Carbohydrate Polymers 17 (1992) 145-149

A differential scanning calorimetry study of melting transitions in aqueous suspensions containing blends of wheat and rice starch

H. Liu & J. Lelièvre*

Department of Food Science, Acadia University, Wolfville, Nova Scotia, Canada B0P 1X0

(Received 5 November 1990; revised version received 8 February 1991; accepted 21 February 1991)

Differential scanning calorimetry (dsc) has been used to study the transitions that take place when an aqueous suspension containing a blend of wheat and rice granules is heated. These starch types gelatinize over distinctly different temperature ranges. The positions of the wheat and rice endotherms in the dsc traces are governed by the melting of granules of different stabilities at different volume fractions of diluent. When the total concentration of starch in the suspensions is relatively low, that is less than about 30% wt, the dsc traces for the blends are simply the sum of the outputs for each of the components in the mixture. However, at higher starch concentrations competition for water occurs and non-additive behaviour is found. Under these conditions the wheat starch, since it gelatinizes first, has access to more water and melts at about the same temperature as controls. The rice granules give an endotherm at higher temperatures than controls since the gelatinized wheat particles have already absorbed much of the aqueous phase.

INTRODUCTION

In recent years, many researchers have used differential scanning calorimetry (dsc) to study the molecular transitions that occur when an aqueous suspension of starch granules is heated (Biliaderis, 1990). These studies show that at relatively high water levels, where the volume fraction of granule polymers is less than about 0·5, a single endotherm is apparent at about 60°C. The precise position of the peak depends on the variety of starch being investigated (Biliaderis, 1990) and on the dsc heating rate (Shiotsubo & Takahashi, 1986). When the volume fraction of polymer is increased, two endothermic transitions become evident. The first occurs at the same temperature as before. The second endotherm is observed at increasing temperatures as the water content is decreased. If the volume fraction of polymer is raised still further, the lower temperature endotherm disappears while the temperature of the second peak continues to increase (Donovan, 1979). In addition to the above endotherms, transitions due to lipid-amylose complexes are found at about 120°C (Donovan *et al.* 1983; Biliaderis *et al.*, 1985). A change in heat capacity accompanies all the endotherms (Slade, 1984; Maurice *et al.*, 1985).

The molecular mechanism responsible for the biphasic endotherm is uncertain. Donovan (1979) suggested that the initial dsc peak results from the stripping of polymer chains from the surfaces of crystallites due to stress, while the second peak represents melting at low diluent volume fractions. However, the melting point of polymers under stress tends to increase, rather than decrease (Mandelkern, 1964), which is inconsistent with this model (Lelièvre, 1985). Another explanation is based on the fact that the crystalline zones in different granules have different stabilities (Evans & Haisman, 1982; Zobel *et al.*, 1988). Water will migrate from one location to another within the sample as the various granules gelatinize. Accordingly the peaks correspond to melting transitions of crystalline material with different stabilities, occurring at different diluent levels. This explanation is consistent with reports that X-ray crystallinity changes occur during the first and second dsc peaks (Liu *et al.*, 1991) and that the loss of birefringence begins with passage through the first endotherm but is not

---

*To whom correspondence should be addressed.

Carbohydrate Polymers 0144-8617/91/$03.50

complete until the second peak has been traversed (Burt & Russell, 1983). Other investigators suggest that the lower temperature peak is a consequence of chain mobilization in the amorphous regions of the granule (Biliaderis *et al.*, 1985; Maurice *et al.*, 1985). According to the model the glass transition, which is responsible for the change in heat capacity, is located at the leading edge of the first dsc peak. Completion of the glass transition permits the crystalline domains to undergo a non-equilibrium melting process giving the second endothermic trace (Slade & Levine, 1988). However, considerable evidence indicates that the heat capacity change occurs during both endothermic peaks and is not associated with a glass transition (Zeleznak & Hoseney, 1987; Liu *et al.*, 1991; Liu & Lelièvre, in press). Russell (1987) interprets the double endotherms observed in limited water systems to be due to disruption of double helices associated with short-range ordering involving amylose and amylopectin followed by melting of crystallites. The most recent suggestion is that recrystallization can contribute to the second endothermic peak (Biliaderis, 1990).

Starch samples are known to be heterogeneous. The stabilities of the crystalline domains vary both within and between granules (Blanshard, 1987). The present paper reports an investigation of the effect of granule heterogeneity on the dsc traces of aqueous starch suspensions. The approach adopted was to study defined blends of two different starch varieties with widely differing gelatinization temperatures. The varieties selected had a different appearance under the microscope, so that the extent to which any one variety had been modified by heating could be observed.

MATERIALS AND METHODS

Starch was isolated from wheat and rice by subjecting wet-milled samples at 10 °C to repeated sieving and centrifuging (Meredith *et al.*, 1978). Microscopic observation confirmed the procedure avoided the production of damaged starch (Meredith *et al.*, 1978). The resultant starch slurry was freeze-dried at below 20 °C to 10% wt moisture. The freeze-drier conditions prevented annealing (Ahmed & Lelièvre, 1978).

Measurements of dsc were made on a Perkin Elmer 2C calorimeter with thermal analysis data station. The resultant traces were normalized to a basis of 1 mg starch per sample, using the data station. The instrument was calibrated by standard procedures (Biliaderis *et al.*, 1986). The heating rate was 10 °C min^{-1}. An empty dsc pan was employed as inert reference.

To study gelatinization, granules were weighed into O-ring stainless steel pans designed to withstand high pressures and suppress the volatilization of solvent. Sufficient water was added from a microsyringe to wet all the granules. Excess water was removed by evaporation and the pans were then sealed. The sample size was 20 mg starch slurry. Samples were allowed to equilibrate for at least 1 h before measurements were made.

Individual granules were examined by microscope to determine their origin, and whether they displayed birefringence and were stained by Congo Red dye (Burt & Russell, 1983).

RESULTS AND DISCUSSION

Figure 1 shows that where one starch is present in excess water, which in this case corresponds to a 30% wt suspension, a single endothermic transition occurs and the wheat starch endotherm takes place about 10 °C below that for the rice starch. The traces for the wheat-rice blends are simply the sum of the dsc outputs for each of the starch components in the mixture. Microscopic observation was found to demonstrate that

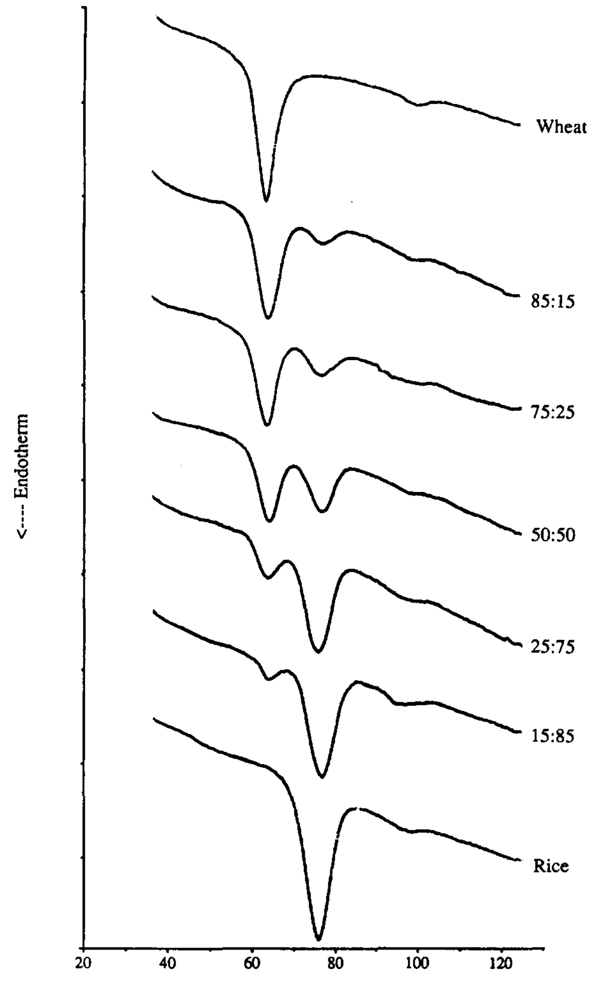

Fig. 1. Differential scanning calorimetry traces for 30% wt starch suspensions. The numbers labelling the traces give the ratios of the weights of wheat to rice in the blends.

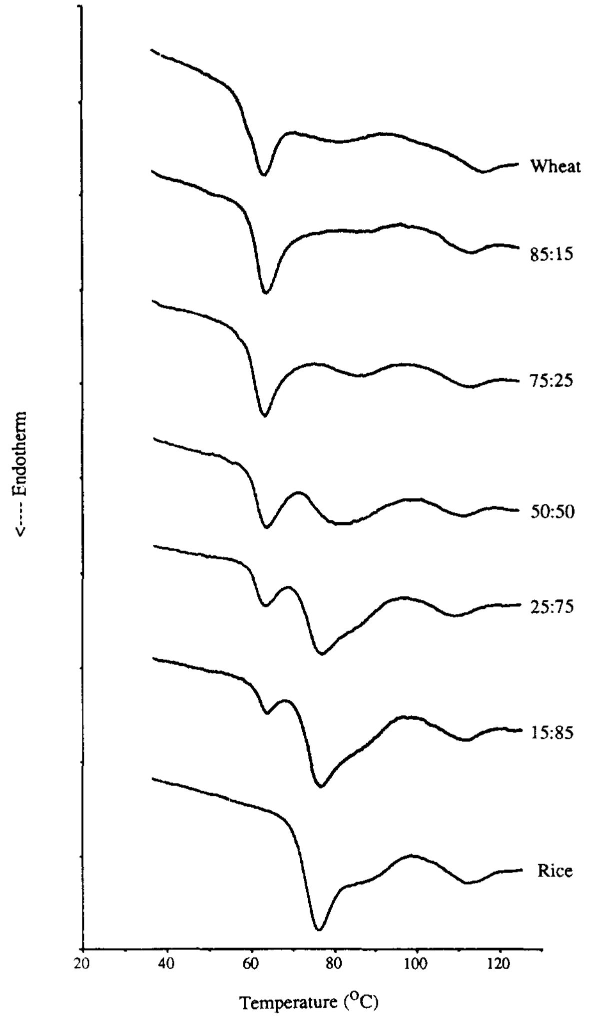

Fig. 2. Differential scanning calorimetry traces for 50% wt starch suspensions. The numbers labelling the traces give the ratios of the weights of wheat to rice in the blends.

wheat starch gelatinizes almost completely before the rice endotherm commences.

In 50% wt suspensions the situation is more complicated (see Fig. 2). The temperature of the first peak in the endotherm is always about the same (63 °C). Birefringence and staining measurements suggest this peak arises solely from the melting transition of wheat starch granules. In contrast, the temperature of the second peak, which is mainly due to the gelatinization of rice starch, increases as the weight fraction of rice in the wheat-rice blend decreases. The area of the first peak in the wheat endotherm begins to increase and then decreases as the weight fraction of this starch in the blend is reduced. The rice endotherm simply becomes smaller as the wheat : rice ratio becomes larger.

Since the water absorbed by wheat and rice granules prior to gelatinization is about the same (BeMiller & Pratt, 1981), the initial water contents of the wheat starch particles in the 100% wheat sample and the 85 : 15 wheat-rice blend are similar. Hence the amorphous regions of the wheat granules will swell to the same extent and be subject to the same degree of stress. If the first dsc peak results from stripping of polymer chains from the surfaces of crystallites due to stress (Donovan, 1979), then the first endothermic peak in the two samples should be similar. The finding that the endotherms differ provides further evidence against this explanation for the dsc traces. The fact that the wheat granules in the 100% wheat and the 85 : 15 wheat-rice blend contain the same water levels, and therefore the same plasticizer contents (Moy & Karasz, 1980), suggests that T_g should be the same in both samples. If a glass transition controls the melting process (Slade & Levine, 1988), then the peaks for the wheat transition in the two samples should be the same. Although the leading edges of the traces are similar, differences then develop. Again, theory and experimental results are in disagreement. Neither can the suggestion that recrystallization (Biliaderis, 1990), nor disruption of double helices followed by melting of crystallites (Russell, 1987), contributes to dsc traces, account for the endotherms given in Fig. 2.

The theory suggesting that the dsc peaks are due to melting transitions of crystalline material with different stabilities at different diluent levels (Evans & Haisman, 1982; Zobel *et al.*, 1988), can explain the results shown in Fig. 2. According to the theory, if the water content of the suspension is sufficiently high, on melting each granule absorbs water without restriction and a single endothermic peak is observed. This occurs when the water content of the starch suspension is greater than about 65% wt (Donovan, 1979). If the water content is less than this level, there is competition between the granules for water. In this case the least stable granules melt first, absorb water and so deplete the remaining more stable starch particles of diluent. The latter particles melt at a higher temperature partly because they are more stable and partly because the effective volume fraction of diluent is reduced. The associated endotherm initially occurs in the form of a trailing shoulder on the first peak. However, as the water content of the sample is reduced, fewer granules are able to gelatinize in an unrestricted water environment and so the first endotherm decreases in size while the second increases and shifts to a higher temperature. If the volume fraction of diluent is reduced sufficiently, only the higher temperature endotherm is apparent.

The dsc trace for pure wheat starch given in Fig. 2 shows a trailing shoulder since water is restricted and less than about the 65% wt level. This trailing shoulder has largely disappeared in the 85 : 15 wheat-rice blend. The rice granules in this blend, having a significantly higher melting temperature, do not compete effectively with the gelatinizing wheat particles for water. To some extent, the rice granules are acting as an inert filler in the suspension when the wheat starch gelatinizes. Hence the behaviour of the wheat granules is equivalent to that in a suspension containing about 45% wt (i.e. 0·85/1 + 0·85) starch, and about 55% wt water. With the water being, in effect, almost unrestricted during the gelatinization of the wheat starch, the first peak is prominent and the second trailing peak is almost absent. The area of this former peak is greater than that for the corresponding endotherm in the 100% wt wheat sample even though the mass of wheat granules is less. Presumably this is because in the 100% wt wheat sample, the limited water conditions cause a smaller mass of granules to gelatinize at the lower temperature. When the rice starch in the 85 : 15 blend melts, most of the water has been absorbed by the gelatinized wheat granules so the transition shifts to a temperature which is about 25 °C higher than for the corresponding pure rice case.

As the proportion of wheat starch in the wheat-rice blend is further reduced, the wheat endotherm remains at the same temperature since water is still, in effect, unrestricted. The peak area reduces in size as fewer granules now undergo the melt. The corresponding endotherm for the rice firstly increases in size as a greater mass of particles gelatinizes, and secondly shifts to lower temperatures as the effective diluent volume fraction increases. However, the first rice peak in the traces of the blends, corresponding to initial melting in excess water, is never particularly prominent as the wheat granules have already absorbed part of the diluent. The temperature of the lipid-amylose endotherm is slightly higher for wheat than rice starch and the position of this peak in the blends presumably reflects this difference.

Figure 3 gives endotherms calculated from the traces for the pure starches according to the weight fractions in the blends. Comparison with the experimental results shows that in contrast to the more dilute suspensions, the calculated and experimental traces do not coincide. The calculated trace predicts the peak due to wheat granules to be smaller and that due to rice granules to be greater than occurs experimentally. This trend suggests that, in effect, the wheat granules undergo less competition for water during gelatinization within the blends while the reverse is the case for the rice particles.

Figure 4 sets out the dsc traces for the 75 : 25 wheat-rice blends as a function of the total percentage of starch in the suspension. As this percentage increases above about 30% wt, the rice endotherm is shifted to higher temperatures. Below about 30% wt, the rice peak is that for melting in unrestricted water. At higher starch concentrations the broad rice peak is that for melting in limited quantities of diluent. Similar trends were obtained for all the other blends, with the different wheat : rice ratios given in Fig. 1. Again the data suggests that within the blends the wheat starch, since it gelatinizes first, has access to more water while the rice granules melt at higher temperatures than controls since the gelatinized wheat particles have already absorbed much of the aqueous phase.

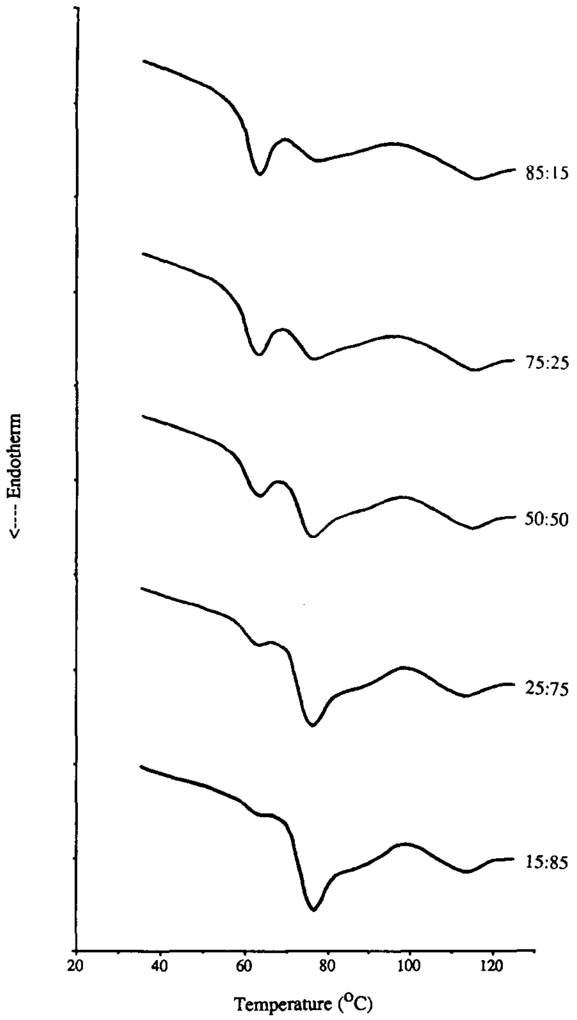

Fig. 3. Endotherms calculated from the 50% wt traces for pure wheat and rice starch given in Fig. 2. The numbers labelling the traces give the ratios of the weights of wheat to rice in the blends.

Clearly, when starch gelatinizes under the heating regimes normally used in dsc instruments, a non-equilibrium process occurs. First, the crystals are not properly annealed and the heating rate is too fast to prevent superheating (Wunderlich, 1981). Second, the water is not evenly distributed within the matrix of starch polymers. The positions of the endotherms in dsc traces are governed by the melting of granules of different stabilities at different volume fractions of diluent.

ACKNOWLEDGEMENT

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

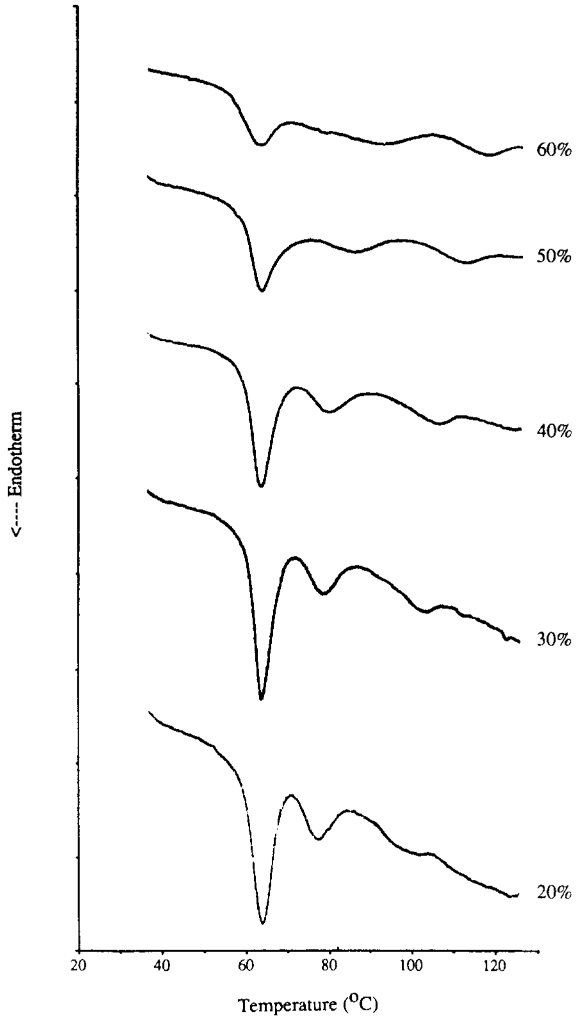

Fig. 4. Differential scanning calorimetry traces for 75 : 25 wheat-rice blends as a function of the total percentage of starch in the suspension.

REFERENCES

Ahmed, M. & Lelièvre, J. (1978). *Starke*, **30**, 78.

BeMiller, J. N. & Pratt, G. W. (1981). *Cereal Chem.*, **58**, 517.

Blanshard, J. M. V. (1987). *Critical Reports on Applied Chemistry*, **13**, 16.

Biliaderis, C. G. (1990). In *Thermal Analysis of Food*, ed. V. R. Hatwalker & C.-Y. Ma, Elsevier Applied Science Publishers, Barking, UK, p. 217.

Biliaderis, C. G., Page, C. M., Slade, L. & Sirett, R. R. (1985). *Carbohydr. Polym.*, **5**, 367.

Biliaderis, C. G., Page, C. M., Maurice, T. J. & Juliano, B. O. (1986). *J. Agric. Food. Chem.*, **34**, 6.

Burt, D. J. & Russell, P. L. (1983). *Starke*, **35**, 354.

Donovan, J. W. (1979). *Biopolymers*, **18**, 263.

Donovan, J. W., Lorenz, K. & Kulp, K. (1983). *Cereal Chem.*, **60**, 381.

Evans, I. D. & Haisman, D. R. (1982). *Starke*, **34**, 224.

Lelièvre, J. (1985). *Starke*, **37**, 267.

Liu, H., Lelièvre, J. & Ayoung-Chee, W. (1991). *Carbohydr. Res.*, **210**.

Liu, H. & Lelièvre, J. (in press). *Carbohydr. Res.*

Mandelkern, L. (1964). *Crystallization of Polymers*, McGraw-Hill, New York.

Maurice, T. J., Slade, L., Sirett, R. R. & Page, C. M. (1985). In *Properties of Water in Foods*, ed. D. Simatos & J. L. Multon, Martinus Nijhoff Publishers, Dordrecht, p. 211.

Meredith, P., Dengate, H. N. & Morrison, W. R. (1978). *Starke*, **30**, 119.

Moy, P. & Karasz, F. E. (1980). In *Water in Polymers*, ed. S. P. Rowland, American Chemical Society, Washington, DC, p. 503.

Russell, P. L. (1987). *J. Cereal. Sci.*, **6**, 133.

Shiotsubo, T. & Takahashi, K. (1986). *Carbohydr. Res.*, **158**, 1.

Slade, L. (1984). *AACC 69th Ann. Meet.*, 30 Sept.-4 Oct., Minneapolis, p. 112.

Slade, L. & Levine, H. (1988). *Carbohydr. Polym.*, **8**, 183.

Wunderlich, B. (1981). In *Thermal Characterization of Polymeric Matierals*, ed. E. A. Turic, Academic Press, Orlando, p. 91.

Zeleznak, K. J. & Hoseney, R. C. (1987). *Cereal Chem*, **64**, 121.

Zobel, H. F., Young, S. N. & Rocca, L. A. (1988). *Cereal Chem.*, **65**, 443.