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Effect of moisture content on the melting and subsequent physical aging of cornstarch

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Differential scanning calorimetry and dynamic mechanical analysis were used to study low moisture (10–50%) gelatinized cornstarch in order to understand the severe embrittlement on aging often seen in these systems. On aging at 22°C, gelatinized starch having 11–20% moisture (T_g = 112–30°C) developed endothermic differential scanning calorimetry peaks characteristic of enthalpy changes due to structural relaxation. The increase in area (enthalpy) of these peaks with time correlated well with decreases in ultimate elongation as measured by tensile tests of extruded starch-water ribbons. The rates of increase of enthalpy and decrease in elongation with time increased with moisture content. At moisture contents of 25% and above (T_g < 15°C), high temperature endotherms characteristic of the melting of recrystallized amylopectin and amylose appeared. These data indicate that embrittlement of gelatinized starch can occur as a result of free volume relaxation during sub-T_g aging as well as a result of plasticizer (water) loss by evaporation.

INTRODUCTION

There has been much interest recently in developing biodegradable plastic materials based on gelatinized starch (Otey *et al.*, 1987; Stepto & Tomka, 1987; Swanson *et al.*, 1988; Lim & Fujio, 1989; Gould *et al.*, 1990; Roper & Koch, 1990; Wiedmann & Strobel, 1991). The potential advantage of such materials is that they may be disposed of by composting on land or hydrolysis at sea rather than accumulating in landfills and waterways. Biodegradability would be a special asset in single-use items such as food packaging, plastic dinner utensils, trash bags, diapers and planting pots. Use of cornstarch in plastics would also reduce our dependence on synthetic polymers made from imported oil.

Films cast from aqueous solutions of gelatinized starch become hard and brittle on drying (Zobel, 1988). To avoid this problem, starch has been blended or grafted with more flexible synthetic polymers. Even many of these compositions slowly become brittle with aging (Swanson *et al.*, 1988). The question arises whether this embrittlement is due solely to loss of water or, in addition, to structural changes in the starch. The latter could include starch recrystallization (retrogradation), changes in hydrogen bonding or free volume relaxation processes.

Previous studies (Kulp & Ponte, 1981; Miles *et al.*, 1985; Zeleznak & Hoseney, 1986; Russell, 1987; Chinnaswamy *et al.*, 1989) of the gelatinization and aging of starch have usually been conducted at high moisture contents (>20%) since this condition is often encountered in food processing. At moisture contents above 20%, the amylopectin within a starch melt slowly recrystallizes to the B-form (Miles *et al.*, 1985; Ring *et al.*, 1987; Chinnaswamy *et al.*, 1989). This occurs because at moisture levels above 20%, the glass transition temperature (T_g) drops below room temperature, allowing the starch sufficient mobility to rearrange into the crystalline form (Slade & Levine, 1988). The decrease in the T_g of starch with increasing water content has been explained on the basis of free volume theory (Orford *et al.*, 1989). At high moisture contents (>60%), the amylose component of starch rapidly phase-separates from amylopectin and recrystallizes

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into the B-form (Miles *et al.*, 1985). Low moisture, extrusion-cooked starch, however, shows an X-ray pattern reflecting the presence of recrystallized amylose-lipid V-forms immediately after cooling (Mercier *et al.*, 1980; Chinnaswamy *et al.*, 1989).

To our knowledge, no studies of gelatinized starch aging at moisture contents below 20% have been conducted. This moisture regime is of particular interest since starch equilibrated at ambient humidities of 20–80% contains about 8–20% moisture (Wittwer & Tomka, 1987). It is anticipated that some increase in stiffness of gelatinized starch will occur on aging due to free volume relaxation. This process occurs in all amorphous and semi-crystalline polymers below their T_g and reflects the slow decrease in volume of a glass towards its equilibrium value (Bendler, 1985). Such physical aging processes can be identified by characteristic endothermic peaks in differential scanning thermograms (Hodge & Berens, 1982; Hutchinson & Kovacs, 1984).

In the present study, we have encapsulated cornstarch at moisture levels of 11–50% in steel pans, heated them in the differential scanning calorimeter (DSC) until all melting processes have occurred, aged the samples for 3 h to 4 weeks at 22°C and finally rescanned them in the DSC. Samples were also removed from the DSC pans after aging and subjected to CP/MAS C-13 NMR and FTIR to determine whether any changes in starch structure had occurred. Tensile tests and dynamic mechanical analyses were also carried out on extruded starch-water ribbons to correlate changes in the DSC curves with changes in mechanical properties.

EXPERIMENTAL

Materials

Cornstarch was Buffalo 3401 from CPC International Inc. It contained approximately 12% water and had a pH of 6·4 in a 50% aqueous suspension. Defatted cornstarch was prepared by soxhlet extraction with methanol according to the method of Schoch (1945). Waxy maize starch was obtained from National Starch and Chemical. Amylose was isolated from cornstarch by the method of Schoch (1945).

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC7 with dry ice coolant and nitrogen purge gas was used. Melting points and enthalpies for indium and water were used for temperature and heat capacity calibration.

The moisture content (wet basis) of starch was determined by drying in a vacuum oven at 100°C for 2 h. Approximately 30 mg of moist starch was weighed into stainless steel DSC pans (part No. 0319-0218, Perkin Elmer Corp., Norwalk, CT). The moisture content was then raised or lowered to the desired level by placing the open pan in a desiccator containing water or drierite. For high moisture levels (30–50%), water (50% by weight of the starch) was pipetted directly into the pan. Pans were then left to air dry to the desired moisture level. Pans were then sealed and left to equilibrate for 1 day prior to melting in the DSC. Unless otherwise noted, samples were heated from 2°C to 220°C (11–14% moisture), 215°C (16% moisture), 210°C (20% moisture) or 180°C (25–50% moisture) at 10°C/min in the DSC. The upper temperature limit was selected for each moisture content to ensure complete melting of amylopectin and amylose without degradation (see Results). After the initial melting, pans were cooled rapidly in the DSC (~200°C/min), aged at 22°C for 3 h to 28 days and then reheated in the DSC at 10°C/min. Pans were reweighed at the end of the experiment. Very small (0·1 mg) weight losses were noted, indicating little water was lost from the pans during heating in the DSC.

Extrusion of starch-water ribbons

Ribbons containing approximately 14 and 17% moisture were prepared as follows. Cornstarch containing 25% moisture was gelatinized at 170–180°C by two passes through a C.W. Brabender two-zone, single screw extruder equipped with a strand die having 17 holes, 1·6 mm in diameter. The mixing screw was 1·9 cm in diameter, had a 20:1 L/D ratio, a compression ratio of 3:1 and was operated at 60 rpm. The strands of gelatinized starch were extruded into a ribbon by a third and final pass through the extruder with zones 1 and 2 maintained at 145 and 149°C and a 25·4 × 0·51 mm slit die heated to 129°C. The moisture level of the ribbon was determined to be 14% after vacuum drying at 110°C for 6 days. A ribbon containing about 17% moisture was prepared as described above except the initial moisture content of the starch was adjusted to 35% and extrusion temperatures were lowered to 128 and 135°C during the second pass through the spaghetti die, and to 81, 88 and 90°C during extrusion through the slit die. Ribbons were cut into 2 × 0·6 cm pieces with a paper cutter for dynamic mechanical thermal analysis and into 7·5 × 1·25 cm pieces for tensile testing. Samples were aged at 22°C inside zip-lock polyethylene bags to maintain constant moisture levels.

Mechanical testing

A Perkin-Elmer DMA7 operating in the three-point bending mode was used for dynamic mechanical thermal analysis (DMTA). An oscillatory frequency of 1 Hz and a strain amplitude of 0·04% were maintained throughout the experiment. Samples were first cooled

to −150°C then scanned at a rate of 3°C/min to 90°C. Similar results were obtained when samples were cooled to 2°C, indicating that sample freezing and thawing did not influence the results obtained at temperatures above freezing.

An Instron 4201 Universal Testing Machine operated at a grip length of 50·8 cm and a crosshead speed of 5 cm/min was used for tensile testing. All samples were tested in the machine direction.

Analytical methods

CP/MAS C-13 NMR experiments were performed using a Bruker MSL-300 spectrometer. Pulse widths, contact times and delay times were 5 μs, 2 ms and 1 or 5 s, respectively. Samples were spun in zirconia rotors at 3500 Hz. Lipid-free cornstarch (20% moisture) was gelatinized in DSC pans as described above, aged for 28 days at 22°C, removed from the pans, pulverized by shaking with a stainless steel ball in a stainless steel vial cooled with liquid nitrogen and equilibrated to 50% relative humidity over 1 week. A control sample was also prepared as above but without the 28-day aging. FRIR spectra were obtained using a Mattson Polaris spectrometer operating at 4 cm^{-1} resolution. A starch sample (1 mg) and 300 mg of KBr were pulverised together by shaking with two stainless steel balls inside a steel vial and were then pressed into a disc.

RESULTS

Melting and degradation of cornstarch

At the start, it was necessary to determine the temperatures at which starch at various moisture contents would melt. This was necessary for our study since we wanted to observe only those DCS peaks which were due to aging of completely gelatinized starch rather than those peaks which might represent incomplete melting. To our knowledge, such melting data for low moisture cornstarch were not available in the literature. Therefore, DSC studies of cornstarch at low and medium moisture levels were conducted to determine the temperatures at which complete melting occurred.

DSC melting curves for cornstarch at moisture levels of 11–50% are presented in Fig. 1. The assignment of peaks to the melting of amylopectin (peak numbers 1, 2, 4), amylose (5), amylose-lipid complexes (3) and degradation (6) are also indicated in Fig. 1. These assignments were made based on DSC data for waxy maize starch, amylose and defatted cornstarch at similar moisture levels (data not shown). Peak 3 was assigned to melting of amylose-lipid complexes since this peak was not present in defatted cornstarch. Previous studies (Biliaderis *et al.*, 1985; Raphaelides & Karkalas, 1988; Russell, 1987) have shown that amylose-lipid complexes usually melt at temperatures of 90–120°C in the presence of excess water. This is similar to the T_m of 110°C for peak 3 at 50% moisture in Fig. 1. Peak 5 was assigned to amylose melting since this peak was not observed in DSC runs of waxy maize and pure amylose had endothermic peaks at similar temperatures. The area of the amylose melting peaks in Fig. 1 varied greatly with repetitive runs and moisture content. Annealing cornstarch at temperatures below the T_m greatly increased the area of the amylose melting peak, indicating that amylose is poorly crystalline in native granules. Peaks 1, 2 and 4 associated with amylopectin melting have been noted previously (Russell, 1987) in studies of waxy maize. Peak 1 was postulated to be associated with the swelling or gelatinization process where starch double helices are disrupted in the amorphous regions. Peak 2 is due to melting of the amylopectin crystallites while peak 4 may represent melting of well-annealed crystals or possibly a different crystalline form. Curve D in Fig. 4 has what appears to be recrystallization exotherm just prior to peak 4, suggesting that recrystallization may be occurring. Peak 6 was found to reflect chemical degradation since starch heated above this temperature and then recovered from the pans showed carbonyl and other new bands in the FTIR spectra.

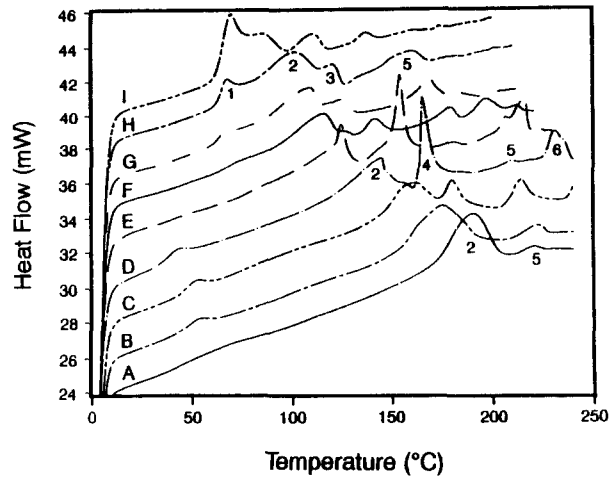


Fig. 1. DSC heating curves for native cornstarch at the following moisture contents: 11·1% (A), 13·8% (B), 16·1% (C), 20·0% (D), 24·9% (E), 29·8% (F), 34·7% (G), 39·6% (H) and 50·2% (I). Peaks are numbered on curves A, D and H to indicate the following melting or degradation processes: amylopectin melting (1,2,4); amylose-lipid complex melting (3); amylose melting (5) and degradation (6).

Peak melting and decomposition temperatures so assigned are plotted in Fig. 2 as functions of moisture content. The melting point depression of starch by water has been successfully fitted (Russell, 1987) by the equation of Flory (1953), although it has been questioned (Biliaderis *et al.*, 1986) whether this equation is applicable, since starch melting at commonly used heating rates is essentially irreversible.

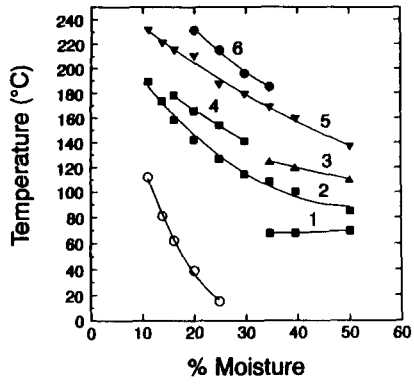


Fig. 2. Plots of peak degradation and melting temperatures for the crystalline components of native cornstarch: degradation, ●; amylose melting, ▼; amylose-lipid complex melting, ▲; amylopectin melting, ■. Plot of the glass transition temperature measured after rapid quenching and immediate reheating of gelatinized cornstarch, ○.

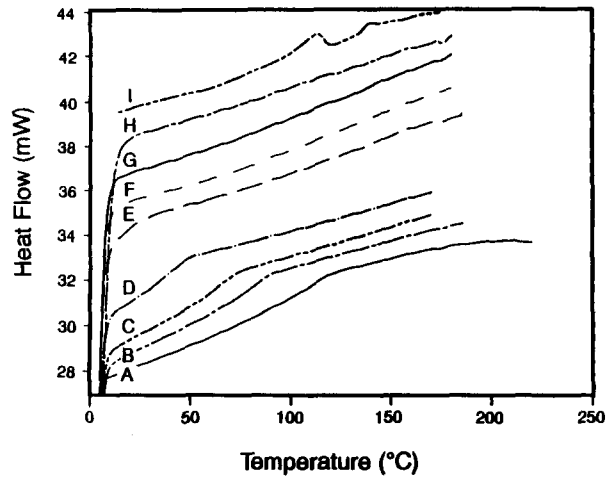


Fig. 3. DSC heating curves of gelatinized lipid-free cornstarch measured immediately after quenching the samples to 2°C. The moisture contents are: 11·1% (A), 13·8% (B), 16·1% (C), 20·0% (D), 25·1% (E), 30·1% (F), 40·1% (G) and 50·4% (H). DSC heating curve for gelatinized cornstarch (with lipids) at 50·4% moisture measured immediately after quenching to 2°C (I).

It was found that cornstarch samples heated above the amylose melting temperature underwent severe degradation. For example, cornstarch at 20% moisture heated to 240°C became black with the consistency of tar and had a large carboxylic acid C=O stretch absorption at 1708 cm^{-1}. The extent of the degradation decreased somewhat as the moisture content decreased. In contrast, methanol-extracted cornstarch heated to 240°C showed no DSC decomposition peak, appeared light brown in color, was solid and showed little change in its FTIR spectrum. Its DSC melting curves were otherwise very similar to native cornstarch. Therefore, it was decided to perform the aging studies on gelatinized methanol-extracted cornstarch. Presumably, unsaturated lipids such as oleic and linoleic, which are native to cornstarch, were oxidized to peroxides at high temperatures. These peroxides could then catalyze decomposition of the polysaccharide components of starch.

Physical aging of gelatinized, methanol-extracted cornstarch

Figure 3 shows DSC curves for methanol-extracted cornstarch which was rapidly cooled to 2°C after melting and then rescanned in the DSC. Step increases in heat capacity due to onset of the glass transition are apparent in samples containing 11–25% moisture. The midpoints of the change in heat capacities are plotted in Fig. 2 as a function of moisture content. Similar changes in T_g with water content have been reported for wheat starch (Zeleznak & Hoseney, 1987). It is interesting to note that no T_g was observed on the initial heating of cornstarch (see Fig. 1), suggesting that most of the polysaccharide is highly ordered. At higher moisture contents (30–50%), T_g drops below the freezing point of water and so a flat DSC trace was obtained. Figure 3 also shows a DSC curve for native cornstarch (with lipids) at 50% moisture which was rapidly cooled to 2°C after melting and then rescanned in the DSC. Melting peaks due to recrystallized amylose-lipid complexes at 111°C and amylose at 137°C are evident. It has been previously demonstrated (Miles *et al.*, 1985) that amylose can recrystallize much more rapidly (min-h) than amylopectin (days). The absence of such peaks in lipid-free cornstarch suggests that lipids may promote the phase separation of amylose from amylopectin.

DSC curves for gelatinized, methanol-extracted cornstarch aged for 1, 7 and 28 days at 22°C and then rescanned in the DSC are shown in Figs 4, 5 and 6, respectively. A new endothermic peak at 36–52°C has appeared in the samples having 20% or less moisture. Values of the maximum temperature (T_{max}) and enthalpy (ΔH) for this new transition have been plotted against log time in Fig. 7. Both T_{max} and ΔH increase linearly with log time. The enthalpy of the new peak also increases with increasing moisture content up to 20% and then disappears completely at higher moisture levels. The disappearance of this endotherm when T_g is less than the aging temperature, T_e (22°C), strongly suggests that the endotherm is due to enthalpy relaxation in the non-equilibrium glassy state. The melting peaks at 60–120°C for samples having 25–50% moisture have been characterized previously (Zeleznak & Hoseney, 1986) and are due to recrystallized amylopectin.

DSC studies of the aging of amylopectin melts for 28 days showed behavior very similar to starch (data not shown). Amylose melts aged for 28 days showed similar DSC curves as aged starch at 11 and 14% moisture but showed large (14 J/g) melting endotherms at higher moisture levels (T_m as in Fig. 2). The absence of this

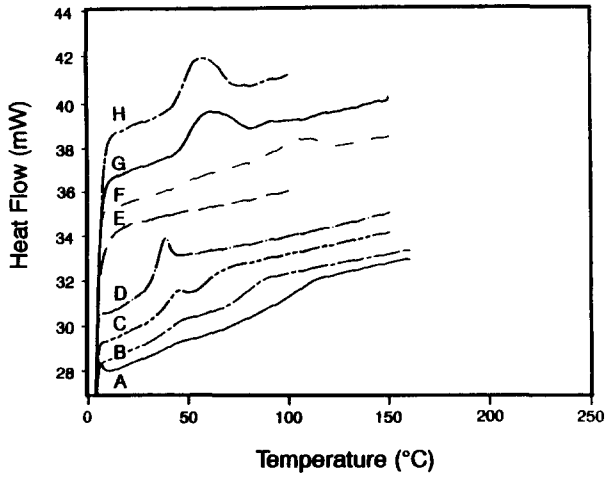


Fig. 4. DSC heating curves of gelatinized lipid-free cornstarch measured after aging for 1 day at 22°C. The moisture contents are as in Fig. 3.

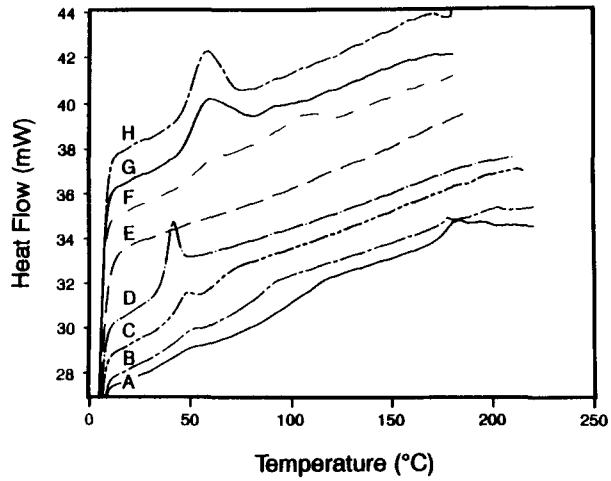


Fig. 5. DSC heating curves of gelatinized lipid-free cornstarch measured after aging for 7 days at 22°C. The moisture contents are as in Fig. 3.

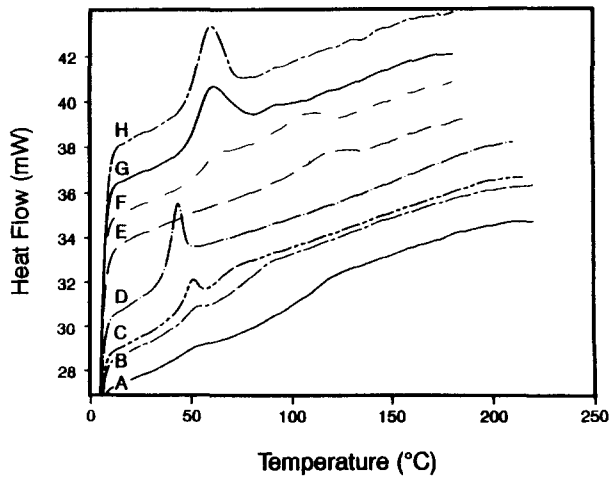
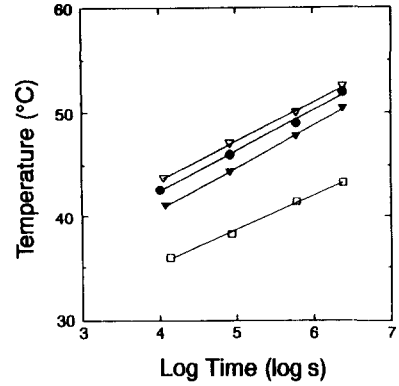


Fig. 6. DSC heating curves of gelatinized lipid-free cornstarch measured after aging for 28 days at 22°C. The moisture contents are as in Fig. 3.



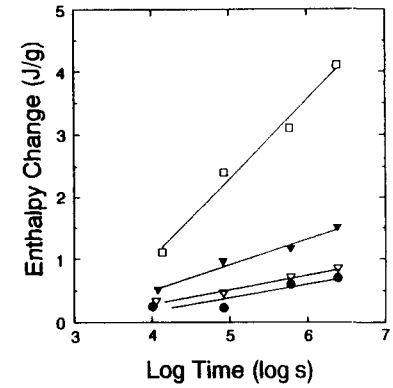


Fig. 7. Dependence of the enthalpy (ΔH) and peak temperature (T_{max}) on time for lipid-free cornstarch at the following moisture contents: 11·1%, ●; 13·8%, ▽; 16·1%, ▼; and 20·0%, □.

amylose melting peak in aged cornstarch melts again suggests that the interaction of amylose with amylopectin prevents amylose recrystallization in cornstarch.

In order to determine if any changes in starch structure or conformation occurred on aging, gelatinized starch which initially contained 20% moisture was examined by CP/MAS C-13 NMR spectroscopy before and after aging for 28 days at 22°C. These spectra, shown in Fig. 8, are nearly identical, suggesting little change in starch structure occurs on aging below the T_g. This supports the hypothesis that the DSC peak which appears on aging is due to free volume relaxation rather than melting of a helix or other highly organized structure. It is interesting to note that the NMR peaks for these rapidly quenched samples are much broader than those obtained for an amorphous amylopectin sample prepared by freeze-drying from solution. This implies that the carbon atoms of the melt-quenched samples have a much wider range of local environments and conformations than are found for more highly relaxed samples prepared by evaporation from aqueous solution.

Plots of dynamic storage modulus, E', and tangent delta versus temperature for freshly made and aged starch ribbons (14% moisture) are shown in Fig. 9. Tan delta, which reflects the energy loss per deformation

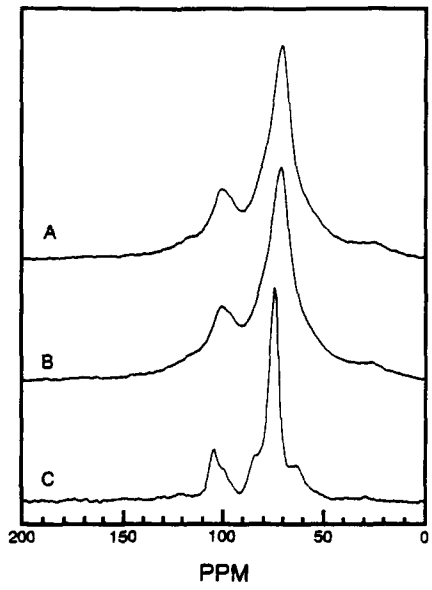


Fig. 8. CP/MAS C-13 NMR spectra of gelatinized lipid-free cornstarch aged for 28 days at 22°C and 20% moisture content (A) and a sample gelatinized as in (A) but without aging (B). A spectrum for a sample of amorphous amylopectin lyophilized from dilute solution is also shown for comparison (C).

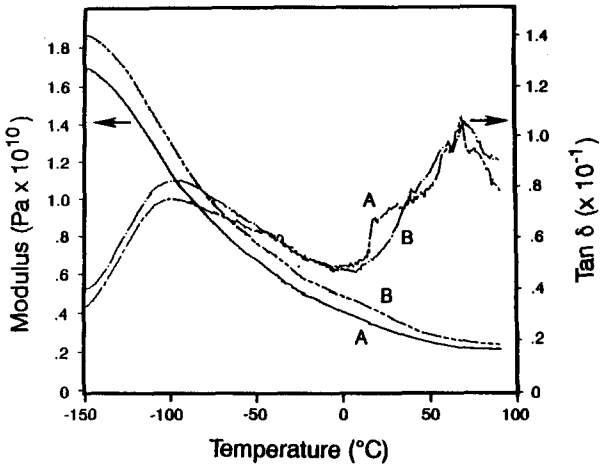


Fig. 9. DMTA curves for samples of extruded starch ribbons (14% moisture) after aging for 1 h (A) and 27 days (B) at 22°C.

cycle, is equal to tan (E''/E') where E'' is the dynamic loss modulus. A maximum in tan delta occurs when $\omega \cdot \tau \sim 1$, where ω = the angular velocity and τ = the relaxation time of the process. E' was slightly larger for the starch ribbon aged for a month than the freshly prepared ribbon, although the difference was close to the experimental error. E' for the aged ribbon also had a slightly more rapid decrease at 40°C. This may represent the same transition to equilibrium amorphous state as observed in the DSC at 40–50°C. The peak in tan delta at −90 to −100°C may reflect the increase in mobility of water in the starch. This is reasonably close to estimates of the glass transition of amorphous water of approximately −140 to −110°C (Orford *et al.*, 1989). As the bound water becomes mobile, motions of the hydroxyl groups of starch would likely begin, thus facilitating the local structural relaxation processes and enthalpy relaxation during sub-T_g aging. Motions of the C-6 hydroxymethyl groups of starch may also be involved (Kohyama *et al.*, 1992). The portion of the DMTA plots much above room temperature are difficult to interpret since moisture is being lost by evaporation.

The effect of time on the modulus, tensile strength, elongation and enthalpy change for extruded starch-water ribbons is shown in Table 1. After 672 h (28 days) of aging at 22°C, the tensile strength and modulus of samples having 14% moisture increased slightly while the elongation decreased from approximately 12 to 7%. Over the same period the relaxed enthalpy increased by 1·1 J/g. At the end of the 28-day period these samples remained quite flexible on bending. At the higher moisture level (17%), the elongation decreased from 12% to only 3% after 7 days while the modulus and tensile strength changed little. The enthalpy increased with time in a manner similar to the data for lipid-free starch in Fig. 7. After 7 days of aging these samples often fractured on bending. Thus the starch ribbons containing the higher moisture level became brittle much more rapidly than those with the lower moisture level. This result correlates well with the more rapid increase in enthalpy with time at the higher moisture level.

Table 1. Effects of moisture content and time on the mechanical properties of extruded cornstarch-water ribbons

Moisture (%)	Time (h)	Young's modulus (MPa)	Tensile strength (N/mm²)	Elongation (%)	N	ΔH (J/g)
14	1	670 ± 210	20·1 ± 4·8	12·3 ± 5·0	3	0
14	672	1090 ± 164	30·1 ± 3·3	7·2 ± 1·0	2	1·1
17	0·5	710 ± 100	17·8 ± 2·6	11·7 ± 7·7	10	0
17	24	790 ± 76	18·9 ± 1·5	4·2 ± 0·5	4	1·1
17	168	830 ± 51	16·7 ± 2·3	3·3 ± 0·7	3	1·5

N is the number of samples tested, ΔH represents the change in enthalpy and the errors represent 1 standard deviation from the mean.

A small (0·4–0·8 J/g) melting peak at 181°C was also measured by DSC for the extruded starch samples. This likely reflects melting of the amylose-lipid complex which recrystallized rapidly during cooling.

DISCUSSION

The development of sub-T_g peaks on aging has been observed for other amorphous and semicrystalline polymers such as poly(vinyl chloride) (PVC) (Illers, 1969; Hodge & Berens, 1981), poly(ethylene terephthalate) (Tant & Wilkes, 1981), poly(acrylonitrile-butadiene-styrene) (Wyzgoski, 1980) and poly(methyl methacrylate)-polystyrene blends (Shultz & Young, 1980). Hodge & Berens (1982) have developed a four parameter kinetic model of the glass transition which accurately reproduces DSC heating curves after sub-T_g aging. The key assumptions of their model are that the relaxation of the polymer can be described by the equation of Williams and Watts (1970)

$$\text{phi}(t) = \exp\left[-(t/\text{tau}_0)^{\text{beta}}\right] \quad (1)$$

where tau_0 is given by the expression of Gardon & Narayanaswamy (1970)

$$\text{tau}_0 = A \exp\left[x\Delta h^*/RT + (1-x)\Delta h^*/RT_f\right] \quad (2)$$

Beta has values of 0 to 1 and is a measure of non-exponentiality. A beta of 1 indicates a single exponential relaxation, while a smaller value reflects a mixture of short and long relaxation times. A and Δh^* are frequency and activation energy parameters which alone determine the T_g. The fictive temperature, T_f, is defined as the temperature at which the measured value of H would be the equilibrium one and for purposes here is equal to H/C_{pl} where C_{pl} is the heat capacity of the polymer above T_g. Thus, $T - T_f$ represents the degree of departure of the glass from equilibrium. The parameter x ($0 < x < 1$) represents the relative dependence of tau_0 on temperature versus polymer non-equilibrium structure (T_f).

Illustrative plots of H or V and $C_p = dH/dT$ for a polymer heated to above T_g, quenched to a temperature T_e below T_g, isothermally aged at T_e and then reheated are shown in Fig. 10. As the polymer is cooled below T_g, relaxation times increase from seconds to hours-years, and thus H and V for the polymer cannot immediately relax to their equilibrium values. As the polymer is isothermally aged at T_e, portions of the polymer having relatively short relaxation times relax, leading to a decrease in V, H and T_f. Presumably these rapidly relaxing components reflect short-range rearrangements in polymer structure. When the polymer is reheated, thermal energy is first reabsorbed as these relaxed structural elements become mobile (giving a peak in C_p) and an additional increase in C_p occurs as the entire polymer molecule becomes mobile (at T_g). The decrease in H on aging can be estimated by measuring the area under the peak in the C_p heating curve.

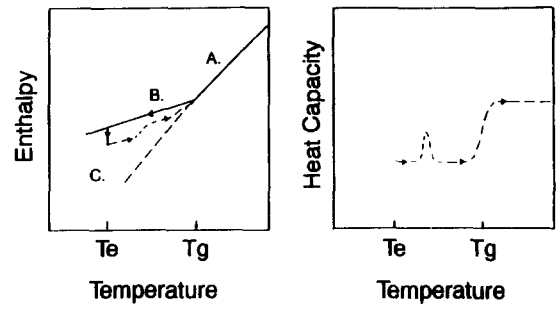


Fig. 10. Schematic drawings of the changes in enthalpy (H) and heat capacity (dH/dT) for a polymer glass after a rapid quench from the melt (A) to a temperature T_e below T_g, isothermal aging at T_e and reheating to above T_g. The initial enthalpy of the glass after quenching to below T_g is given by the line B while the equilibrium enthalpy is given by the dotted line C.

When small values for beta and x (0·1–0·5) are selected, the mathematical model described above (Hodge & Berens, 1982) predicts the trends observed in Fig. 7. These include: (1) the linear increases in ΔH and T_{max} as log time increases; and (2) the increase in ΔH and decrease in T_{max} as $T_g - T_e$ decreases (due to increasing moisture content). To achieve quantitative agreement between theory and experiment would require experimental determination of Δh^* and extensive numerical simulations. It is noted, however, that PVC aged for 6 days at 23°C (Hodge & Berens, 1982) has a DSC curve (T_{max} = 59°C, $C_{p\,max}$ = 0·19, T_g = 90°C) similar to starch at 13·8% moisture aged for 7 days (T_{max} = 50°C, $C_{p\,max}$ = 0·3, T_g = 82°C), where $C_{p\,max}$ is given as a fraction of ΔC_p. The corresponding values of beta, 0·25, and x, 0·11, indicate the presence of both fast and slow relaxation mechanisms and a strong structural dependence of the relaxation rate, respectively. This could reflect some type of local ordering in the moist starch, such as improvements in hydrogen bonding.

The demonstration that enthalpic relaxation processes occur for starch plasticized with water has a number of important implications. When starch-water melts are cooled below T_g, H, V and T_f will slowly decrease, leading to a slow increase in average relaxation time (eqn 2). Such increases in relaxation time cause increases in viscosity, modulus and yield stress and decreases in impact strength and elongation at break. Changes in properties involving large deformations such as yield stress, impact strength and elongation are affected the most (Illers, 1969; Struik, 1985). The rate of aging will increase with moisture content and temperature up to $T_e < T_g$. Therefore, high ambient humidity and hot weather would accelerate this type of aging for

extruded starch having typically 8–15% moisture. For low humidity levels (10–40%), loss of water by evaporation would cause a large increase in T_g and constitute an additional cause of embrittlement. There is obviously a need to measure other mechanical properties, such as impact strength as a function of aging time and moisture level. Controlling the initial moisture level of extruded or molded test specimens is difficult, however. In addition to changes in mechanical properties with aging, decreases in permeability to gases and liquids are predicted and observed due to a decrease in the free volume between polymer molecules (Illers, 1969).

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