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Transitions in frozen gelatinized-starch systems studied by differential scanning calorimetry

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Differential scanning calorimetry (d.s.c.) has been used to study the transitions that occur when gelatinized-starch systems are heated from −20°C to +20°C. The samples contained from 10 to 70% polymer. With gelatinized suspensions containing less than about 30% starch, a glass transition due to plasticization of amorphous polymer was detected at about −5°C. The ice in the specimen melted at about the same temperature as pure ice. In the case of samples of intermediate concentration, containing, say, 45% starch, an exotherm due to crystallization of unfrozen water occurred once the glass-transition temperature had been exceeded. This exotherm only had a significant area when the sample was frozen at a relatively high rate. The melting of the ice in these specimens was characterized by a biphasic endotherm. It was established that, when starch is gelatinized in a d.s.c. pan, water evaporates and can condense on the pan lid. Division of moisture between the sample and the lid was found to be responsible for the twin ice-melting endotherms. Experiments showed that concentrated amorphous polymer caused the melting temperature of the ice in the specimen to decrease below that of pure ice, whereas the crystalline domains had less effect. When the concentration of gelatinized polymer was increased still further, for example, to 70%, polysaccharide–water interactions inhibited freezing, and no transitions were detected in the d.s.c. trace.

INTRODUCTION

Although many differential scanning calorimetry (d.s.c.) studies of aqueous starch systems have been made in the gelatinization region (Blanshard, 1987; Biliaderis, 1990), the technique has been little used to investigate these materials at lower temperatures. However, some other frozen aqueous biopolymer systems have been studied by d.s.c., and the traces so obtained have been reviewed in detail (Guegov, 1981). Various transitions have been identified. As the temperature is raised from, say, −100°C, a glass transition is usually the first to be detected (Luyet & Rasmussen, 1968; Rasmussen & Luyet, 1969). Once the amorphous material has undergone this transition, devitrification may be the next event to take place. Devitrification entails crystallization and results in an exothermic peak. The phenomenon is only apparent when rapid-cooling regimes are employed (MacKenzie, 1981). Other features, such as 'antemelting' and 'incipient' melting, may take place before the final transition, which is due to melting of the water component, is reached (MacKenzie, 1977). In the presence of some polymer structures, the melting of water may give rise to two or more peaks (Taniguchi & Horigome, 1975; Ahad, 1978; Radosta & Schierbaum, 1990).

The objective of the present study is to probe transitions occurring in frozen starch–water systems. These transitions are both of practical importance to the frozen-foods industry and of intrinsic scientific interest. In addition, since sub-freezing profiles reflect polymer–polymer and polymer–water interactions, they may provide further insight into events taking place during gelatinization.

MATERIALS AND METHODS

Starch was isolated from rice, wheat, and maize as described previously (Liu *et al.*, 1991). D.s.c. measurements were made by using a Perkin-Elmer d.s.c.-2C

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calorimeter equipped with a thermal-analysis data station in accordance with the procedure given in detail elsewhere (Liu *et al.*, 1991). The instrument was calibrated so that the onset of melting of pure ice occurred at 0°C. The d.s.c. pans were stainless-steel capsules, fitted with a rubber-seal O-ring, which can withstand pressure and suppress the evaporation of water. To prepare samples, the required amount of starch (on a dry-weight basis) was weighed into the pans. Sufficient water was added by a syringe to wet all the granules. Excess water was removed by evaporation, and when the desired weight was obtained, the pans were sealed hermetically. All the suspensions were left at room temperature to equilibrate for at least one hour before d.s.c. measurements were made. An empty pan was used as an inert reference to balance the heat capacity of the sample pan. Samples of gelatinized starch were prepared by heating suspensions from ambient temperature to 145°C at a rate of 10°C min^{-1}. Once the maximum temperature had been reached, the samples were immediately cooled at a rate of 320°C min^{-1} to −20°C. The resultant frozen systems were then heated at a rate of 2°C min^{-1} to about 20°C.

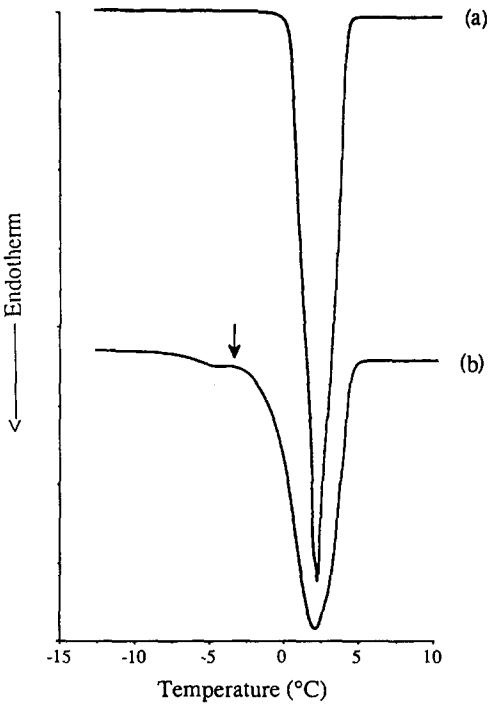

Fig. 1. D.s.c. traces obtained on heating pure ice, curve (a), and a frozen gelatinized-rice-starch system containing 30% (w/w) polymer, curve (b). Traces are normalized to 1 mg of water. Heat-flow axis 750 $\mu J\ s^{-1}$ per division. The arrow marks the temperature used for rescan experiments.

RESULTS AND DISCUSSION

Figure 1(a) gives the melting trace for pure ice. Figure 1(b) shows that the d.s.c. profile obtained on heating a frozen sample of gelatinized 30% starch has a minor baseline shift at the leading edge of a single major endothermic peak. Such a baseline shift is not present in ungelatinized starch suspensions of the same concentration (data not shown). Similar results were found with more dilute samples and with all the starch varieties investigated. As expected, the peak due to melting of ice in the starch system is at the same temperature as, but is of smaller area and is broader than, that for pure water. This is because freezing of some of the water is inhibited by interactions with the polymer (Derbyshire & Duff, 1973).

The minor baseline shift that precedes the endotherm shown in Fig. 1(b) has been attributed to a glass transition (Slade & Levine, 1988). If softening of amorphous polymer does cause this heat-capacity change, then the baseline shift would be expected to be reversible but to exhibit non-equilibrium effects. To check for such reversibility, freshly gelatinized samples were frozen to −20°C and then heated to the temperature just above the point at which the baseline shift appears to be complete but before that of the start of the ice-melting endotherm. This temperature is marked in the figure. The sample was then recooled to −20°C and rescanned. The resultant trace was found to remain the same as shown in Fig. 1(b), supporting the designation of the baseline shift as a glass transition. Heating to a higher temperature in the preliminary partial scan was not found to change the trace either.

The d.s.c. trace obtained on heating a frozen gelatinized sample that contains 45% starch is shown in Fig. 2(a). Similar results were obtained with all the varieties of starch investigated. The nature of the transitions responsible for the peaks shown in Fig. 2(a) was studied by using the rescanning technique already described for the 30% suspensions. Different thermal profiles were obtained in some cases as shown in Fig. 2(b). The procedure indicates that the initial baseline shift that precedes the first endothermic peak is a glass transition as found for the 30% suspensions. Comparison with traces for other frozen aqueous systems suggests that the exothermic peak that directly follows the glass transition is due to crystallization of water (Guegov, 1981). This water does not freeze initially because the sample undergoes a high rate of temperature decrease (MacKenzie, 1981). Heating to temperatures above that of the glass transition, or that of the exothermic peak, but before that of ice-melting, allows freezing to occur. These temperatures are marked A, B, and C, respectively, in Fig. 2(a). It is for this reason that the exothermic peak is not reversible and does not reappear in the corresponding rescan traces, Fig. 2(b). However, if the sample is heated to higher temperatures in the initial partial scan so that significant ice-melting occurs, temperatures D, E, and F in Fig. 2(a), rescanning gives

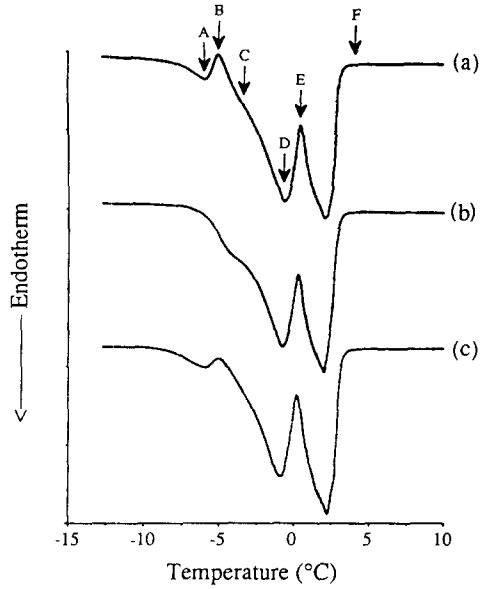

Fig. 2. (a) The d.s.c. trace obtained on heating a frozen gelatinized-wheat-starch system containing 45% polymer (w/w). (b) The trace obtained on heating to point A, B, or C on curve (a), cooling to −20°C, and reheating. (c) Heating curve for a gelatinized sample frozen to −20°C at a cooling rate of 0·5°C min^{-1}. All traces are normalized to 1 mg water. Heat-flow axis 750 $\mu J\ s^{-1}$ per division.

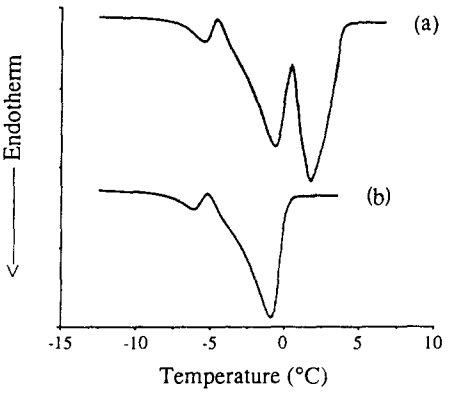

Fig. 3. (a) The d.s.c. output obtained on heating a frozen gelatinized-rice-starch system containing 45% (w/w) polymer. (b) Rescan of the same sample with a new pan lid. Traces are normalized to 1 mg of water in the original sample. Heat-flow axis 750 $\mu J\ s^{-1}$ per division.

the original trace. The cooling rate is again too high for all the water to freeze. When gelatinized samples containing 45% starch are frozen at slower rates, the exotherm is less evident, as would be expected (see Fig. 2(c)).

The two major endothermic peaks shown in all the traces in Fig. 2 are reversible and may reflect the melting of ice in different locations. One possibility is that water condenses on the lids of the sample pans when they are heated to 145°C and cooled. A feature of the d.s.c. pans used in the present study is that they can be opened and resealed with a new lid without damaging the pan base. Opening of the sample pans concerned showed that water had condensed on the sample lid. On resealing the sample pan with a new lid, a single peak was obtained (see Fig. 3). The single peak is about the same as the low-temperature one in the biphasic case and is located at a lower temperature than that for the melting of pure ice. The effect of water on the sample lids is not evident in the more dilute samples, presumably because the melting of ice in the two locations occurs at about the same temperature.

Clearly, water evaporates from the sample during the course of a conventional d.s.c. gelatinization run. This evaporation may have a significant effect on the traces so obtained when the concentration of starch is relatively high. In concentrated mixtures, there appears to be competition between the granules for water during gelatinization (Evans & Haisman, 1982; Liu & Lelièvre, 1992). The least-stable granules melt first, absorb water, and so deplete the remaining more-stable starch particles of diluent. The latter particles melt at higher temperatures, partly because they are more stable and partly because the effective volume fraction of diluent is reduced. Evaporation of water will deplete the more-stable particles of water still further.

To investigate the extent of evaporation during a conventional gelatinization experiment, a 45% suspension was heated to a point along the gelatinization endotherm and then immediately frozen at 320°C min^{-1} to −20°C and rescanned. A direct estimate of the water that had evaporated from the sample was made by weighing the water condensed on the lids (see Fig. 4(a)). The data suggest that significant evaporation occurs early in the gelatinization process. The extent of evaporation would be expected to depend on factors such as the thermal treatment received by the sample, the sample size, and the pan dimensions. The rescanning traces shown in Fig. 4(b), (c) suggest that the second endothermic peak, due to ice melting on the lid, is apparent when the initial partial-gelatinization scan reaches a temperature along the leading edge of the gelatinization scan. However, water has evaporated from the sample before the second peak is apparent. Since the first granules that gelatinize absorb a relatively large amount of water to form a homogeneous zone within the sample, ice in this zone melts at the same temperature as in dilute starch systems, which is a similar position to that of pure ice. Hence, in the early stages of the partial-gelatinization-scan experiment, melting of ice does not lead to a doublet trace.

When the gelatinized 45% starch–water mixture was stored at room temperature prior to freezing, the endotherm due to melting of ice gradually changed and ultimately gave a single peak (see Fig. 5(a)). Comparison of Fig. 5(a) and Fig. 3(a) shows that with storage the higher-temperature ice-melting peak and the exothermic peak due to water crystallization

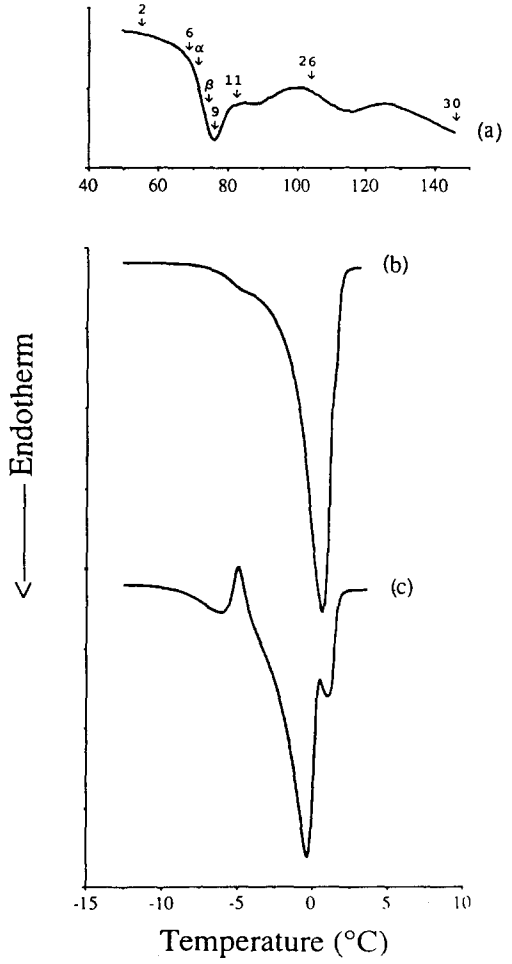

Fig. 4. (a) The d.s.c. trace recorded on heating a suspension containing 45% (w/w) rice starch. The numbers above the trace give the percentage of water in the sample that was found to condense on the sample lid. A single ice-melting peak is evident (see 4(b)) when the suspension is heated to the temperature α during gelatinization, while in the case of β biphasic melting of ice is apparent (see Fig. 4(c)). Curves (b) and (c) are normalized to 1 mg water, and their heat-flow axis is 750 μJ s^{-1} per division.

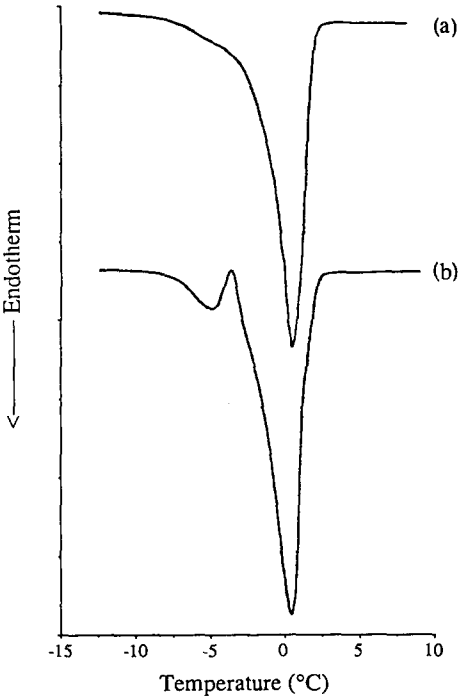

Fig. 5. D.s.c. traces obtained on heating frozen gelatinized rice starch at 45% (w/w) polymer. (a) Gel stored at room temperature for one week. (b) A 45% (w/w) system made from a gelatinized sample containing 10% starch, by evaporation. Traces are normalized to 1 mg of water. Heat-flow axis 750 μJ s^{-1} per division.

disappears, whereas the glass transition remains. During storage, the polymer crystallizes (Slade & Levine, 1987), and, in addition, moisture gradients within the sample pan are at least partially eliminated since time is available for water to diffuse from one region to another. No water was found on the lids of pans that had been stored in the manner corresponding to Fig. 5(a). When the stored gel was heated to 145°C, frozen to −20°C, and rescanned, it was found that the dual ice-melting and the exothermic peaks return, and the trace is similar to that obtained before holding (data not shown). The heating process destroys the crystallinity that has developed in the sample and causes water to condense on the sample lid again.

In a further experiment, a fresh gel containing 45% starch was prepared by heating a 10% starch suspension to 145°C, cooling to 20°C, removing the sample lid, and allowing water to evaporate until the desired polymer concentration was obtained. The melting trace for the sample so prepared exhibits a glass transition and exothermic and single endothermic peaks (see Fig. 5(b)). The exothermic peak is absent in Fig. 5(a). This suggests that it is the concentrated amorphous-polymer regions that are responsible for the inhibition of water crystallization during freezing. When the polymer becomes ordered and polymer-polymer interactions replace polymer-water interactions, the capacity to alter ice crystallization appears to be reduced.

Freezing of gelatinized samples containing more starch, e.g. 70%, to −50°C and reheating gave essentially flat traces (data not shown). Little water was found on the sample lid. The water appears to be strongly absorbed by the starch and therefore remains largely associated with the polymers during heating. The concentrated polymer system prevents much of the water from freezing in the experiment (MacKenzie, 1977; Guegov, 1981). A glass transition was not detected, perhaps because insufficient water was present to plasticize the amorphous starch regions (Slade & Levine, 1988). However, previous work has shown that glass transitions are difficult to detect in concentrated starch systems (Zeleznak & Hoseney, 1987).

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REFERENCES

Ahad, E. (1978). *J. Appl. Polym. Sci.*, **22,** 1665–76.
Biliaderis, C.G. (1990). In *Thermal Analysis of Food*, ed. V.R. Hatwalker & C.-Y. Ma. Elsevier Applied Science Publishers, Barking, UK, pp. 168–220.
Blanshard, J.M.V. (1987). *Critical Rep. Appl. Chem.*, **13,** 16–54.
Derbyshire, W. & Duff, I.D. (1973). *Chem. Soc. Faraday Discuss.*, **57,** 243–54.
Evans, I.D. & Haisman, D.R. (1982). *Stärke*, **34,** 224–31.
Guegov, Y. (1981). In *Advances in Food Research*, Vol. 27, 1981. Academic Press, New York, pp. 297–352.
Liu, H. & Lelièvre, J. (1992). *Carbohydr. Polym.*, **17,** 145–9.
Liu, H., Lelièvre, J. & Ayoung-Chee, W. (1991). *Carbohydr. Res.*, **210,** 79–87.
Luyet, B. & Rasmussen, D. (1968). *Biodynamica*, **10,** 167–91.
MacKenzie, A.P. (1977). *Phil. Trans. R. Soc. Lond. B.*, **278,** 167–89.
MacKenzie, A.P. (1981). In *Microprobe Analysis of Biological Systems*, ed. T.E. Hutchinson & A.P. Somlyo. Academic Press, New York, pp. 397–421.
Radosta, S. & Schierbaum, F. (1990). *Stärke*, **42,** 142–7.
Rasmussen, D. & Luyet, B. (1969). *Biodynamica*, **10,** 319–31.
Slade, L. & Levine, H. (1987). In *Industrial Polysaccharides*, ed. S.S. Stivala, V. Crescenzi & I.C.M. Dea. Gordon & Breach Science Publishers, New York, pp. 387–430.
Slade, L. & Levine, H. (1988). *Carbohydr. Polym.*, **8,** 183–208.
Taniguchi, Y. & Horigome, S. (1975). *J. Appl. Polym. Sci.*, **19,** 2743–8.
Zeleznak, K.J. & Hoseney, R.C. (1987). *Cereal Chem.*, **64,** 121–4.