layer of gold. The coated specimens were analyzed with a scanning electron microscope (JJM 35C, JEOL, Tokyo, Japan) at 15kV.

RESULTS AND DISCUSSION

A typical DSC scan and rescan of the protein-starch extrudate is shown in Fig. 2. The thermogram of the first scan shows two thermal transitions consisting of an endothermic transition and a glass transition. The endothermic transition interferes with the wide

glass transition and masks its onset. This endothermic transition is related in the literature to either enthalpy relaxation (Berens and Hodge 1982; Kalichevsky et al 1992; Shogren 1992; Thiewes and Steenken 1997) or carbohydrate-water interactions (Appelqvist et al 1993). The rescan indicates that the glass transition is a fast reversible transition but the endothermic event is not. This is in agreement with all the above-mentioned studies. It has been demonstrated before (Berens and Hodge 1982; Kalichevsky et al 1992; Shogren 1992; Appelqvist et al 1993; Yuan and Thompson 1994; Thiewes and Steenken 1997) that the irreversibility of the endothermic transition is a process that lasts for several hours. Therefore, to analyze the T_g correctly, there is a need to run two successive scans and to use the second one for the analysis.

Using the DSC measurements for T_g analysis, we studied the effect of the SME on the T_g of protein-starch extrudates. The results presented in Fig. 3 show that the SME input during extrusion cooking did not affect the T_g . These results do not support previous studies, which reported a decrease in T_g with an increase in SME (Kaletunc and Breslauer 1993, 1996; Barrett and Kaletunc 1998). The explanation given by these authors for the decrease in T_g is based on earlier studies showing that fragmentation for starch occurred during extrusion and this process was more extensive the higher the SME (Davidson 1984; Gomez and Aguilera 1984, 1983; Wen et al 1990). Because there is a correlation between molecular weight and

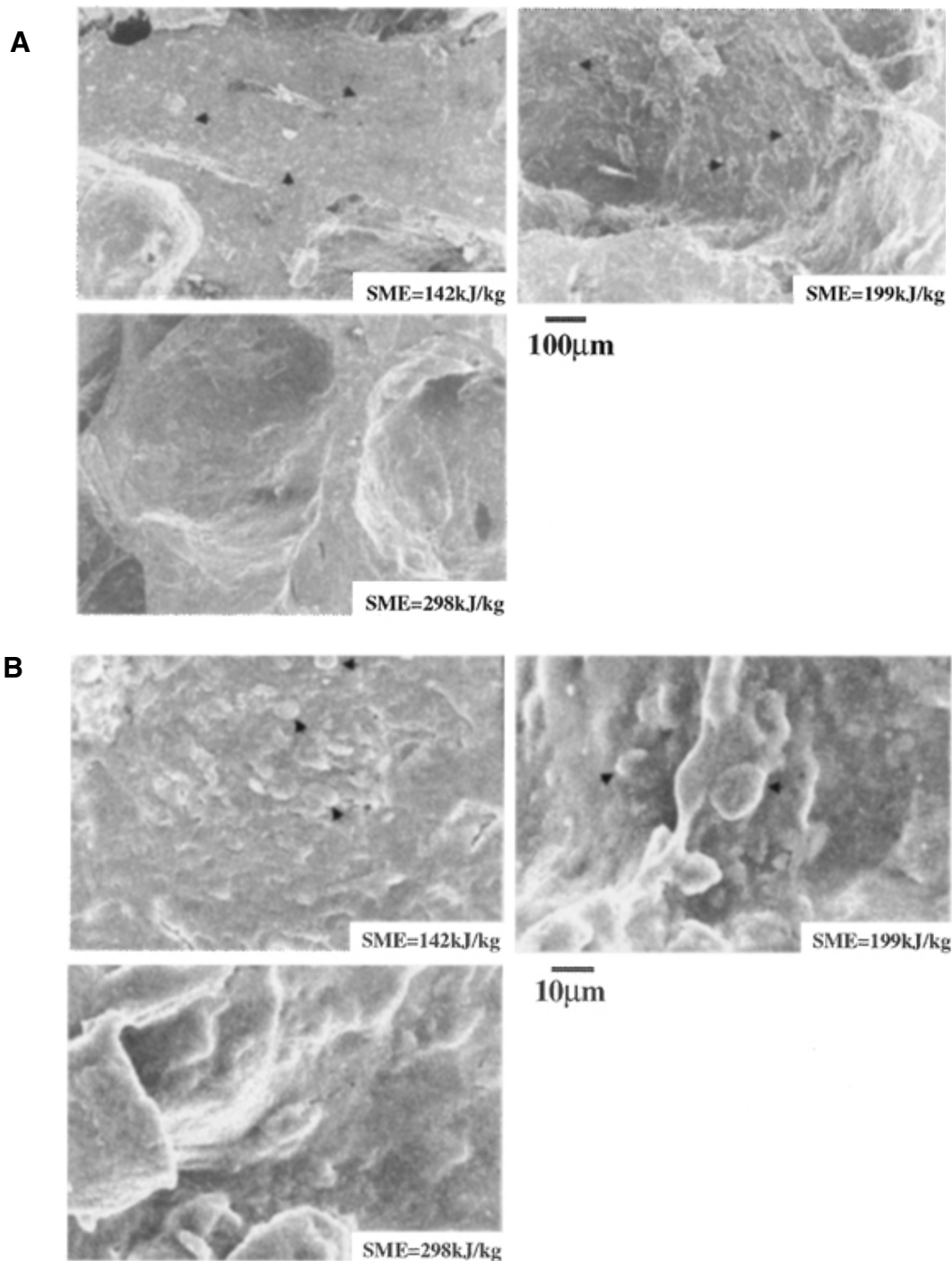


Fig. 6. Scanning electron microscopy at 10 μm (A) and 100 μm (B) of extrudates at different specific mechanical energy (SME) levels.

T_g (Slade and Levine 1988; Finegold et al 1989; Orford et al 1990), a correlation was expected between the SME and T_g .

One reason for the different result could be the compositional differences between the formulation used in our study and the cereal flours used by Kaletunc and Breslauer (1993, 1996) and Barrett and Kaletunc (1998). Higher moisture, fat, and protein content in our formulation might be a cause for less fragmentation as compared with the earlier studies.

Another possible explanation could be the relationship between T_g and molecular weight. To explore this hypothesis, we checked the effect of the molecular weight of glucose polymers (dextran) and its dimer (maltose) on their T_g (Figs. 4 and 5). Dextran, like starch, is composed of glucose units; however, its backbone contains mostly α -1:6 bonds (Linden and Lorient 1999), unlike starch that contains mostly α -1:4. We chose to use dextran instead of starch

because dextran offers a range of molecular weights and serves as a good model to study the effect of molecular weight on T_g for a glucose polymer system. At low molecular weights, we found a large increase in T_g with the increase in molecular weight. This effect reached a plateau at the molecular weight of 67,300 at T_g 92°C for $a_w = 0.326$, indicating that there was a threshold value of molecular weight above which there was no effect on T_g .

This finding is in agreement with Boyer (1974) and Kumler et al (1977), who plotted T_g versus molecular weight of polystyrene according to the equation (Fox and Flory 1950):

$$T_g = T_g(\infty) - K_g/MW \quad (2)$$

where $T_g(\infty)$ was the glass transition of limiting molecular weight and K_g is a constant representing the limiting molecular weight and has units of $(\text{g/mol}) \times (^\circ\text{C})$. They found that three intersecting

straight-line regions could explain the T_g versus MW relationship with each region exhibiting a different value of K_g . The slope of the higher molecular weight region represented a plateau region. Cowie (1975), who found it applicable to a wide variety of synthetic polymers, expanded this theory to other polymers. For food applications, Roos and Karel (1991) reported a K_g value of 52,800 (g/mol) \times ($^{\circ}$ C) for maltodextrins, over the low molecular weight region (<3,000). However, they did not report effects of higher molecular weights.

Wen et al (1990) characterized the molecular size distribution of starch as a function of the extrusion conditions that caused fragmentation of starch during extrusion by using gel filtration chromatography. They found that the main fraction of starch that underwent fragmentation was amylopectin. The fragments were eluted in the chromatography before amylose, which showed a molecular weight higher than that of amylose (50,000–200,000 MW) (Fennema 1985). These results are in accordance with a previous study of Davidson et al (1984), who found that molecules break down mainly at the α -1:6 bonds of the amylopectin, so the fragments could not be too small.

Because fragmentation of the starch molecules leads to macromolecules of $>5 \times 10^4$ to 10^5 MW (Fennema 1985; Van Lengerich 1990; Politz et al 1994), and because our results showed that the limiting molecular weight affecting the T_g was 10,500–67,300, one should not expect to find effects of SME on T_g of starch.

SME Effect on Starch Gelatinization

We also studied the effect of the SME on the microstructure and the starch gelatinization in the extrudates (Fig. 6). Starch gelatinization is strongly affected by SME during extrusion. The higher the SME (142–298 kJ/kg), the higher the degree of gelatinization during extrusion. Starch granules were as small as few micrometers at SME 142 kJ/kg; they became more swollen at SME 199 kJ/kg; and at SME 299 kJ/kg, the gelatinization process looked complete. These results are in concordance with those of Gomez and Aguilera (1983, 1984), who studied the gelatinization of corn starch. Clearly SME plays an important role in starch gelatinization, and mechanical energy catalyzes the gelatinization reaction by rupturing intermolecular hydrogen bonds. This result has been observed by many authors (Wang et al 1992) and is consistent with earlier reports.

CONCLUSIONS

Extrusion SME input did not affect the T_g of mixed protein-starch extruded products in this study despite previous studies reporting decreased T_g due to starch fragmentation. In dextran systems with MW above 67,300, there was no effect of a_w on T_g . Other authors demonstrated that starch fragmentation during extrusion generates fragments of $>5 \times 10^4$ to 10^5 MW and we found that the limiting molecular weight affecting T_g was 1×10^4 to 6.7×10^4 , so one should expect no effects of extrusion on the T_g of starch matrices. The detectable effect of SME on the gelatinization of starch was probably due to the disruption of intermolecular hydrogen bonds by mechanical forces, which catalyzed the gelatinization process, a fact reported by many authors.

LITERATURE CITED

Appelqvist, I. A. M., Cooke, D., Gidley, J., and Lane, S. J. 1993. Thermal properties of polysaccharides at low moisture. 1. An endothermic melting process and water-carbohydrate interactions. *Carbohydr. Polym.* 20:291-299.

Barrett, A. H., and Kaletunc, G. 1998. Quantitative description of fracturability changes in puffed corn extrudates affected by sorption of low levels of moisture. *Cereal Chem.* 75:695-698.

Berens, A., and Hodge, I. M. 1982. Effects of annealing and prior history on enthalpy relaxation in glassy polymers. 1. Experimental study on (poly)vinyl chloride. *Macromolecules* 15:756-761.

Boyer, R. F. 1974. Variation of polymer glass temperatures with molecular weight. *Macromolecules* 7:142-143

Cowie, J. M. G. 1975. Some general features of T_g -MW relations for oligomers and amorphous polymers. *Eur. Polym. J.* 9:297-300.

Davidson, V. J., Paton, D., Diosady, L. L., and Larocque, G. 1984. A model for mechanical degradation of wheat starch in a single screw extruder. *J. Food Sci.* 49:453.

Fennema, O. 1996. *Food Chemistry*. Pages 191-204. Marcel Dekker: New York.

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. I* 85:2945-2951.

di Gioia, L., Cuq, B., and Guilbert, S. 1997. Effect of hydrophilic plasticizers on thermomechanical properties of corn gluten meal. *Cereal Chem.* 75:514-519.

Gomez, M. H., and Aguilera, J. M. 1983. Change in the starch fraction during extrusion-cooking of corn. *J. Food Sci.* 48:378-381.

Gomez, M. H., and Aguilera, J. M. 1984. A physicochemical model for extrusion of corn starch. *J. Food Sci.* 49:40-43.

Kaletunc, G., and Breslauer, K. J. 1993. Glass transitions of extrudates: Relationship with processing-induced fragmentation and end-product attributes. *Cereal Chem.* 70:548-552.

Kaletunc, G., and Breslauer, K. J. 1996. Construction of a water-flour state diagram. Application to extrusion processing. *J. Therm. Anal.* 47:1267-1288.

Kalichevsky, M. T., Jaroszkiewicz, E. M., Ablett, S., Blanshard, J. M. V., and Lillford, P. J. 1992. The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydr. Polym.* 18:77-88.

Kumler, P., Keinath, S. E., and Boyer, R. F. 1977. ESR studies of polymer transitions. III. Effect of molecular weight and molecular weight distribution on T_g values of polystyrene as determined by ESR spin-probe studies. *J. Macromol. Sci.-Phys.* B13(4):631-646.

Noel, T. R., Ring, S. G., and Whittam, M. A. 1993. Relaxations in supercooled carbohydrate liquids. In: *The Glassy State in Foods*. J. M. V. Blanshard and P. J. Lillford, eds. Nottingham University Press: Nottingham, UK.

Orford, P. D., Parker, R., and Ring, S. G. 1990. Aspects of the glass transition behavior of mixture of carbohydrates of low molecular weight. *Carbohydr. Res.* 196:11-18.

Politz, M. L., Timpa, J. D., White, A. R., and Wasserman, B. P. 1994. Non-aqueous gel permeation chromatography of wheat starch in dimethylacetamide (DMAC) and LiCl: Extrusion-induced fragmentation. *Carbohydr. Polym.* 24:91-99

Roos, Y., and Karel, M. 1991. Water and molecular weight effects on glass transition in amorphous carbohydrates and carbohydrate solutions. *J. Food Sci.* 56:1676-1681.

Shogren, R. L. 1992. Effect of moisture content on the melting and subsequent physical aging of cornstarch. *Carbohydr. Polym.* 19:83-90.

Slade, L., and Levine, H. 1988. Non-equilibrium behavior of small carbohydrate of small carbohydrate-water systems. *Pure Appl. Chem.* 60:1841-1864.

Thiewes, H. J., and Steeneken, P. A. M. 1997. The glass transition and the sub- T_g endotherm of amorphous and native potato starch at low moisture content. *Carbohydr. Polym.* 32:123-130.

Van Lengerich, B. 1990. Influence of extrusion processing on in-line rheological behavior, structure and function of wheat starch. In: *Dough Rheology and Baked Product Texture*. H. Faridi and J. M. Faubion, eds. Van Nostrand Reinhold: New York.

Wang, S. S., Chiang, W. C., Zheng, X., Zhao, B., Yeh, A. I., and Cho, M. H. 1992. Application of an energy equivalent concept to study the kinetics of starch conversion during extrusion. Page 165 in: *Food Extrusion Science and Technology*. J. L. Kokini, ed. CHIPS Books: Kingwood, TX.

Wen, L. F., Rodis, P., and Wasserman, B. P. 1990. Starch fragmentation and protein insolubilization during twin-screw extrusion of corn meal. *Cereal Chem.* 67:268.

Yuan, R. C., and Thompson, D. T. 1994. Sub- T_g thermal properties of amorphous waxy starch and its derivatives. *Carbohydr. Polym.* 25:1-6.