Low Temperature Exotherm in Starch / Water Systems: A Retrogradation Marker

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Synopsis

DSC measurements at slow ($< 1.0°C$ min^{-1}) heating speeds reveal a crystallization exotherm in the $-4--6°C$ region for starch/water systems. The same exotherm is not observed for other polysaccharides such as guar and is sensitive to chemical modification of the starch sample. The DSC thermograms have been interpreted in terms of three different levels of water organization in the starch matrix.

INTRODUCTION

Many papers[1-5] have been published on the structure of water in polymeric matrices or the specific case of water/starch interactions in natural starches, copolymers containing starch, and modified starches. The term "bound water" is often employed to describe at least some of the water in such systems, although a single, precise widely accepted definition of this term does not exist.[6] On a physicochemical basis any such definition must be related to an alteration of the physical properties of water as a consequence of its interaction with the polymeric matrix. In practice, this is not a sufficiently restrictive requirement. Berendsen,[7] for example, suggests 11 slightly different definitions of bound water. A simple bimodal separation into mobile (freezing) and bound (nonfreezing) phases can arise from the shape or number of melting endotherms in the 0°C vicinity in differential scanning calorimetry (DSC), from scanning electron microscopy (SEM), or from nuclear magnetic resonance (NMR) measurements.[1,2,8,9]

More complex systems involving water of at least three different types have also been proposed.[10-12] Andrade and co-workers,[10] for example, distinguish between bound-, bulk-, and an intermediate (interfacial)-water forms in hydrogels using DSC, specific conductivity, and dilatometric techniques. Quantitation of the water in each of these phases is not reproduced by workers in other laboratories.[11,12] In a related study, Drost–Hansen developed a three-layer model of water near solid/water interfaces from a multidisciplinary approach involving infrared, NMR, surface conductance, viscosity, mechanical damping, and dielectric studies. In the case of cellulose acetate[4] a four-state model with free, weakly interacting, and bound water, the latter being further divided into a phase including dissolved salts and a second which rejects them.

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TABLE I
Description of Hydroxypropylated Starches

Sample	Batch	Type of starch	% Hydroxypropyl subst. (w/w)
A	18QQ-33	HP waxy corn starch (Staley)	1.29
B	18QQ-34	HP waxy corn starch (Staley)	2.34
C	18QQ-39	HP waxy corn starch (Staley)	4.02
D	18QQ-40	HP waxy corn starch (Staley)	6.06

Our present study of the starch system also utilizes DSC as a primary tool but differs from the preceding ones in the very slow scanning speeds used. These permit a closer approach to equilibrium conditions. The presence of a "crystallization" exotherm and two subsequent melting endotherms is established, and chemical factors governing shape of these is explored.

EXPERIMENTAL

Samples

Powdered samples of native starches s, i.e., corn (CS) starch, waxy corn (WCS) starch, and potato (PS) starch were donated by the National Starch and Chemical Company, Bridgewater, NJ (courtesy of Dr. M. K. Rutenberg). A series of hydroxypropyl waxy corn starches were donated by the A. E. Staley Manufacturing Co., Decatur, IL (courtesy of Dr. K. Niekamp) and their properties are summarized in Table I. A sample of guar gum purified from Celanese Jaguar 8 by repeated low speed centrifugation followed by ethanolic precipitation was donated by Dr. G. A. Hardy, Celanese, Summit, NJ.

Methods

All DSC experiments were carried out with a Perkin-Elmer DSC-4 calorimeter. Large volume (75 μL) sample pans with O-ring seals to prevent evaporative losses were used throughout. An empty but sealed pan of this type served as the reference. The DSC head was purged continuously with dry N_2.

In a typical experiment a weighed starch sample was mixed with distilled water in the sample pan. The sample was then heated rapidly (100°C min^{-1}) to 95°C, held at that temperature for 3 min (to permit complete gelatinization) and then quenched at 320°C min^{-1} to -15°C. The sample was held at this temperature for several minutes to reestablish thermal equilibrium. The sample was then heated at a uniform rate, usually 0.5°C min^{-1}, from -15 to 5°C. Sample pans were weighed empty, as well as before and after the slow scan. In all cases, no loss of mass was observed during the slow-speed scan.

RESULTS AND DISCUSSION

DSC thermograms were recorded for the WCS/water system over the temperature range $-15-+5$°C at several heating rates ranging from 10.0 to 0.2°C min^{-1} (see Fig. 1). At 1.0°C min^{-1} the single broad endothermic
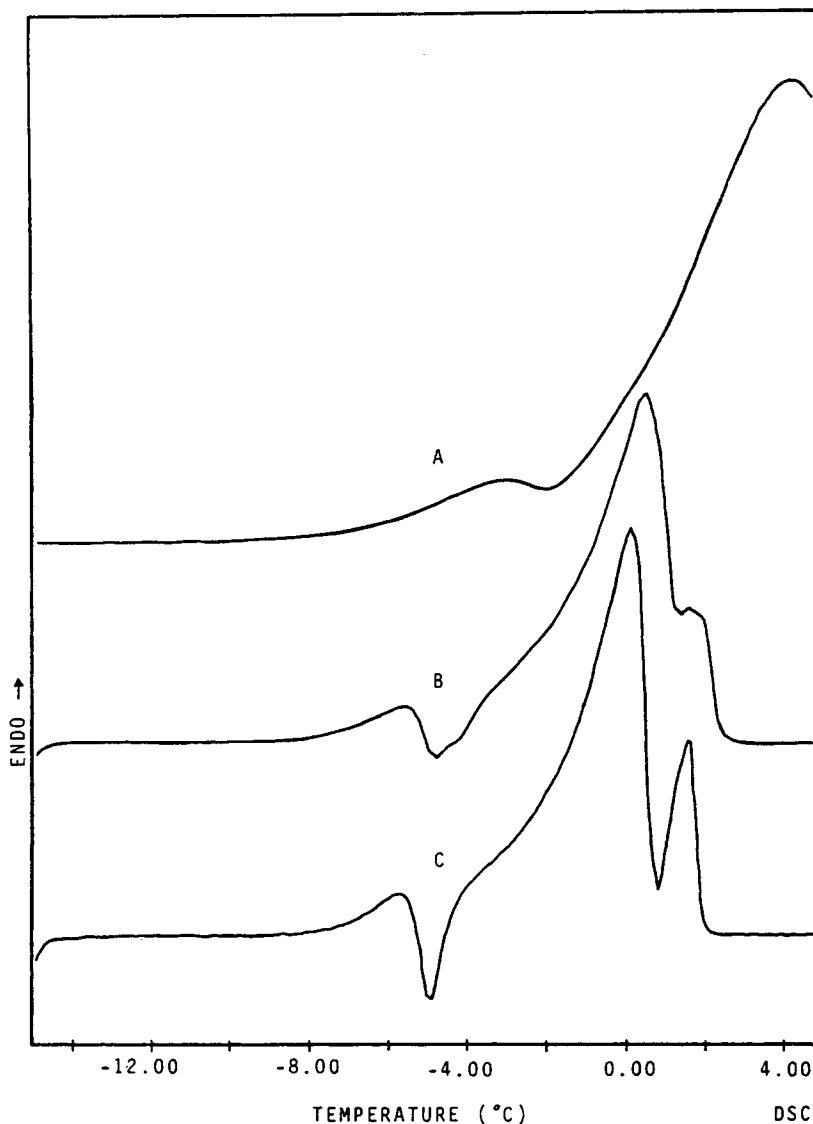
Fig. 1.   DSC thermograms of WCS/water mixtures (50/50 in w/w) showing the influence of heating rate (°C min^{-1}): (A) 5; (B) 1; (C) 0.5.

transition with its peak at 3.9°C began to resolve into two separable endotherms. Reduction of the heating rate to 0.5°C min^{-1} resulted in the separation of a rather sharp endothermic peak centered at 1.5°C appearing as a well-defined shoulder of a broad endothermic maximum (T_{peak} = 0.2°C). The low-temperature tail of this peak has a readily discernible exotherm (T_{peak} = -4.7°C) superimposed upon it. Further reduction in the heating role to 0.2°C min^{-1} sharpened the resolution but did not affect the observed transition temperatures. For this reason subsequent experiments were carried out at 0.5°C min^{-1}.
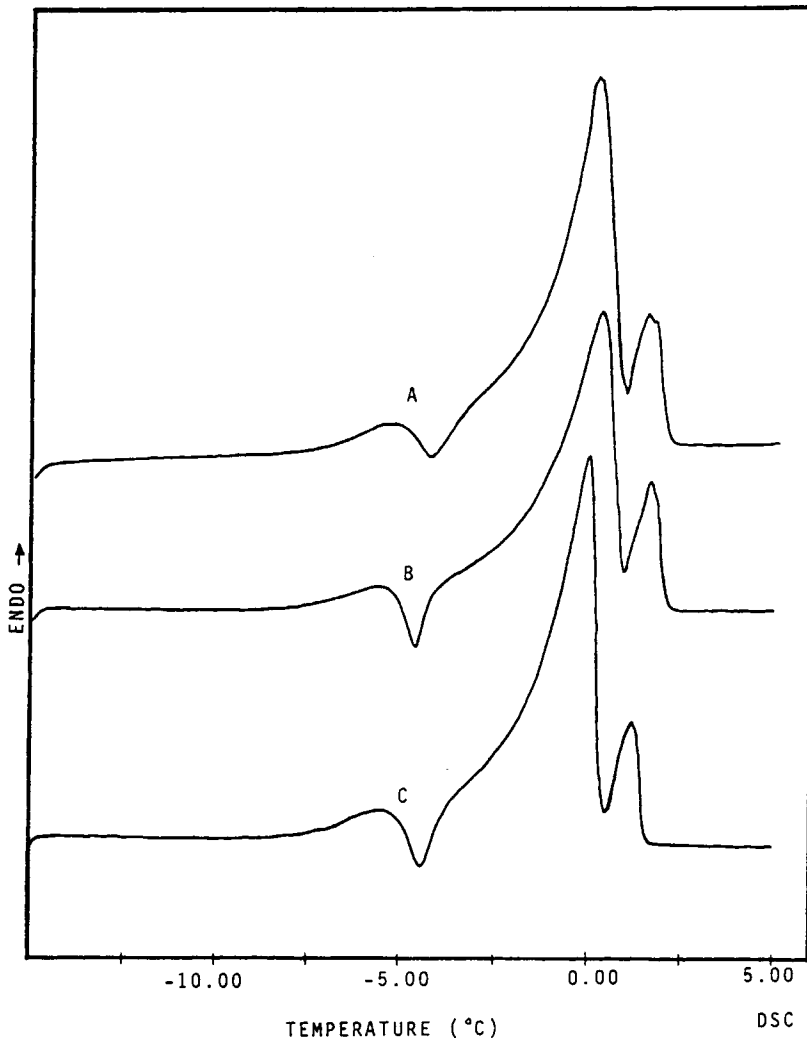
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Fig. 2. DSC thermograms for 50/50 starch/water gels with (a) potato (PS), (b) corn (CS), and (c) waxy corn (WCS) starches.

Figure 2 shows the DSC heating curves for three different starches, CS, WCS, and PS, each prepared as an approximately 50/50 (w/w) aqueous mixture which was heated to form a gel and then quenched as described. In each case the thermogram exhibits a well-defined endotherm at $1.3 \pm 0.2°C$, a second larger and broad endotherm ($T_{peak} = 0.0 \pm 0.2°C$) with a low-tempera-ture tail and an exothermic peak at $-4.7 \pm 0.2°C$. X-ray diffraction studies of similarly treated samples shows that each has a B type diffraction pattern. The considerable similarity of the three thermograms suggests that composi-tional differences such as the lipid or protein content does not play a role in these changes. As shown in Figure 3, the same effect is not observed with other polysaccharide/water systems such as guar/water, nor is it an artifact arising from some interaction of water with the sample container. In addition,
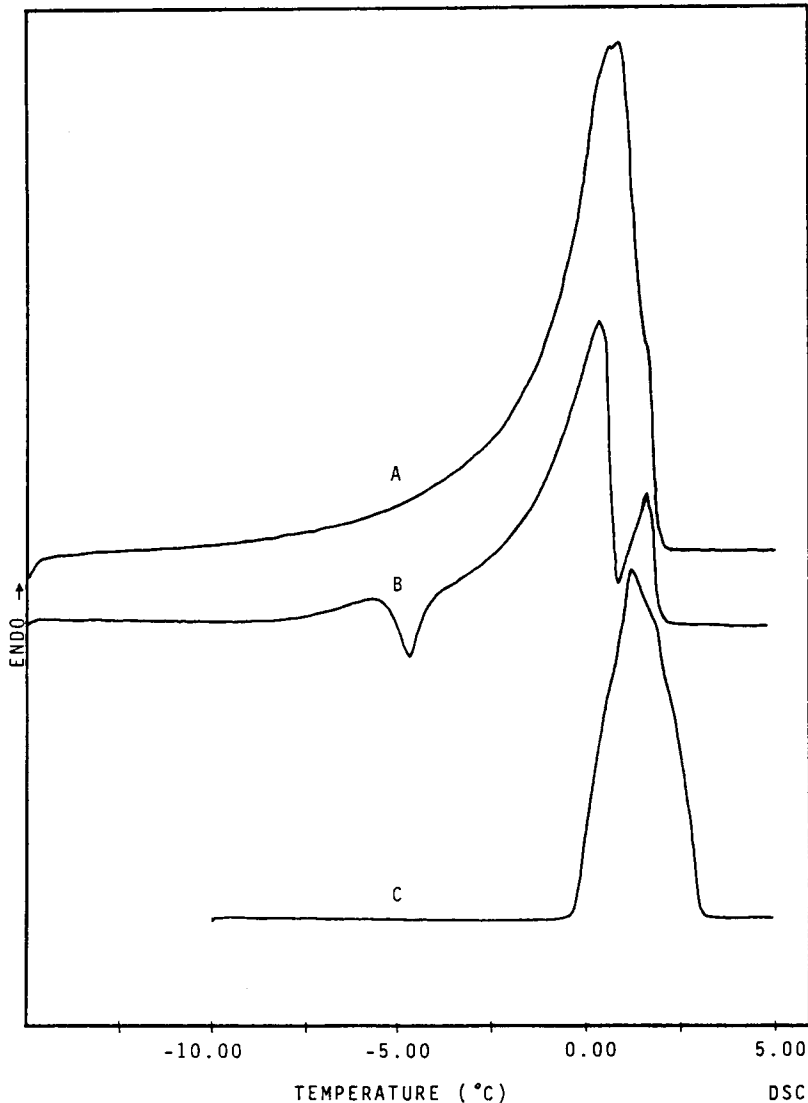
Fig. 3. DSC thermograms of (a) guar/water (33/67; w/w), (b) WCS/water (50/50 in w/w), and (c) distilled water.

the position of the water peak for distilled water [Fig. 3(C)] establishes that the high temperature (1.5°C) peak in the starch/water samples corresponds to free water in the "stiff gel." The latent heat of fusion calculated from this peak is 79.6 cal g^{-1}. The second endotherm we therefore assign to the melting of the starch/bound water phase. The considerable asymmetry arises, in our opinion, from the fact that this is not a true single phase at all but rather a complex melange of microcrystalline domains in an amorphous matrix. In this context, it is difficult to distinguish between the "bound" and "interfacial" water phases as described by Andrade and co-workers.[10] Their technique of measuring the residual water content upon disappearance of the endotherms

at −5 and 0°C is not applicable in a system where different polymer phases arise as a consequence of lost water. There are always at least two distinct polysaccharide phases. The crystalline domains are essentially linear B-amylose segments with the branch points of the amylopectin either on the crystallite surface or in the amorphous matrix. The matrix in turn may also have local separations into amyloselike regions. Crystallization of such domains provides one explanation for the occurrence of an exothermic peak at −4.8°C, 4.5–5.0°C below the peak position in the bound water melting endotherm.

The magnitude of the exothermic peak, in particular, is influenced by derivitization of the starch. As shown in Figure 4 for a series of hydroxypropylated WCS samples, the area of the exothermic peak decreases steadily with
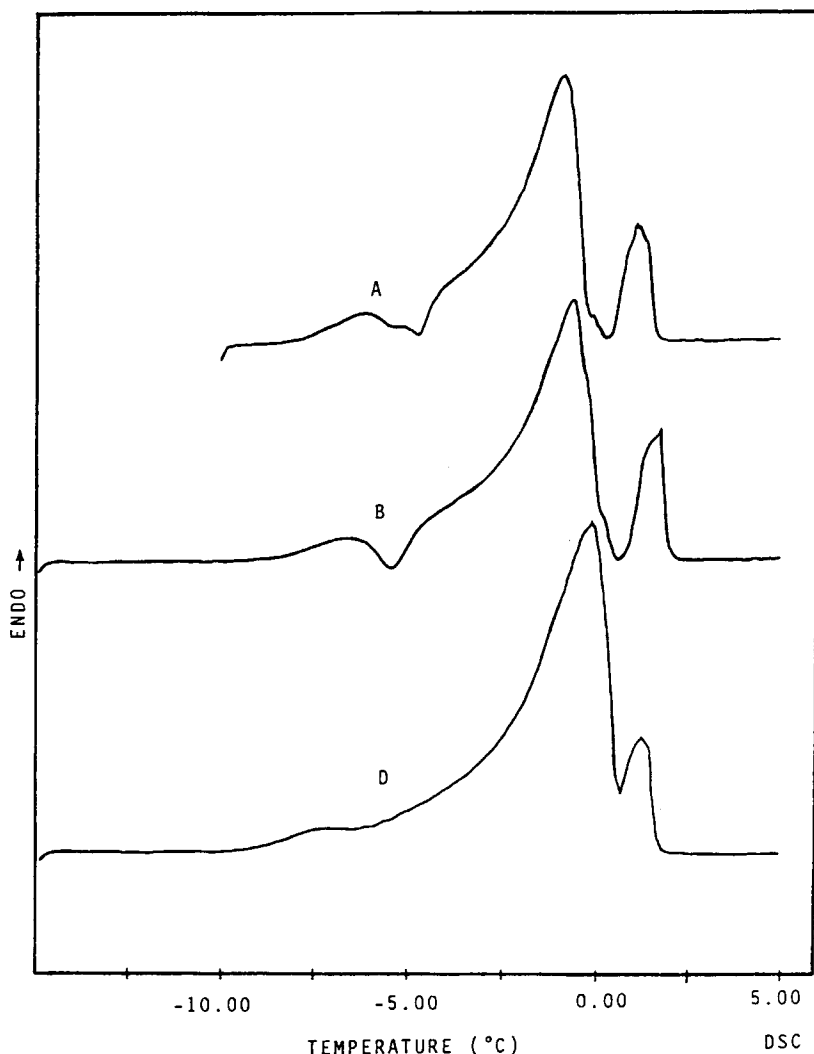

Fig. 4.   DSC thermograms of HPWCS/water mixtures with varying degrees of hydroxypropylation. Symbols refer to Table I designations.

increasing hydroxypropyl content. At a level of 6.06% (w/w) substitution the exothermic peak is no longer evident. We interpret this result as an indication that the 6% hydroxypropylated material is protected from retrogradation. In this context, we are using the term retrogradation to reflect a dehydration and reversion of cooked starch into an insoluble phase. The fact that the endotherm for interfacial water is largely unaffected suggests that much of this water is associated with the noncrystalline domains in agreement with the low level of crystallinity observed in these samples. Such organization may be expected to correspond to water association with either molecular or double-
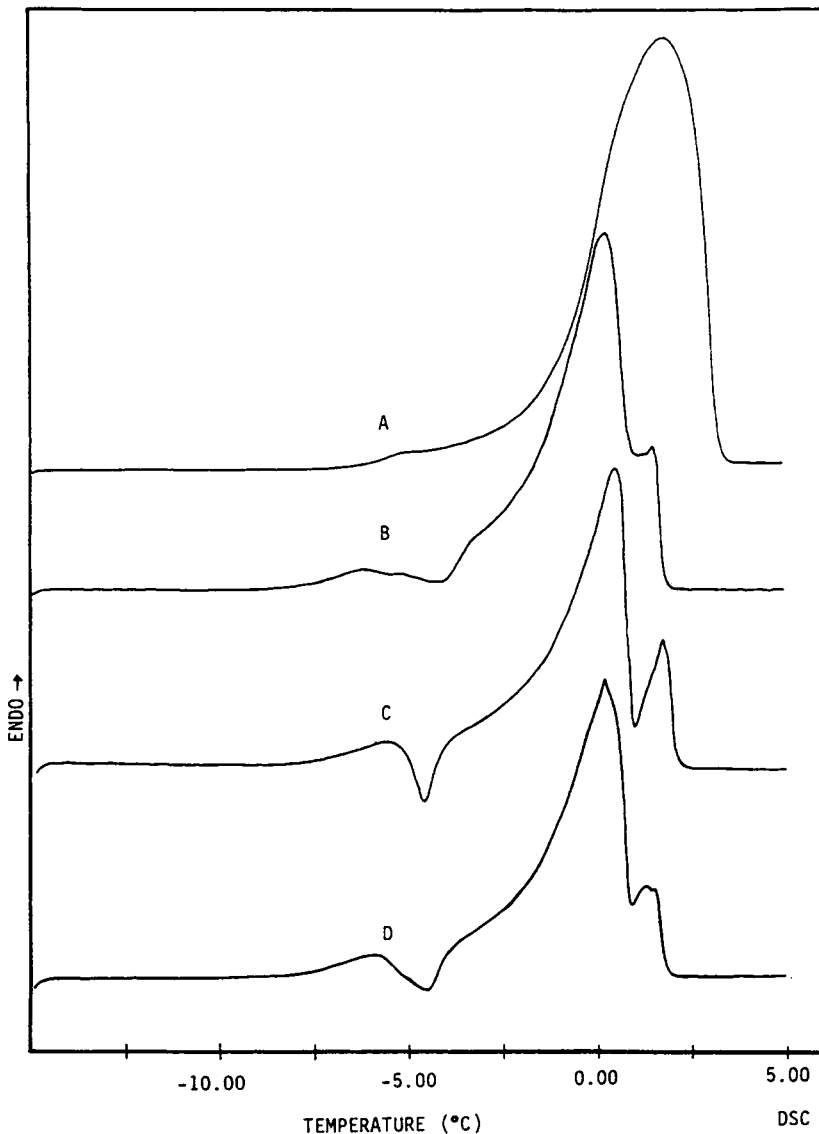
Fig. 5.   DSC thermograms of WCS/water mixtures showing the influence of starch/water ratios: (A) 44/56; (B) 50/50; (C) 53/47.

helical starch but not to participation in a regular crystal lattice. Only the weaker, readily masked, exotherm appears to correlate reliably with the crystallization process.

In Figure 5 we see the influence of changes in the water content of starch/water gels on the DSC profile. After normalization of the exothermic transitions on a per gram of starch basis, results were identical for all samples. Further increases in the water content to a 25/75 starch/water composition results in complete disappearance of a *detectable* exotherm and merging of the two endothermic peaks into a single broad peak.

Our results clearly point to the weak exothermic transition as a marker for the crystallization process and, hence, for retrogradation. Since the method is simple, comparatively rapid and its results are readily reproducible, the technique should be considered as a possible method for testing the ability of additives or derivatives to regulate the tendency of a starch product to undergo retrogradation.

REGISTRY NUMBERS

Hydroxypropyl starch, 9049-76-7; waxy corn starch, 9037-22-3; corn starch, 9005-22-8; guar gum, 90000-39-0; potato starch, 9005-25-8.

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