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Wheat starch gelatinization under microwave irradiation and conduction heating

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Abstract

Wheat starch–water dispersions at excess water conditions were heated under mixing to different temperatures by either microwave energy at 2000 W or by conduction heating in order to compare both heating methods.

The effects of microwaves and conduction heating on starch gelatinization were evaluated using different techniques; It was possible to obtain the same viscosity for both heating methods but the required time was much shorter for microwaves heated starch dispersions. No unique structures due to the heating method were observed under the microscope. At the beginning of the heating process an increase in the mobility of the starch protons occurred, slightly higher for microwaves heated samples. Likewise, DSC experiments revealed an increase in the enthalpy for short times microwave heated samples. The heating method caused no differences in the mechanism of gelatinization; nevertheless the crystallinity disappeared at a higher rate when heated with microwaves.

Keywords: Starch; Microwave heating; Conduction heating; Gelatinization; Dielectric properties; Differential scanning calorimetry; X-ray; Nuclear magnetic resonance; Transmission electron microscopy

1. Introduction

Being one of the most plentifully used ingredients, starch imparts structure, texture, consistency and appeal to many food systems.

Most of the unique properties of starch arise from the fact that it is composed of two distinct polymer fractions, amylose [(1–4)-linked α-D-glucan] and amylopectin [(1–4),(1–6)-linked α-D-glucan. The conventional model of starch is that the granule appears to be made up of concentric layers of alternating low-density amorphous shells and high density semi-crystalline shells. The width of a high-density layer is estimated to be in the range 120–400 nm thick. Amylopectin is located both in the amorphous and semi-crystalline shells. In the amorphous shells amylopectin is predominantly in the double helical form, although its crystallinity is reduced possibly due to increased interactions with amylose. The semi-crystalline shells consist of alternating amorphous and crystalline lamellae. Previous studies have indicated that in wheat starch the amorphous and crystalline lamellae are ≈22 and 68 Å thick, respectively, giving an overall repeat of about 90 Å (Cameron & Donald, 1993). The crystalline lamellae are believed to consist of the ordered double helical amylopectin side chain clusters and are alternated with more amorphous lamellae consisting of the amylopectin branching regions according to the amylopectin model of Robin, Mercier, Charbonnière, and Guilbot (1974).

There is an additional level of organisation, between that of the lamellae and the growth shells termed "blocklets" (Gallant, Bouchet, & Baldwin, 1997). The blocklets appear as more or less spherical structures in both shells; in the amorphous and in the semi-crystalline shells. According to the most recent studies, the blocklets which are amylopectin-based are suspended in an amylose-based supporting matrix (Ridout, Parker, Hedley, Bogracheva, & Morris, 2004). Support for this model has come from the recent

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atomic force microscopy (AFM) studies performed by Ridout, Gunning, Parker, Wilson, and Morris (2002, 2003, 2004).

On heating starch in excess water conditions the granules swell, the starch polymers are partially solubilized and leached from the granules, and finally the starch granules disintegrate. The irreversible change taking place on heating is commonly denominated gelatinization.

Heat transfer in conductive heating is driven by the differences between the low internal and high external temperatures. This tends to be a slow heat transfer mechanism. However, heating that occurs as a result of microwave irradiation is caused by molecular friction resulting from the dielectric coupling of molecules as they orient themselves with the oscillating electromagnetic field with frequencies in the microwave region of the radiation spectrum (Goebel, Grider, Davis, & Gordon, 1984). The internal generation of heat, as a consequence of absorption of microwave energy, results in a bulk heating throughout the whole sample, causing a faster heating rate than in conductively heated samples.

Microwave heating of a material depends on its dielectric constant (ε') which determines how a material couples with microwaves, and on the dielectric loss factor (ε'') which expresses the ability of the material to absorb microwave energy and transform it into heat (Mudgett, 1982).

In the present study, starch granule gelatinization by microwave and conduction heating was investigated. A better understanding of the molecular and structural changes that occur in the starch granules during heating would enable effective control of its functional behavior during processing.

2. Materials and methods

2.1. Sample preparation and heating conditions

All samples were studied at a wheat starch (excelsior, supplied by Avebe, UK) concentration of 9% (w/w), except for those used to obtain the flow curves when, for practical reasons, a concentration of 4.5% (w/w) was used. For all the samples the water mass was 45 g since water is a critical component of a food with regard to heating by microwave energy.

Starch dispersions inside non-microwave absorbing plastic bags (17 × 5 cm) were placed directly in a waveguide, which acts as a heating chamber, of a specially constructed microwave oven. The 2450 MHz oven was operated with 2000 W incident microwave power. The heating chamber is divided in two sections connected by a semi-cylindrical slot (8 mm diameter, 20 mm height). Mixing was carried out with a compressed air system connected to the waveguide, which forced the sample from one section to the other every 1.5 s through the semi-cylindrical slot. Shearing was provided to promote mixing of every part of the starch/water suspension and also transfer heat throughout the entire sample mass. For conduction heating, water could be circulated through channels in the lid of the chamber by connecting to a water bath in order to heat conventionally.

2.2. Measurements of dielectric properties

In order to obtain samples exhibiting degrees of structure loss, samples were prepared by microwave irradiation, heating up to temperatures corresponding to various extents of gelatinization. After heating, samples were immediately cooled down in cold water to prevent any further gelatinization and dried in a fan oven at 35 °C.

The dielectric properties of starch suspensions were determined during drying using a dielectric probe and a network analyzer (made by Hewlett Packard) at 2450 MHz. The dielectric probe was calibrated by using air, short circuit and water at 20 °C before dielectric measurements were done.

2.3. Rheology

Viscosity of the hot sauce was measured immediately after the heating process (to prevent any retrogradation effects, which may occur on cooling). The sample was equilibrated at 60 °C in the MV1 sensor geometry in the Haake VT550 for 5 min. Measurements were taken by increasing the shear rate. A shear rate sweep was performed from 0.01 to 1000 s^{-1}.

2.4. Microstructure evaluation

Dispersions were sampled for microscopic evaluation. A single layer of granules was observed with a polarizing microscope using both ordinary and polarizing light after diluting the samples 10 times in distilled water. Observations were realized with 10× magnification at ambient temperature.

2.5. TEM

Starch granules that had been subjected to heat treatment either by conventional means or by microwaves were prepared for transmission electron microscopy in the following manner.

Several drops of suspended starch granules were placed into a 0.1% aqueous solution of ruthenium tetroxide and fixed for 30 min. The samples were rinsed in distilled water and prestained in 1% aqueous uranyl acetate overnight. The granules were then suspended in 2% warm agar and allowed to set. Dehydration was via ascending grades of ethanol (70%, 90% and 100%), followed by 100% acetone which acts as an ante-medium between the alcohols and the resin. Samples were then soaked in a 50/50 mixture of Araldite epoxy resin and acetone followed by pure resin. Finally the samples were embedded and polymerised at 60 °C for 48 h.

Ultrathin sections were cut on a Reichert Ultracut E at 100 nm thick using a Diatome diamond knife, they were

collected on 200 mesh copper grids and stained with Reynolds lead citrate.

All the sections were examined using a Jeol 1200 EX transmission electron microscope operated at 100 kV. Images were recorded using a Gatan Bioscan CCD camera DigitalMicrograph software.

2.6. DSC measurements

Samples prepared for DSC analysis were cooled immediately after removal from the oven in dry ice to minimize further temperature increases. DSC analysis was carried out with a Perkin-Elmer DSC7 instrument. The DSC was programmed to heat from 20 up to 100 °C at 10 °C/min, with data analysis performed using standard software. Samples of ≈30 mg were weighted into a Perkin-Elmer DSC aluminum sample pan on a microbalance. The pan was hermetically sealed and immediately examined in the DSC. An empty sample pan was used as reference. The heats of transition (ΔH) were determined from the areas of the thermograms. To obtain the area, a baseline was constructed as a smooth line from the beginning to the end of the transitions. Enthalpy of gelatinization was related to the dry starch. The peak temperature is defined as the point of maximum endothermic heat flow relative to the baseline. Measurements of these values are based on the mean of three runs. The sample moisture content was established by recording the weight loss after storage in a vacuum oven at 80 °C for 24 h after puncturing the DSC pan.

2.7. NMR spectroscopy

Starch dispersions (9% w/w) were prepared in NMR sample tubes. The tubes were sealed and placed directly in a specially constructed waveguide of a microwave oven. The 2450 MHz oven was operated with 2000 W incident microwave power. Starch dispersions prepared conventionally were heated conductively in a preheated water bath at 70 °C. The temperature was checked with a thermocouple. After heating, the samples were cooled down to 20 °C to stop the gelatinization process.

The spin–spin relaxation was measured for circa 0.5 g of each sample using a Mara-ultra (23 MHz) TD-NMR spectrometer at 25 °C. The samples were allowed to settle in the NMR tube on cooling immediately after heating by either conduction or microwave method. 32 k data were acquired using a CPMG pulse program with a τ of 100 μs and a recycle delay of 10 s.

2.8. X-ray

X-ray experiments were carried out on station 16.1 at the Daresbury Laboratory. Starch slurries in water were sealed in modified aluminum DSC pans with a mica window. Two gas-filled proportional wire chambers were used to collect the diffraction patterns. X-rays scattered through wide angles were detected by an Inel detector. Simultaneously, X-rays scattered through smaller angles were detected by a quadrant detector, located at a distance of 2.4 m from the sample. The low divergence, high intensity beam of radiation with approximately the wavelength of CuK_α ($\lambda = 1.5$) was collimated with slits. To provide accurate temperature information a thermocouple was inserted into the sample. The sample was heated in situ using a Linkam THM600 hot stage.

Simultaneous in situ measurements of SAXS and WAXS patterns were made while heating from 20 to 90 °C at 5 °C/min heating rate.

3. Results and discussion

3.1. Temperature profiles

Representative time–temperature profiles for microwave (MW) and conventional (CV) heated samples are shown in Fig. 1. As would be expected, times to reach a certain temperature were much shorter using microwave irradiation than conductive heating.

For conventional heating samples, the temperature increased gradually during heating. For microwave heating samples, after reaching the gelatinization temperature, the sample temperature increased more rapidly.

The increasing rate of temperature rise in microwave-heated samples was believed to be caused by increased efficiency of energy conversion in starch granules after the changes in crystallinity accompanying the phase transition.

Fig. 2 shows the dielectric properties values *versus* water content in dry basis (*g* water per gram of dry starch) for starch dispersions with different degrees of gelatinization.

It is observed in this figure that ε' for all the different degrees of gelatinization were the same as those of the native starch dispersions. The loss factor ε'' had greater values for samples with a higher degree of gelatinization than for those with a lower degree of gelatinization. The increase in the dielectric loss factor results in a much shorter time to reach a particular temperature. When the starch granules are more crystalline, as they are in the less advanced stages of starch granule transformations, microwave interaction is smaller because there are rigid, more crystalline structures within the unchanged granules (Goebel et al., 1984).

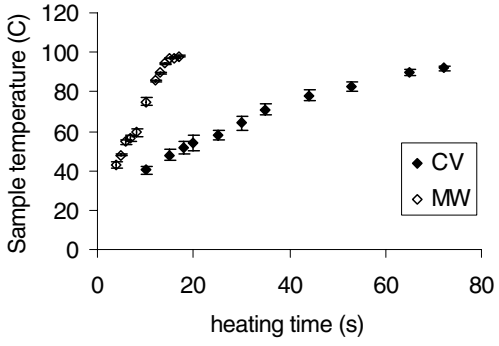

Fig. 1. Time–temperature profiles of starch dispersions (4.5%) during conventional (CV) and microwave (MW) heating.

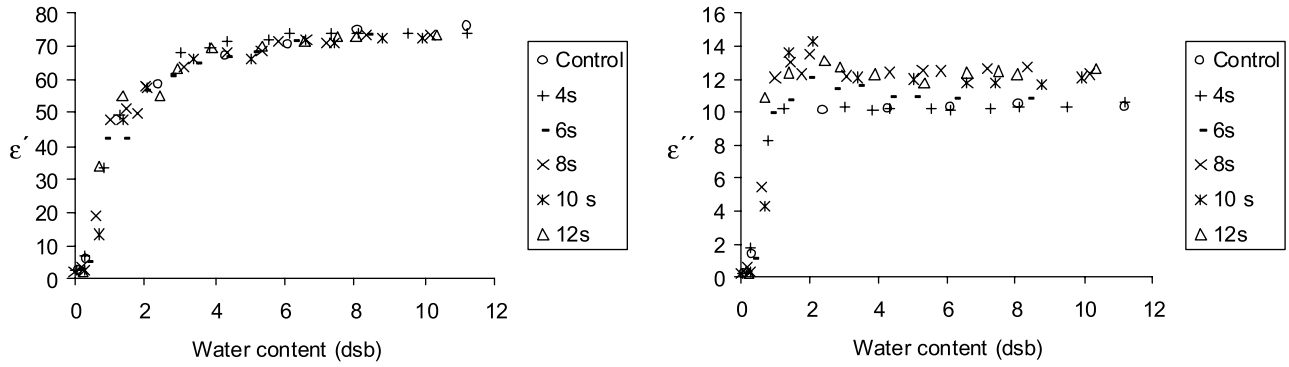

Fig. 2. Dielectric properties during drying of starch dispersions heated for different times at 2000 W microwave power.

The dielectric properties were also greatly affected by the presence of water during drying. As water content decreased, the sample had decreased ability to rotate and couple with the electromagnetic energy. However the presence of water also affected indirectly the dielectric properties by altering the viscosity of the system. In this sense, the increased value of the loss factor at low water content could be due to the increased viscosity of the gelatinised sample.

3.2. Rheological characterization

Fig. 3 shows the results of the viscosity of preheated samples to preset temperatures determined at 60 °C and at an arbitrary shear rate of 200 s^{-1}. The sample temperature in each paired comparison was kept constant to minimize any difference caused by the stages in granule swelling.

As the cooking time increased, the viscosity raised dramatically. The increase in viscosity is generally ascribed to the granules imbibing more free water as they swell (Miller, Derby, & Trimbo, 1973).

The different heating times for both heating methods did not result in significant differences in the obtained viscosity values although the process of gelatinization is known to be affected by the rate of heating; Doublier, Llamas, and Le Meur (1987) observed that when a slow temperature increase is applied, the final swelling values are the lowest.

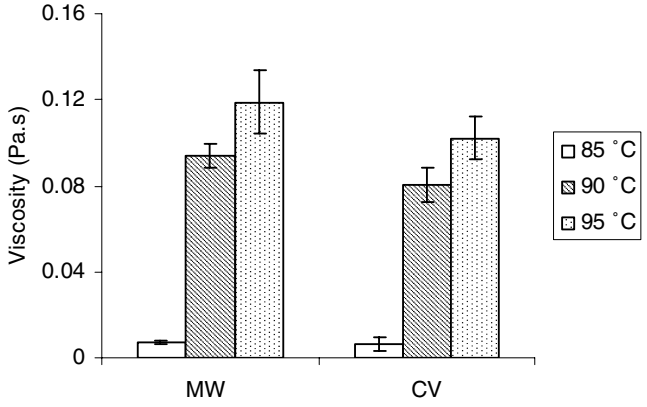

Fig. 3. Apparent viscosity for microwaves and conventional preheated starch solutions. The viscosity was determined at 60 °C and at a shear rate of 200 s^{-1}.

Zylema, Grider, Gordon, and Davis (1985) also observed that the degree of swelling of the conductively heated samples was similar than in the microwave-heated samples when heated with equalized heating times.

3.3. Microstructure evaluation

The stages of swelling that were identified under the light microscope suggested that the same overall sequence of swelling was occurring independently of the heating method. No structures unique to a giving heating method were found. Fig. 4 shows micrographs during starch gelatinization under microwave heating.

The size of the native wheat starch granules can vary greatly. The granules are clear and colorless but in the presence of iodine amylose and amylopectin stain blue and violet, respectively. At the beginning of the gelatinization process, small granules began to swell into disc shapes and then folded into saddle shapes. As they swelled, the swollen starch granules became increasingly susceptible to shear disintegration. On heating to 80 °C, most granules became strongly swollen and distorted and the individual starch granules were less easily distinguishable. By further heating to 95 °C the starch granules appeared disintegrated and melted together with an homogeneous appearance, the starch paste usually consisted of swollen gelatinised granules or, occasionally, granular fragments dispersed in a predominantly amylose solution.

This sequence is similar to that described by Zylema et al. (1985), Goebel et al. (1984), Conde-Petit, Nuessli, Handschin, and Escher (1998) for wheat starch gelatinization under microwaves and conventional heating.

Starch samples isolated after heating to defined stages of the gelatinization process were also examined by transmission electron microscopy to visualize at high resolution the effects of molecular structure loss.

The amorphous regions of the granule appear light in the resulting TEM images (Fig. 5), whilst the more electron dense crystalline regions appear darker. The presence of the lamella ≈7–9 nm thick is observed. This variation is due to the fact that not all sections are exactly perpendicular to the direction of the banding. TEM images of the lamellae indicate that the region between the side chain clusters within

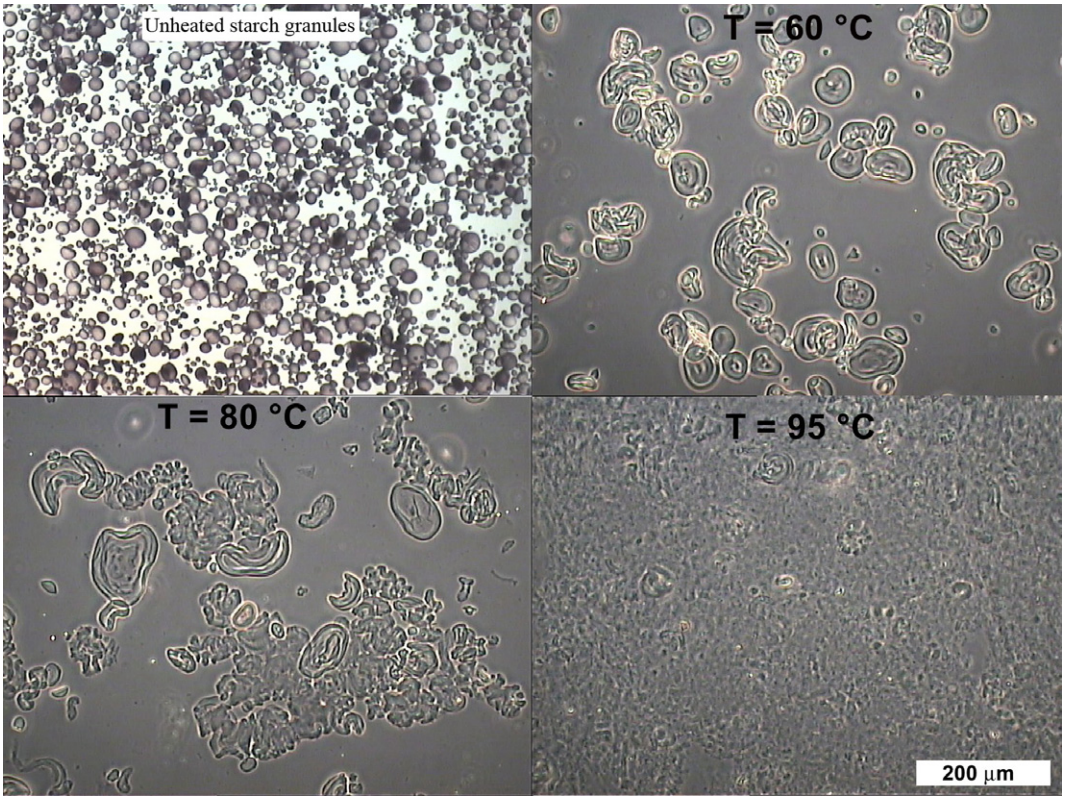

Fig. 4. Light micrographs of wheat starch gelatinization under microwaves heating at 2000 W.

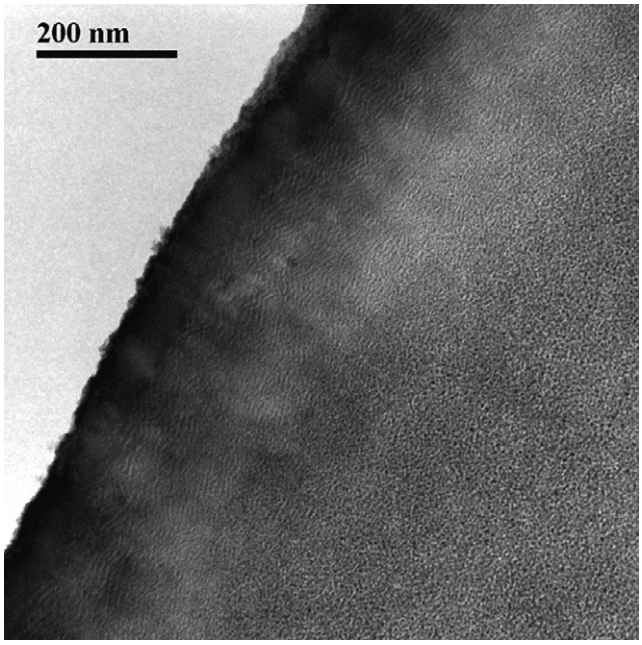

Fig. 5. Control wheat starch granule (unheated) showing periodic banding in the outer crystalline layer (≈7–9 nm).

the lamellae is also of an amorphous nature and that the crystalline lamella are therefore not continuous.

A similar starch structure is observed for conventional heated samples than for microwaves heated samples (Fig. 6) therefore no significant differences could be attributed to the heating regimes.

It is well known that granules swell dramatically when heated in water, prior to their ultimate disintegration. However, during this initial swelling process, little loss of crystallinity occurs since the 7–9 nm repeat distance remained unchanged after heating at 52 °C. Thus the swelling, which can readily be seen by optical microscopy must be occurring within the amorphous growth rings as was previously reported by Donald, Kato, Perry, and Waigh (2001).

3.4. DSC transitions

Detection of the heat flow associated with phase transitions allows for the determination of the temperature range over which transitions occur and the enthalpy change involved in such transitions.

The enthalpy change for this phase transition for native wheat starch, from the present measurements was 11.9 ± 0.9 J/g starch and the obtained value for the peak temperature was $59.0\,^{\circ}\mathrm{C} \pm 0.7$. Values are similar to those found in previous studies (Cooke & Gidley, 1992; Donovan, Lorenz, & Kulp, 1983; Jankowski & Rha, 1986; Jenkins & Donald, 1998; Noel, Ring, & Whittam, 1993; Yost & Hoseney, 1986).

The endothermic enthalpy values and the peak temperature obtained from the DSC traces, are plotted in Fig. 7 as a function of the product temperature at the end of the heating process for each heating method.

As the heating times increased, there was a concomitant increase in the degree of starch gelatinization, as is seen by

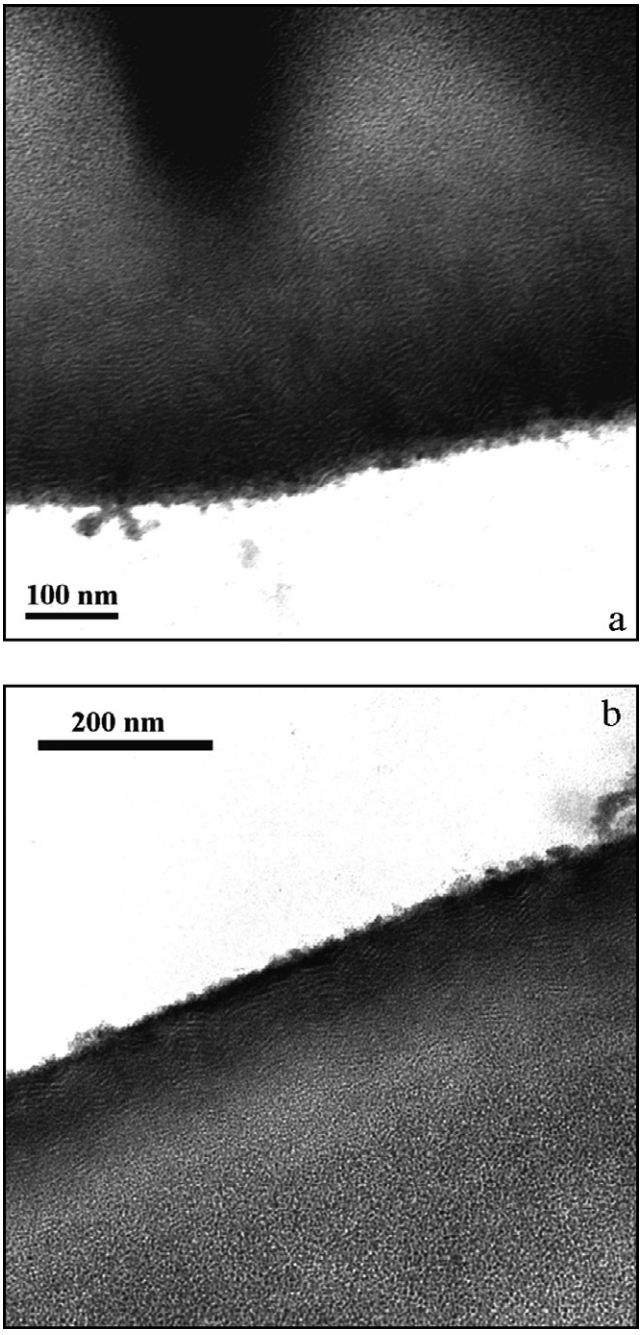

Fig. 6. Conventional (a) and microwave (b) heated wheat starch granule showing periodic banding in the outer crystalline layer (≈7–9 nm).

the reduction in the endotherm peak surfaces. A progressive shift of the endotherm to higher temperatures was observed once the onset of the endothermic transition was reached which could be due to the more perfect structure of the remaining crystals.

Microwave heating carried out to temperatures below the peak of the DSC endotherm resulted in enthalpy levels 25% greater than the corresponding values for native starch.

The high gelatinization enthalpy indicated that more energy was required for the gelatinization of these starch granules compared to the energy required for the gelatinization of conductive heated samples.

The reason for these differences may be related to fast heating rates. To probe this hypothesis a starch solution was heated up while stirring on a hot plate. To eliminate differences in heating rates distilled water temperatures were adjusted so the time to reach a particular temperature in the sample was the same as for a similar sample heated by microwave irradiation.

The endothermic parameters obtained from the DSC are plotted versus the sample temperature reached during heating in Fig. 8.

From these results it was concluded that high heating rates show an increase in the enthalpy above the levels of the native starch granules. Two possible explanations exist as to why the enthalpy of gelatinization increases as a starch sample is more rapidly heated. One possibility is that the starch granules are annealing when exposed to these temperatures (Blanshard, 1987). If the crystalline regions are increasing in size, this could explain an increase in the energy required to disorder the system. Overall, the more ordered nature of starch granules post annealing restricts water penetration and consequently gelatinization temperatures are elevated (Tester et al., 2001). To probe this hypothesis a starch solution was heated up while stirring on a hot plate up to 40 °C and held for different times. Results from this experiment are shown in Fig. 9.

An annealing effect was discarded since an increase in the enthalpy values was not observed after 3 h of holding the starch solution at 40 °C. A second possible explanation involves hydration of the starch granules.

Donovan (1979), Evans and Haisman (1982) have suggested that the enthalpy associated with gelatinization is the result of multiple thermal processes occurring within the same time frame. In essence, the gelatinization endotherm represent the difference between the endothermic energy associated with the transition (melting of the crystallites, granule swelling and denaturation) and the exothermic energy associated with the transition (hydration of starch molecules).

It seems likely that the extent of hydration of starch granules is greater when processing at rapid heating rates since water diffusivity is higher at higher temperature values. This being the case the starch solutions would exhibit a greater endothermic response because of a more complete hydration; the exothermic portion of the gelatinization process would be smaller, allowing more of the endothermic events to be recorded.

3.5. Proton NMR relaxation study

Time domain nuclear magnetic resonance spectroscopy was used to study the starch–water distribution before and after heating by microwave and conduction heating methods. The transverse relaxation time (T_2) was measured by CPMG pulse sequence and only observes the 'mobile' protons.

Distributive exponential fits to the CPMG data show several mobile proton populations. In the unheated starch

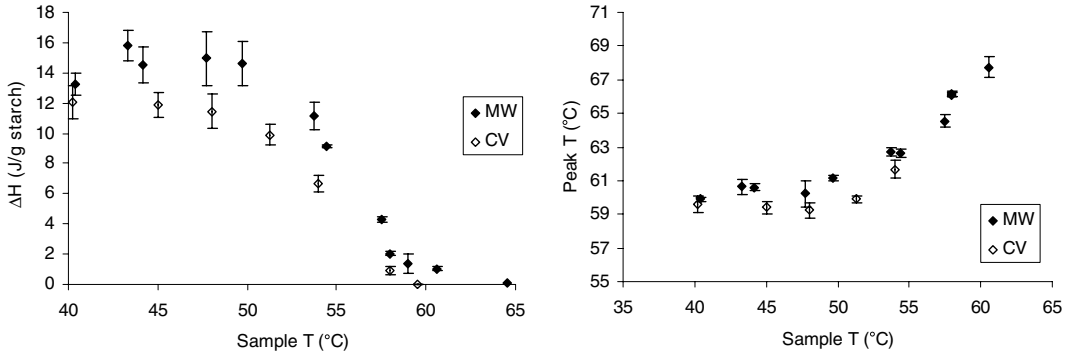

Fig. 7. Gelatinization enthalpy and temperature for starch solutions *vs* sample temperature after heating conventionally or with microwaves at 2000 W.

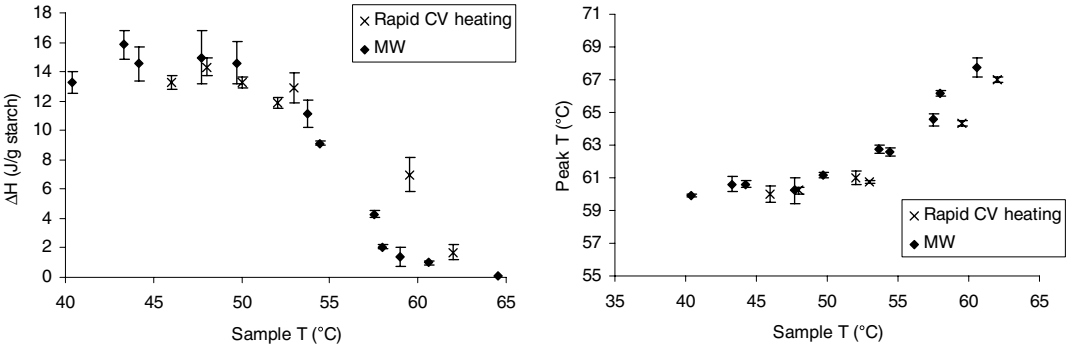

Fig. 8. Gelatinization enthalpy and temperature for starch solutions *vs* sample temperature after rapid heating conventionally or with microwaves at 2000 W.

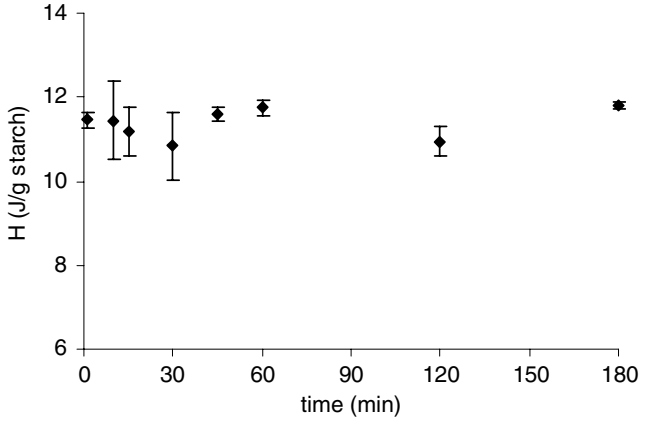

Fig. 9. Enthalpy values of starch solution hold for different times at 40 °C.

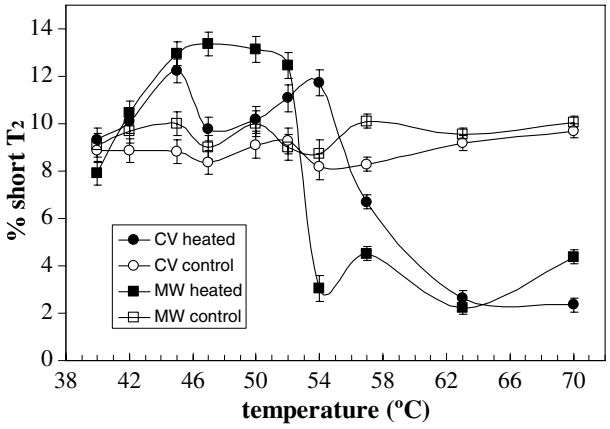

Fig. 10. The relative proportion of short T_2 component with microwave and conventional heating. The error bars indicate the uncertainty in acquisition and fitting not sample heterogeneity. The line interpolating the data is just a guide to eye.

slurries these can be approximated to mobile extra granular water ($T_2 > 0.1$ s) and less mobile intragranular water ($T_2 < 0.1$ s) as previously discussed by Tananuwong and Reid, 2004. Further detailed assignment should not be attempted as it requires an assumption that there is no chemical exchange of protons on the time scale of the NMR experiment and that the decay is exponential, which is not strictly true, particularly when the protons are less mobile.

The intensity of the short T_2 component relative to the total intensity varies with heating, as shown in Fig. 10. The control data also shown in Fig. 10 are from the same samples, before heating. Both microwave and conduction heating increases the relative proportion of the intragranular population. The microwave heated samples have slightly more intragranular protons and have more completely gelled at 54 °C than the conduction heated samples. This could be interpreted as an increase in hydration of the granules before gellation by microwave heating.

However, analysis of microwave heated starch–D_2O slurries suggests that the increase in intragranular population is from mobilized starch protons rather than from a

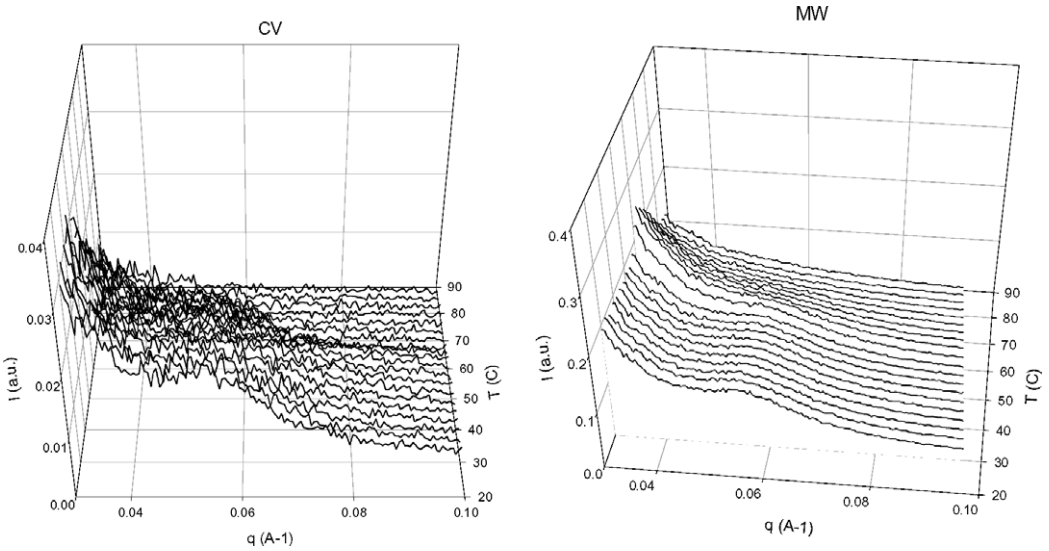

Fig. 11. Changes in small-angle X-ray scattering with increasing temperature of conventional and microwave preheated wheat starch.

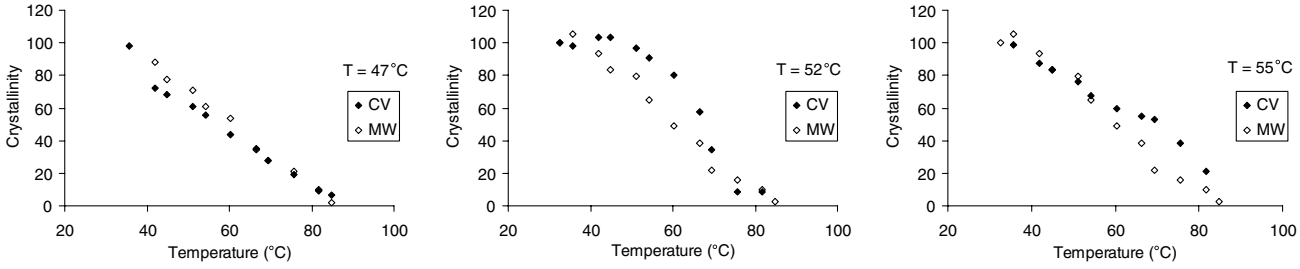

Fig. 12. Crystallinity *vs* temperature for conventional and microwave preheated wheat starch suspensions.

change in water population. These data show a partial gelatinization of the starch at short heating times by microwave heating. This observation is reproducible but subtle, particularly with respect to the variance in the data due to the heterogeneity of the samples and heating methods.

3.6. X-Ray diffractometry

The wheat starch structure was further investigated by X-Ray in which samples were taken to temperatures similar to those used for DSC and NMR experiments. Fig. 11 shows SAXS curves for wheat starch heated conventionally or by microwaves up to 52 °C chosen to represent the general behaviour observed for all the samples.

For both samples it can be seen in this figure a single peak, associated with the regular lamellar spacing within the granule. It is observed that this peak becomes less pronounced in the same way during gelatinization, at no temperature is it observed to shift in position thus showing that the heating method has not altered the gelatinization mechanism.

Simultaneously with the collection of SAXS data, WAXS profiles were also collected. The crystallinity index was calculated for each sample independently as a function of temperature. These plots are shown in Fig. 12 for preheated samples up to preset temperatures below the peak endotherm observed in the DSC thermograms. Values of crystallinity index, based on the method of Wakelin, were obtained from the gradient of a fitted line to a plot of $(I_u - I_a)_{2\theta}$ versus $(I_c - I_a)_{2\theta}$, where I_u, I_a and I_c are the scattered intensities at a given value of 2θ for the data set, and for the amorphous and crystalline reference samples respectively. These reference samples were chosen as the last (fully gelatinised) and first (ungelatinised) data points as a function of temperature, respectively.

It is observed in this figure that the rate of change of crystallinity with temperature is a bit higher for the microwave samples which can be related with a more advanced gelatinization process of the starch granules as revealed by the NMR results.

4. Conclusions

Both, conventional and microwave heating caused starch gelatinization. The same sequence of gelatinization stages was observed for both heating methods. Starch gelatinization caused an increase in viscosity; under the conditions applied, the same viscosity values could be obtained but the required time to achieve a high viscosity was four times higher for conventional heated samples.

Before any swelling and hydration of the starch granules occurred, an increase in the enthalpy values was observed for microwave heated samples, during this stage NMR results revealed a mobilization of the starch protons, slightly greater for microwaves heated samples.

X-ray experiments showed that the heating method did not alter the gelatinization mechanism, however the rate of loss of crystallinity with temperature was higher for microwaves heated samples which could be due to a more complete gelatinization as revealed by the NMR results.

Acknowledgment

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