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Identification of the thermal transitions in potato starch at a low water content as studied by preparative DSC

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ABSTRACT

The aim of this work was to identify the transitions in the complex DSC profiles of potato starch at a low water content. Preparative DSC involves the thermal processing of samples in stainless steel DSC pans in a way that allows their subsequent structural characterization. The low temperature (LT), dual melting (M1–M2), and high temperature (HT) endotherms observed in DSC profiles of potato starch with 16% water were assigned to enthalpy relaxation, melting with preservation of granular identity, and transition of the melted granules into a molecular melt, respectively. Granular melting was accompanied by a strong reduction of swelling capacity. Significant molecular degradation was observed after the HT transition. There is evidence that HT does not represent a true thermodynamic transition, but is due to a volume change in the sample. In contrast to potato starch, maize starch with 16% water gave inhomogeneous samples after processing, presumably because of its low packing density.

1. Introduction

Starch is a versatile and cheap raw material with numerous applications, e.g. as thickener, texturizer, and adhesive (Thomas & Atwell, 1999). The starch biopolymers are packed in semi-crystalline granules that are insoluble in cold water. For almost any application the ordered granule structure is disrupted by heating with water. This process is known as gelatinization or melting (Parker & Ring, 2001). The latter term is used when the water content is low. Indeed, the water content may vary from very high in thickening applications (>90%), to intermediate in bread making (40–45%), and to quite low in the making of expanded products and bioplastics (15–30%). Hence it is no surprise that the gelatinization and melting phenomena have been studied over a wide range of water contents. Starch is unique among biopolymers in the sense that water-assisted melting results in only partial molecular solubilization. As long as the heating and shear conditions are not too severe, the granules lose their crystallinity but maintain their individuality. Complete molecular dissolution is only attained at temperatures exceeding 130 °C. This is accompanied by significant molecular degradation unless strict precautions are taken (Hanselmann, Burchard, Ehrat, & Widmer, 1996). Both transitions also occur at water contents as low as 15–20% (Willenbücher, Tomka, & Müller, 1995). Thus, we can define three states for starch–water systems: the intact granular state, the melted granular state, and the solution state.

From an application point of view, knowledge of the temperature range of the melting transitions at practical conditions is of the utmost importance. This is most conveniently studied by differential scanning calorimetry (DSC) which allows coverage of the entire range of water contents at temperatures up to about 200 °C. Since the pioneering work of Donovan (1979), the gelatinization and melting of starch at intermediate and low water contents have been the subject of numerous DSC studies. It is well established that complex DSC heating profiles arise as the mass fraction of water in the wet starch falls below 0.6 (Donovan, 1979; Evans & Haisman, 1982; Biliaderis, Page, Maurice, & Juliano, 1986).

The majority of the previous DSC studies had their upper temperature limit at $\leqslant$160 °C. However, several workers have observed a significant thermal event in the temperature range between 150 and 225 °C in starch with water contents between 12% and 20% (Willenbücher et al., 1995; Thiewes & Steeneken, 1997; Yu & Christie, 2001; Vermeylen et al., 2006a). It has been reported that this event represents the transition from melted granules into a molecular melt, i.e., from the melted granular state into the solution state (Willenbücher et al., 1995). This was inferred from microscopy. However, no images were presented.

In the present work we aimed at the exploration of the thermal transitions at low water content up to 210 °C in somewhat more detail. This was achieved by applying the concept of 'preparative DSC'. This involves the use of DSC as a tool for the thermal processing of starch samples that allows easy withdrawal of samples from

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stainless steel pans and subsequent sample analysis at the 20 mg scale. A water content of 16% (wet basis) was selected because the glass transition temperature (T_g) at this water content is higher than ambient temperature (Thiewes & Steeneken, 1997). This prevents structural changes due to recrystallization during storage of heated samples at ambient temperature.

2. Materials and methods

2.1. Materials

Potato starch and normal maize starch were gifts from AVEBE and Cargill, respectively. Starch with 16% water (wet basis) was prepared either by dehydration at ambient temperature or by addition of the calculated amount of distilled water and equilibration for 1 week in a closed container with occasional mixing. The water content was checked from the weight loss of the starch after heating (130 °C, 2 h) in a free-ventilating oven. A solution of 0.2621 g/l $CaCl_2$. $2H_2O$ in distilled water served as simulated tap water. Aerosil R972 (Degussa) was used as a flow conditioner.

2.2. Preparative DSC

Stainless steel large volume pans (Perkin Elmer) were fitted with thermally inert silicon rubber rings. These inserts (height 2 mm) were cut from silicon rubber tubing (type S 5/1 SIK 8360) with an internal diameter of 5 mm and a thickness of 1 mm. Starch with 16% water (ca. 25 mg) was then weighed into the pan, which was sealed. Heating scans were performed in a Perkin Elmer DSC 7 or Pyris 1 from 20 °C to the selected final temperature at 10 °C/min with an empty pan without insert as a reference. After attaining the final temperature the sample was cooled immediately to 20 °C at 200 °C/min. The pan was opened, the insert was removed by tweezers, and the sample was transferred to a screw-cap tube of known weight by means of a spatula. Maximum final temperature was 210 °C. DSC profiles were corrected by subtraction of the profile of an empty pan with insert against an empty pan without insert as a reference. Conventional heating scans were run on samples (50 mg) in pans without insert from 20 to 210 °C against an empty pan without insert as a reference.

2.3. Optical microscopy

Samples in screw-cap tubes were dispersed in distilled water (1 ml) with optional treatment in an ultrasonic bath, except those heated to 210 °C, which were viewed without dilution. Images were taken with a Nikon Eclipse 600 optical microscope equipped with a Nikon FDX-35 camera.

2.4. Swelling capacity and solubility

The swelling capacity q at 92 °C was determined in duplicate by the Blue Dextran dye exclusion method according to Evans and Haisman (1979) with modifications. To a starch sample of known mass (typically 20 mg dry matter), untreated or heated in the DSC and contained within a screw-cap tube, a Blue Dextran solution in distilled or in simulated tap water (0.06%, 2.5 g for heated starch, 5 g for untreated starch) was added. The sample was suspended by treatment in an ultrasonic bath (3 min). The suspension was then rotated at 92 °C (45 min) on a wheel in an oven, cooled to room temperature, and centrifuged in a swing-out rotor (Sigma 4K10, 3000 rpm, 15 min). An aliquot of the supernatant (2 ml) was centrifuged (Sigma 3MK) at 15,000 rpm for 15 min to remove any suspended material. The absorbance of an aliquot of the supernatant was measured at 620 nm and compared to that of a standard 0.06% Blue Dextran solution in distilled or in simulated tap water. Calculated values of q were not corrected for solubilized matter. It was assumed that the water content of the starch sample was not altered by the heating in the DSC.

A similar sample preparation was applied for the determination of the solubility S at 92 °C in duplicate, except that distilled or simulated tap water was added instead of the Blue Dextran solution. An aliquot of the supernatant of the centrifugation at 15,000 rpm was diluted with distilled water and analysed for solubilized starch by the anthrone colorimetric assay with glucose as a standard (Fales, 1951). It was ensured that the concentration of simulated tap water was the same in blank, standard, and sample solutions.

2.5. Molar mass

Molar mass distributions of starch heated to 210 °C were determined by size exclusion – multi-angle laser light scattering with refractive index detection (SEC-MALLS-RI) on a Dawn-F multi-angle laser light scattering detector (Wyatt) and an ERC-7500 refractive index detector. The SEC equipment consisted of three columns: PLGel Guard, PLGel Mixed-C, and PLGel Mixed-E (Polymer Laboratories). DMSO/aqueous 1 M $NaNO_3$ at a ratio 9/1 (v/v) was used as the elution medium at a flow rate of 0.5 ml/min. Column and detector temperatures were 95 and 50 °C, respectively. Mass-average molar mass (M_w) was calculated from the molar mass distribution using the standard software of the instrument. Two methods were applied for the preparation of sample solutions: the sample was dispersed in distilled water (1 ml) and heated at 92 °C until complete dissolution. DMSO (9 ml) was added after cooling (a); the sample was dispersed in distilled water (1 ml) in an ultrasonic bath (5 min) and DMSO (9 ml) was added (b). All solutions were filtered over 0.2 μm (PTFE) prior to analysis.

2.6. Density

The mass density of intact starch and starch heated to 210 °C was determined in triplicate by micro-pycnometry at 20.0 °C in a pycnometer with a nominal volume of 1.5 ml. Sample size was 20–50 mg. The true volume was determined in fivefold with degassed distilled water. Distilled water and low viscous paraffin oil were used as the immersion media. Densities were calculated on a wet basis (water content 16.16%).

Bulk densities of starch in DSC pans were calculated using a pan volume of 70 μl (without insert).

3. Results and discussion

3.1. Preparative DSC

Because the stainless steel large volume pans required for DSC of water-containing samples at temperatures >100 °C have a smaller diameter at the top than at the bottom, it was impossible to remove the samples from the pans without damage to the sample. Fitting the pans with a thermally inert silicon rubber insert gave satisfactory results: the insert could be easily removed from the pan with tweezers, which allowed a trouble-free transfer of the heated starch sample to a screw-cap tube for further characterization. With insert, the sample mass at complete filling was 20–25 mg, whilst in conventional DSC without insert it was 50 mg.

Preparative DSC was compared to conventional DSC in order to establish the effect of the insert and the reduced sample mass. For potato starch the M1 and M2 transitions were comparable in both types of experiment, but a small shift in the HT endotherm was observed, which was considered acceptable. The homogeneity of potato starch heated to the completion of M1 was checked by scraping off the pellet in three separate layers, which were examined by optical microscopy. Differences in degree of gelatinization between granules were noticed in each layer, but there were no differences between layers. This suggests that heated potato starch samples are reasonably homogeneous.

3.2. DSC heating profile of potato starch

A DSC heating profile of potato starch is shown in Fig. 1. The temperatures indicated by the arrows correspond to the completion of the transitions designated as LT, M1, M2, and HT (=low temperature, melting 1 and 2, and high temperature) and were selected as the final heating temperatures in sample preparation by preparative DSC.

3.3. LT and M transitions in potato starch

Fig. 2 shows optical micrographs of potato starch heated to the completion of the LT and M1 and M2 endothermic transitions. No visible change in birefringence was observed by heating through LT. This observation, together with the location of LT below T_g (Fig. 1), supports our previous conclusion that LT is related to enthalpy relaxation due to slow physical ageing below T_g (Thiewes & Steeneken, 1997), which is a universal phenomenon for all amorphous and semi-crystalline materials (Struik, 1978). This makes the conclusion of some workers that this transition is associated with a melting process at low water content unlikely (Willenbücher et al., 1995; Randzio, Flis-Kabulska, & Grolier, 2002).

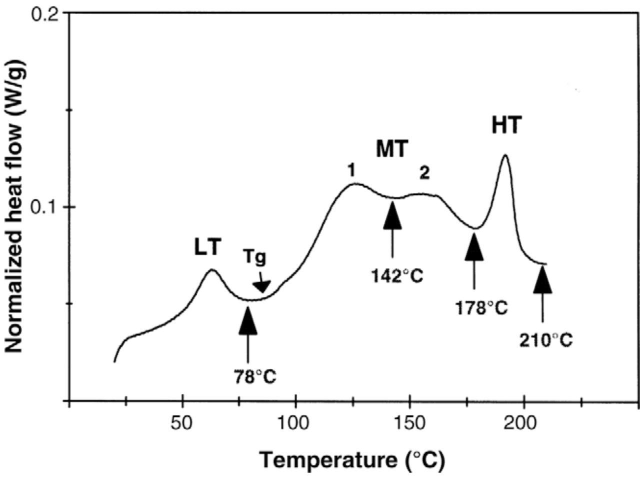

Fig. 1. DSC heating profile of potato starch with 16% water. Letters denote the thermal transitions. T_g is the glass transition temperature according to Thiewes and Steeneken (1997). Arrows indicate the final heating temperatures for thermal processing by preparative DSC.

M1 and M2 represent the granule melting transitions. After M1 the birefringence has largely disappeared (not shown), but the sample still has a powder-like appearance. Fig. 2 suggests that melting has started in the interior of the granule but is not yet complete after M1. Similar results have been obtained by static heat-moisture treatment of potato starch (20–26% water, 100–130 °C, 24 h). However, a significant birefringence remained after this treatment (Vermeylen, Goderis, & Delcour, 2006b). Heating through the M2 transition, i.e., to 178 °C, is sufficient for complete granule melting, but granule individuality is still preserved at that temperature.

Table 1 displays the swelling capacity q and the solubility S at 92 °C. It was attempted to determine q also at ambient temperature, but the amount of swelling was too low to obtain reliable results with the available sample size. Our results show that q in hot water is dramatically reduced on heating through the M transition. This, together with the microscopic observations discussed above, indicates that heating with 16% water in the DSC may provoke similar effects as a pronounced heat-moisture treatment (Jacobs & Delcour, 1998). S is also reduced by the thermal treatment, but increases somewhat when heating through the M2 transition. We observed a distinct medium effect on q which is due to the polyelectrolyte effect exerted by the phosphate ester groups in potato starch. This effect is screened by the ions in simulated tap water. The sensitivity of q to the medium diminished as the heat treatment advanced. This is likely a consequence of the increasing degree of physical cross-linking (Flory, 1953), but a removal of the phosphate groups by thermal de-esterification could play a role as well.

Our results nicely complement the wide- and small-angle X-ray scattering observations (WAXS and SAXS) on these transitions in potato starch at low water content (Zobel, Young, & Rocca, 1988; Vermeylen et al., 2006a). Thereby it is helpful to view an intact starch granule as an assembly of 'amorphous' and 'crystalline' growth rings, the latter being composed of stacks of alternating crystalline and amorphous lamellae with a spacing of 9 nm (Cameron & Donald, 1992). The WAXS and SAXS observations can be summarized as follows: a decrease in crystallinity from the start of the melting endotherm (a), a gradual change from B- to A-type

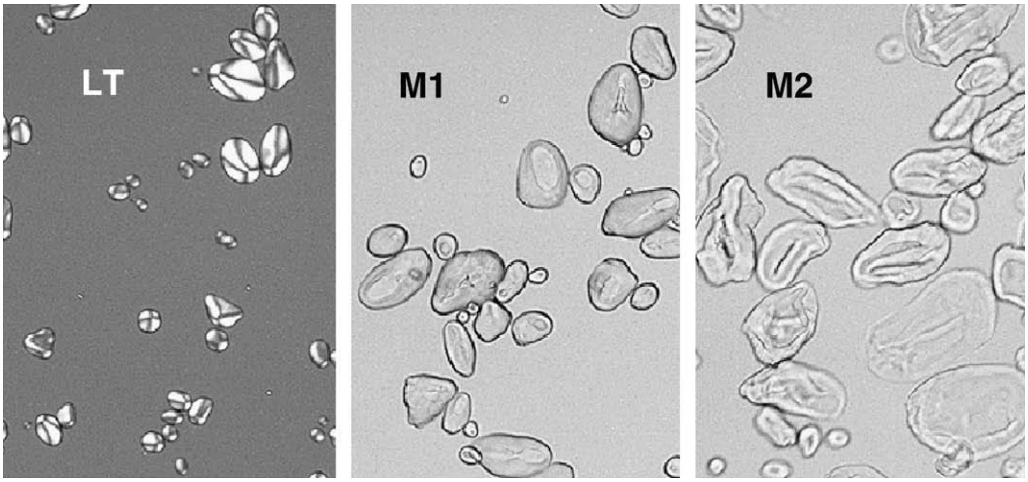

Fig. 2. Optical micrographs of potato starch with 16% water heated through the LT, M1, and M2 transitions. Polarization optics (left); bright field optics (centre and right).

Table 1
Swelling capacity q and solubility S at 92 °C of potato starch with 16% water heated through the M transitions.[a]

Suspending medium	Distilled water		Simulated tap water	
Final heating temperature (°C)	q (g/g)	S (%)	q (g/g)	S (%)
Untreated	82.4	23.6	20.1	8.3[b]
142 (M1)	12.9	9.4	5.5	7.5
178 (M2)	5.0	12.6	4.9	12.5

[a] Standard deviations in q and S are 0.95 g/g and 0.92%, respectively.
[b] Value is lower than that obtained in experiments at a larger scale.

Table 2
Density ρ, solubility S, and mass average molar mass M_w of potato starch heated with 16% water through the HT transition.

Final temperature (°C)	ρ (g/cm^3)	S (%)	M_w (10^3 g/mol)
Untreated	1.54 ± 0.03[a]	8.3[b]	170,000[c]
210 (HT)	1.28 ± 0.10[a]; 1.30 ± 0.08[d]	99.6[b]; 95.5[e]	274[b]; 185[e]

[a] In distilled water ($n = 3$).
[b] In simulated tap water at 92 °C.
[c] M_w of potato amylopectin according to Yoo and Jane (2002).
[d] In paraffin oil ($n = 4$).
[e] In simulated tap water at ambient temperature with ultrasonic treatment.

crystallinity (b), an increase of the 9 nm lamellar order on heating until well into the melting transition followed by a decrease (c), and partial recrystallization into the A-type on cooling without recovery of lamellar order (d). The latter observation suggests that crystallites formed on cooling are distributed at random within the granules. This would explain the profound decrease in q on heating through the M transitions. Obviously, a random distribution of crystallites provides a much more effective physical cross-linking than the ordered arrays of crystallites in the intact granules.

3.4. HT transition in potato starch

On going through the HT transition, potato starch with 16% water changes its appearance from a particulate to a homogeneous hard solid and its appearance turns from opaque into glossy. This suggests the disruption of granule individuality, which marks the transition into a true molecular melt (Willenbücher et al., 1995). It was not possible to disperse the pellet in water without the occurrence of dissolution. For that reason microscopy was performed on the intact dry pellet. Fig. 3 shows a continuous structure with randomly dispersed 'particles', which are supposed to be gas bubbles. The heated starch was analysed for density, solubility, and molar mass and the results were compared to those for untreated starch (Table 2). The density of untreated starch was somewhat higher than the literature value of 1.47 g/cm^3 for potato starch with 16% water (de Willigen & de Groot, 1967). This is acceptable given the small sample size. We observed a significant decrease in density after heating through HT. This supports our contention that gas bubbles are entrapped in the melt. These arise from the voids between the starch granules in the original sample. Similar density values were obtained irrespective of the immersion medium, water or oil. This suggests that penetration of water into the glassy pellet at quiescent conditions is negligible at the time scale of the density determination. However, the melted starch is almost completely soluble in water after heating to 92 °C or after treatment in an ultrasonic bath. Table 2 also shows that the transition into the solution state is accompanied by severe molecular degradation. A similar effect was observed when potato starch with 80% water was transferred into the solution state by heating to 180–220 °C (Steeneken & Woortman, 2008).

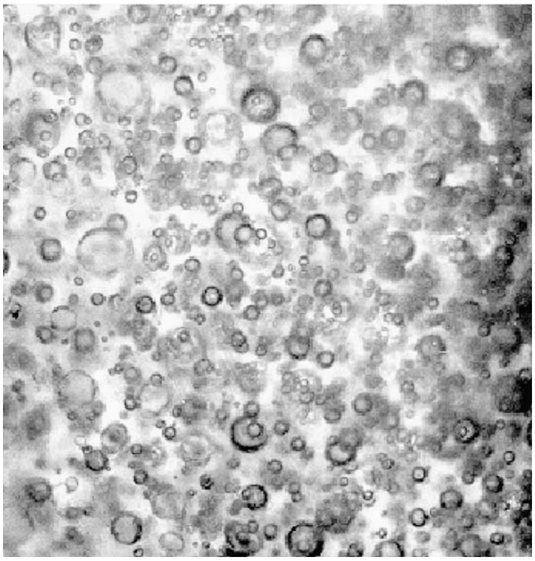

Fig. 3. Optical micrograph (bright field) of potato starch with 16% water heated through the HT transition.

Fig. 4 shows that the HT transition may be also observed at water contents at least as high as 35%, provided that the final temperature of the DSC scan is high enough. Our results also indicate that the location and magnitude of HT depend on the source of potato starch. This is in accordance with the results of Willenbücher et al. (1995), who reported that the location of HT depends on the type of counter cation at the phosphate ester group. In comparison to Fig. 1, LT and M2 have disappeared and M1 is preceded by a tail that represents the last trace of the gelatinization transition G. This latter transition represents gelatinization in excess water accompanied by the uptake of water (Donovan, 1979; Evans & Haisman, 1982; Jenkins et al., 1994). As the equilibrium water content of intact starch granules is ca. 30% (BeMiller & Pratt, 1981), the initial amount of excess water is very small in starch with 35% water. This explains that the G transition is barely observable in the samples of Fig. 4 and has vanished in starch with 16% water. M1 represents melting at a constant limiting water content. The disappearance of M2 in Fig. 4 is due to a lowering of the optimum temperature for starch recrystallization at increasing water content (Farhat, Blanshard, & Mitchell, 2000). Finally, LT has vanished because T_g has dipped below room temperature at a water content of 35% (Zeleznak & Hoseney, 1987).

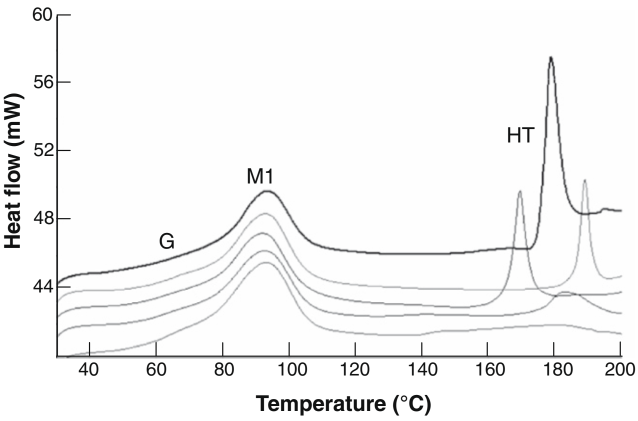

Fig. 4. DSC heating profiles of five potato starches with 35% water. Letters denote the thermal transitions.

Because it seemed unlikely to us that the transition between two amorphous states would be accompanied by a sizable enthalpic effect, we studied the effect of a variation in bulk density of the starch with 16% water in the DSC pan on the magnitude of the HT transition in experiments without insert. Loose filling, tapping after loose filling, and filling with added flow conditioner (0.02%) resulted in approximate bulk densities of 0.6, 0.85, and 1.0 g/cm^3, respectively. The magnitude ΔH of the HT endotherm decreased in that order from 3.9 via 2.5 to 1.1 J/g. There was no effect of sample mass on ΔH. This suggests strongly that this endotherm does not represent a true thermodynamic transition, but is rather a – quite useful! – artefact associated with a sudden volume change due to the disappearance of part of the voids between the granules during the transition to a molecular melt. The void fraction and hence the expected volume change is less at higher packing density. The observation that potato starch with 16% water heated in silicon oil at a 1:1 ratio still displays a HT transition suggests that a volume change is not the only explanation for HT. In fact, potato starch settled in this medium during heating. Maize starch with 16% water, having a smaller particle size, did not show a HT transition when heated in silicon oil, at least not below 210 °C.

3.5. Observations on maize starch

Some preliminary experiments were done on maize starch with 16% water. It was observed that DSC profiles recorded with and without insert did not coincide. This indicates that the conditions of preparative DSC do not truly represent the events that occur in a common DSC experiment. Because, in contrast to potato starch, the maize starch pellets shrunk on heating, an insert was not required for their removal from the pans. Inspection of the samples heated through the M transition without insert revealed that these were inhomogeneous: about half of the granules were still birefringent and melting had occurred predominantly in the upper part of the sample. The most likely explanation for sample inhomogeneity is the high cohesiveness of maize starch powder in comparison to potato starch powder, which is related to its smaller particle size. This leads to a lower bulk density. The observed inhomogeneous melting precluded a study as that for potato starch at the time of the present investigation. It also questions the validity of conventional DSC experiments with maize starch at the conditions employed. A possible solution is to increase the packing density by addition of a flow conditioner and/or compression of the powder sample. Other options are to reduce sample size and heating rate (Yu & Christie, 2001). Whatever the selected approach, it should always include a test for sample homogeneity after thermal processing.

4. Conclusions

DSC heating profiles of starch with low water content are complex, featuring a number of endothermic transitions. The LT endotherm is due to enthalpy relaxation that occurs on ageing below T_g. The M and HT endotherms represent the melting of starch granules and the transition into a molecular melt, respectively. In potato starch with 16% water, the individuality of the granules is preserved until the end of the M2 transition, i.e., at least up to 178 °C. Heating through the M transition is accompanied by a strong reduction in swelling capacity, analogous to a heat-moisture treatment. This reduction parallels the overall decrease in crystallinity and the partial recrystallization on cooling without restoration of the lamellar order, which were reported by other workers (Zobel et al., 1988; Vermeylen et al., 2006a). This suggests that randomly dispersed crystallites are much more effective as physical cross-links than crystallites in ordered arrays that exist in the intact granules. The transition into a molecular melt is accompanied by significant molecular degradation. It is likely that the HT endotherm, which persists at water contents up to at least 35%, does not represent a true thermodynamic transition, but is an artefact due to a volume change in the sample.

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