

# The Glass Transition in Starch<sup>1</sup>

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## ABSTRACT

Cereal Chem. 64(2):121-124

An investigation of the glass transition temperature ( $T_g$ ) of wheat starch revealed that  $T_g$  was extremely sensitive to the percentage of moisture present. It was possible to detect the  $T_g$  by differential scanning calorimetry only within a narrow moisture range (13–22%). The glass transition occurred below room temperature at moisture contents greater than 22%, and the transition was broad and ill-defined below 13% moisture. This may

indicate that inter- and intrachain hydrogen-bonding is facilitated as water is lost from amorphous regions of starch. A comparison of granular and pregelatinized starches showed that a higher degree of crystallinity elevated  $T_g$  and enhanced the system's sensitivity to moisture. These findings are consistent with reports for synthetic semicrystalline polymers and contradict the suggestion that  $T_g$  immediately precedes melting in starch.

Starch is a semicrystalline polymer. It is composed of highly branched amylopectin molecules, the partially crystalline component, and nearly linear amylose molecules that are apparently amorphous in the granule. It is generally believed that the crystalline regions in a starch granule are interspersed in a continuous amorphous or gel phase (Banks and Greenwood 1975, French 1984). A perfectly crystalline polymer melts at a defined temperature. Discontinuous changes in volume and enthalpy, primary thermodynamic variables, accompany melting. Thus, melting is a first-order transition. In an amorphous polymer at lower temperatures, the molecular motion of the polymer chains is "frozen" in a random conformation, rendering it glassy and immobile. When thermal energy is applied, molecular motion is initiated and the molecules have sufficient energy to slide past one another (Levine 1983). At this point, the polymer becomes viscous, rubbery, and flexible. This physical change reflects the increase in segmental motion of major (20–50 carbons) segments of the polymer backbone and is called the glass transition. At the glass transition there is a discontinuous change in heat capacity (the first derivative of the enthalpy with respect to temperature) and in the thermal expansion coefficient (rate of change in volume with respect to temperature). Although the glass transition is associated with the changes in these second-order variables, it is considered to be a kinetic phenomenon (Eisenberg 1984). Starch, a semicrystalline polymer, should exhibit both transitions. The first-order transition of starch crystallites is well documented (Stevens and Elton 1971, Donovan 1979), but a glass transition of the amorphous regions has not.

Although polymer chemists have not yet achieved a thorough understanding of the theory of the glass transition, there is much known about the parameters that influence it. In general, these parameters alter the rigidity of the polymer backbone, which, in turn, alters the glass transition temperature ( $T_g$ ). This occurs when the molecular motion of the polymer, which defines its  $T_g$ , is hindered by cohesive forces along the chain and between chains. Stiffer chains require higher temperatures to achieve the level of molecular motion necessary for the glass transition. Researchers have found that the presence of bulky sidegroups or cross-links between chains will decrease chain mobility and increase  $T_g$ , whereas flexible sidegroups decrease  $T_g$  (Armeniades and Baer 1977). It is also known that water and other low molecular weight solvents exert a plasticizing effect on many polymers and depress the  $T_g$  (Fuzek 1980). The presence of crystallites suppresses the change in specific heat ( $C_p$ ) at  $T_g$ , and increases the  $T_g$  by interaction at the amorphous-crystalline interface (O'Reilly et al 1964, Buchanan and Walters 1977). It is thought that crystalline regions act as physical cross-links that add rigidity to the

amorphous region and have an effect similar to that of chemical cross-links (Jin et al 1984). Ten Brinke et al (1983) reported that the large  $T_g$  depression by a small amount of diluents is greatly enhanced in a cross-linked system. They saw a pronounced widening of the glass transition region in cross-linked polymers, with changes in  $C_p$  becoming "vanishingly small." The effect of cross-linking was to reduce the number of chain units that could be thermally activated and, thus, contribute to the change in  $C_p$ . All of these factors influence  $T_g$  by altering molecular geometry, flexibility, or polymer interchain forces. Most of this work was conducted on synthetic polymers but should be applicable to a biopolymer such as starch. If a glass transition occurs in starch, it should exhibit a response to factors such as degree of crystallinity and diluent concentration.

The principles of glass transitions and their application to starch have recently been investigated. Maurice and co-workers (1985) examined waxy maize starch by thermomechanical analysis and differential scanning calorimetry (DSC) and reported a change in the coefficient of thermal expansion and in the temperature of the thermal transitions observed by DSC. They concluded that a glass transition occurs just prior to melting and that water acts as a plasticizer and lowers both thermal transitions. Biliaderis and co-workers (1986) recently reported similar evidence for a glass transition in rice starch. The goal of this study was to examine wheat starch by DSC for the occurrence of a glass transition and to characterize the influence of crystallinity and water on  $T_g$ .

## MATERIALS AND METHODS

The native and commercially pregelatinized (drum-dried) wheat starches used in this study were from Midwest Solvents, Atchison, KS. Waxy corn starch was obtained from National Starch (no. 132/26), and normal corn starch was from Sigma (lot 84F-0202, no. S-4126). They were heated in a differential scanning calorimeter (Perkin-Elmer DSC-2, FTS Systems Flexicooler with temperature controller) to detect the incremental change in  $C_p$  associated with the glass transition. The instrument was calibrated with indium. Samples were typically heated at 10°C/min from 2 to 127°C at a sensitivity of 0.5 mcal/sec, but certain samples were heated to as high as 152°C. After the first heating, the samples were immediately cooled at 20°C/min and rescanned within the same range. The temperature of the glass transition was taken from the second scan of each sample by measuring the midpoint of the shift in  $C_p$  (Fig. 1). The standard deviation of determining  $T_g$  values was 1.84°C.

### Preparation of Native Starch Samples

Wheat starch samples were prepared with a range of moisture contents from approximately 13 to 30%. Starch (5.0 ± 0.1 mg) was weighed into a tared, aluminum DSC sample pan. Distilled water was added with a microsyringe until all the granules were wetted and uniformly distributed across the bottom of the pan. The pan containing the known weight of starch plus water was placed on the weighing platform of a Cahn-21 electrobalance. The water was

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allowed to evaporate until the total weight of the system reached the weight calculated to give the desired moisture content. The percent moisture in the stock starch had been determined previously (AACC 1983, Method 44-15A). The dry weight (mg) of each starch sample could then be calculated. Given the dry weight, the total weight of starch plus water necessary to obtain the desired moisture (wet basis) in the final sample was calculated. When the starch/water mixture approached the desired weight, the pan was hermetically sealed and reweighed to determine the final weight. The actual moisture content could then be calculated. Samples were held at 25°C for at least 2 hr before scanning in the DSC. The other granular starches used in this study, waxy corn and normal corn starch, were prepared in a similar manner.

### Preparation of Pregelatinized Starch Samples

A moisture series of commercially pregelatinized wheat starch was prepared differently from the granular starches because of the difficulty in adding water directly to pregelatinized starch. A 5.0 ( $\pm 0.1$ ) mg sample of starch, of known moisture, was weighed into an aluminum DSC pan. The weights of the pan and lid were also known. The sample pan and lid were placed on the sample pan carrier of the hermetic sealing assembly, and the carrier was transferred to a small, sealed chamber where the sample was hydrated over water. The holding time depended upon the desired moisture level. Upon removal from the chamber, the lid was applied to diminish moisture loss, and the pan was quickly sealed and reweighed. The final sample moisture was determined as described above. The sealed samples were held overnight to allow moisture equilibration throughout the starch, then heated in the DSC.

## RESULTS AND DISCUSSION

When starch is heated in excess water (>67%) there is a sharp endothermic transition representing the melting of the starch crystallites. Concurrent with melting is an increase in heat capacity, which has sometimes been construed as evidence of a glass transition. However,  $T_g$  is a reversible event, and, therefore, a

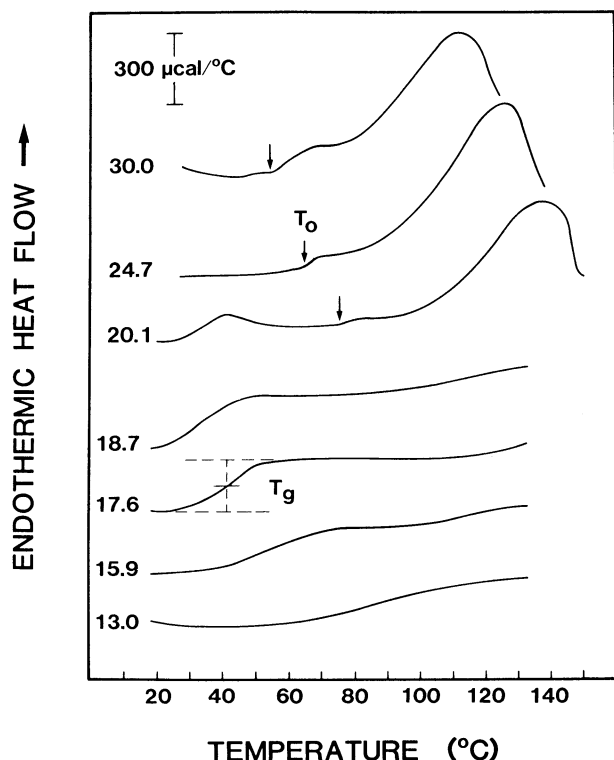


Fig. 1. Differential scanning calorimetry thermograms of native wheat starch at various water contents. The arrow indicates the onset temperature ( $T_o$ ) of gelatinization at 30.0, 24.7, and 20.1% moisture. The glass transition ( $T_g$ ) is shown in samples at 20.1, 18.7, 17.6, 15.9, and 13.0% moisture.

glassy polymer can be heated, cooled below its glass point, and exhibit a glass transition during a second heating also. Yost and Hosney (1986) pointed out that when gelatinized starch is cooled and rescanned in the DSC there is no discontinuous change in heat capacity. Therefore, the increase in heat capacity observed during gelatinization does not represent the classic glass transition. Rather, it merely indicates that the heat capacity of a starch/water suspension is lower than that of gelatinized starch.

It is generally accepted that in partially crystalline polymers softening of the amorphous phase must precede the onset of melting ( $T_o$ ) of the crystalline regions. The rule of thumb regarding the two transitions is as follows:  $0.5 < T_g/T_o < 0.67$  (O'Reilly et al 1964). Therefore, it would be atypical to find that  $T_g$  in starch immediately precedes the melting of the crystallites, as has been suggested (Maurice et al 1985).

Maurice et al (1985) pointed out that water acts as a plasticizer in the starch/water system by depressing thermal transitions. Evans and Haisman (1982) found that, in potato starch, the onset of crystallite melting was depressed by water up to levels of about 37%. Above that level,  $T_o$  was constant. This was explained by the fact that starch granules in cold water will only absorb about 35% water. At that moisture level, water has exerted its maximum plasticizing effect on  $T_o$  because the water content of the granule cannot increase. Additional water forms a separate phase, outside the granule. When we heated low-moisture starch dispersions (20, 25, 30%) in the DSC, the decrease in the  $T_o$  of gelatinization was proportional to the increase in moisture content (Fig. 1). In the starch containing 20% moisture, two thermal events were observed. The onset of melting occurred at about 80°C, and a shift in heat capacity at about 30°C, an apparent glass transition. As plasticizer concentration was increased to 25 and 30%,  $T_o$  was depressed. Presumably, the decrease in  $T_o$  was accompanied by a corresponding decrease in  $T_g$ . At those higher moisture levels, however,  $T_g$  would occur below room temperature and, therefore, could not be detected by this method.

According to polymer literature, as moisture content is decreased, there is a concomitant increase in  $T_g$ . In the series of starch samples with moisture contents ranging from 12 to 24%, a clear shift in heat capacity occurred in samples within the 13 to 22% moisture range (Fig. 1). There was a progressive increase in the glass transition temperature with decreasing moisture levels, giving a typical  $T_g$  versus moisture curve (Fig. 2). At moisture levels greater than 22%,  $T_g$  occurred below room temperature. These findings clearly indicate that a glass transition occurs in starch.

Evidence from semicrystalline synthetic polymers shows that as the degree of crystallinity increases, the  $T_g$  also increases (Jin et al 1984). Conversely, as the ratio of amorphous to crystalline regions increases,  $T_g$  should decrease. We investigated the glass transition of commercially pregelatinized wheat starch, a noncrystalline entity, and compared it to native wheat starch. The pregelatinized

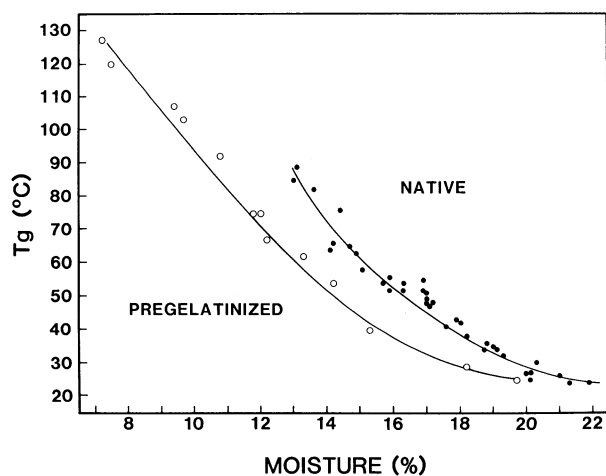


Fig. 2. Plot of the response of the glass transition temperature ( $T_g$ ) to sample moisture in native and pregelatinized wheat starch.

starch at moisture contents ranging from 7 to 20% was scanned in the DSC to determine  $T_g$ . When  $T_g$  was plotted against percent moisture the resulting curve for native starch was somewhat higher (Fig. 2). Both curves appeared to become asymptotic at room temperature. The difference in  $T_g$  apparently reflects the relative difference in degree of crystallinity between the two starches. The pregelatinized starch was noncrystalline (no DSC peak), whereas native starch is 15 to 35% crystalline material (Banks and Greenwood 1975). The results for starch are consistent with what has been observed with synthetic polymers, i.e., that  $T_g$  is elevated by increasing crystallinity.

The persistence of a well-defined glass transition at low moisture levels in the pregelatinized starch may also be indicative of its noncrystalline nature. In this starch,  $T_g$  was detected in samples of 7% moisture and above. Below 7%, the aluminum sample pans failed because of the pressure generated by heating to the high temperatures needed to attain  $T_g$ . In contrast, in the native starch with less than 13% moisture, the change in heat capacity was both too gradual and too small to determine  $T_g$ . The trend toward widening of the glass transition region as plasticizer level is decreased has been interpreted as an effect of cross-linking in a diluent/polymer system (ten Brinke et al 1983). The loss of water from the amorphous regions may lead to the formation of interchain and intrachain hydrogen-bonding (French 1984). These bonds would restrict chain mobility and, thus, elevate  $T_g$ . In starch, crystalline regions are probably interspersed throughout the amorphous regions. In effect, the crystalline areas act as physical cross-links in the polymer network. The crystallites are not involved in the glass transition except to the extent that they act as tie points that restrict the movement of the polymer backbone. Therefore, in polymers with a higher degree of crystallinity, there is more restriction of segmental motion, resulting in increased  $T_g$ . This is similar to the effect of diminished moisture. Moreover, as was observed in the comparison of native and pregelatinized starch, the effect of decreased moisture is enhanced in a more highly crystalline system.

The observed relationship between crystallinity and  $T_g$  supports the conclusions of ten Brinke et al (1983). It is also consistent with the data obtained from normal and waxy corn starches. The latter, a more crystalline entity (Abbott et al 1986), as evidenced by a larger enthalpy ( $\Delta H = 4.00$  cal/g), exhibited a  $T_g$  that exceeded by 5°C that of normal corn starch ( $\Delta H = 2.96$  cal/g) at equal moistures.

Clearly, starch undergoes a glass transition at a temperature considerably lower than the onset of melting. These findings contradict the recent reports of Maurice and co-workers (1985) and Biliaderis and co-workers (1986). The latter followed the thermal events in rice starch over a wide moisture range (0–90%) and reported that the  $T_g$  occurs just prior to crystallite melting. They maintained that at water contents lower than 30%  $T_g$  showed a monotonic increase, but above 30%,  $T_g$  remained constant. However, the  $T_o$  exhibits the same response at moisture levels less than 30%. The authors did not report  $T_o$  values for the moisture series, but it appears that they have equated  $T_o$  and  $T_g$ . In view of our data, it is likely that the increase in heat capacity they observed is associated with granule swelling and the initiation of crystallite melting, and not with a glass transition. Starch/water mixtures do exhibit an increase in heat capacity during gelatinization, but it is not associated with  $T_g$ . At appropriate moisture levels (13–22%), starch exhibits a classic reversible glass transition in the DSC. In addition,  $T_g$  decreases with increasing moisture content and in samples of lower crystallinity. The starch  $T_g$  also exhibits the stress-relief peak often associated with glass transitions. It is interesting to note that whereas Biliaderis et al (1986) reported results over a wide moisture range, they showed no data points between 10 and 20% moisture, precisely the region where it is possible to detect  $T_g$  by DSC.

According to polymer literature, there is typically a wide difference between  $T_g$  and  $T_o$  for any given semicrystalline polymer. It is also well known that such polymers can be annealed. The annealing of crystals occurs in the temperature interval between  $T_g$  and  $T_o$ . Several researchers have documented that

annealing of crystallites occurs in starch (Gough and Pybus 1971, Yost and Hosney 1986). Yost and Hosney (1986) found that the initiation of annealing in wheat starch occurs between 42 and 47°C, well below the normally reported  $T_o$  values. They pointed out that because annealing can only occur after  $T_g$  has been exceeded and the amorphous regions have become mobile, it is highly unlikely that annealing could occur if  $T_g$  immediately preceded  $T_o$ .

Biliaderis and co-workers (1986) used thermomechanical analysis (TMA) to further support their contention that  $T_g$  occurs just prior to crystallite melting. They attributed the initial sharp volume increase to the glass transition. It is well known that the volume versus temperature curve changes as material goes through a glass transition. However, it is also well known that there is a discontinuous change in volume as crystals melt. Their TMA and DSC curves infer that they have interpreted  $T_o$  and  $T_g$  to be coincident. Our data on  $T_g$  clearly refute this. Therefore, it appears that the first abrupt expansion seen by TMA must be the discontinuous volume change typical of crystallite melting. The volume change resulting from swelling of the amorphous regions at  $T_g$  has already occurred.

After this initial increase in volume, there is an intermediate volume expansion plateau, followed by another sharp increase in volume at about 100°C. The second increase appears to coincide with the melting of the amylose-lipid complex, rather than with the melting of the crystallites as Biliaderis and co-workers (1986) suggest.

In waxy starch the volume expansion began at  $T_o$  and did not plateau but continued to increase rapidly throughout gelatinization. As Biliaderis and co-workers (1986) explained, this supports the theory that amylose plays a stabilizing role in the starch gel structure. It also substantiates the interpretation of the second sharp rise in volume as corresponding to the dissociation of the amylose/lipid complex.

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[Received July 7, 1986. Accepted October 30, 1986.]