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Short-range structure in (partially) crystalline potato starch determined with attenuated total reflectance Fourier-transform IR spectroscopy

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Abstract

A fast and direct method, based on infrared spectroscopy, for quantitative determination of starch short-range structure has been developed. The IR spectrum of starch is sensitive to changes in short-range structure in the C–C and C–O stretching region at 1300–800 cm^{-1}. The IR absorbance band at 1047 cm^{-1} is sensitive to the amount of ordered or crystalline starch and the band at 1022 cm^{-1} is characteristic of amorphous starch. The ratios (R) of the heights of the bands at 1047 and 1022 cm^{-1}, which expresses the amount of ordered starch to amorphous starch, and 1047 and 1035 cm^{-1}, which is a measure of the amount of ordered starch, showed a linear regression with the amount of potato starch having B-type crystallinity as determined with wide-angle X-ray diffractometry. The IR spectrum and thus the short-range order is also sensitive to water content. In particular, the band at 994 cm^{-1}, which is related to intramolecular hydrogen bonding of the hydroxyl group at C-6, is water sensitive. It is possible to quantify the IR data in terms of short-range order (S_{IR}) over a range of 10–50% water. The method has been applied to quantify the changes in short-range structure during the melting of potato starch with 18 or 26% (w/w) water. The amount of short-range structure and the changes during melting in the (partially) destructured starch samples concur with differential scanning calorimetry and wide-angle X-ray diffractometry measurements.

Keywords: Starch; Structure; IR spectroscopy; X-ray diffractometry; Water; Melting

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1. Introduction

Our research is focused on the relationship between the structural parameters and the properties of thermoplastic starch materials. Structural parameters, such as crystallinity and helicity, contribute significantly to the physical, rheological, and mechanical properties of the starch products. The plasticizer (water) content influences several properties of thermoplastic starch materials, such as the melting and glass transition temperatures and consequently the mechanical properties. The aim of this study is to obtain a better understanding of the qualitative and quantitative changes in starch molecular structures, both long-range and short-range, during processing conditions relevant to the production of thermoplastic starch products. A comparison of short-range and long-range order is made by a combination of FTIR spectroscopy and X-ray diffractometry.

Starch is the main energy reserve of all higher plants and is gaining much attention as an interesting constituent of biodegradable thermoplastic materials. The two main components are amylose and amylopectin [1]. Three crystal structures (A, B, C) have been described, depending on starch origin and the type of processing of the starch products [2–4]. Differences between these polymorphs are found in the hydrogen-bonding pattern, the water content, and in the conformation of the polysaccharide chain. A-starches are usually found in grains, whereas B-starches are found in tuberous plants. C-starch is more rare and found in some plant sources such as pea [5]. Single helical V-type structures are obtained when amylose crystals are prepared from complexes [6,7]. Recently, these structures have also been found in thermoplastic materials. The short chains of amylopectin are thought to be arranged in crystallites responsible for the crystallinity of the native starch granule. The three-dimensional structure of B-type starch, which occurs in potato starch, is proposed to consist of a hexagonal unit cell containing 12 glucose residues located in two double helices [3,8].

Crystallinity (X_c), which can be interpreted as long-range order, in a semi-crystalline biopolymer like starch, is defined as the ratio between the mass of the crystalline domains and the total mass of the material. Wide-angle X-ray diffractometry methods have been used for the determination of starch crystallinity [9] based on a method that corrects for the loss of intensity of crystalline peaks due to deviations of the atoms from their ideal positions [10]. Several investigators [11–14] have used indices of relative crystallinity (X_c^{rel}) based on methods in which the area of the crystalline diffraction relative to the total area of the diffractogram is taken as a measure of crystallinity [15,16]. Quantitative multi-component analysis has been applied by using the relative intensities of the various crystalline components [17,18]. Although the last two methods give no absolute measure of crystallinity, they can be used as a measure of relative crystallinity. Values of 15–45% crystallinity based on wide-angle X-ray diffractometry have been obtained for several starches [9,11–14,17,19–22]. The crystallinity of native potato starch has been determined as 22% [9].

The IR spectrum of starch has been shown to be sensitive to changes in structure on a molecular level (short-range order), such as starch chain conformation, helicity, crystallinity, and retrogradation processes, as well as water content [23–28]. The spectrum of native potato starch shows bands in the region 2900–3000 cm^{-1} (CH stretching) and at 1150, 1124, and 1103 cm^{-1} (CO, CC stretching with some COH contributions), 1077, 1047, 1022, 994, and 928 cm^{-1} (COH bending and CH_2 related modes), and 861 cm^{-1} (COC symmetrical stretching and CH deformation) [29,30]. It is not possible to assign the bands unambiguously because most bands result from highly coupled vibrational modes. A limiting factor is the overlapping, poorly resolved bands in the spectrum of starch. FTIR spectroscopy coupled with sampling methods, such as attenuated total reflection, and the possibility to enhance resolution by deconvolution, have broadened the fields of application of the IR spectral information.

2. Experimental

Materials.—Starch samples containing 18% water (w/w) of different crystallinities were obtained by mixing native potato starch (Farina, Avebe) with pre-gelatinized potato starch (Farina, Avebe) and with a commercially available amorphous maltodextrin (Paselli SA-2, Avebe). Mixtures were obtained in the range 0–100%.

Native potato starch containing 18 or 26% water (w/w) was thermally treated at various temperatures. The starch samples (10 g) were hermetically sealed in a closed stainless steel container and heated in an oil bath, with a heating rate of 5°C per min, to 90, 110, 130, 150, 170, and 195°C. The samples were quenched in ice–water and stored at $-22°C$ before measurements.

Differential scanning calorimetry (DSC).—The DSC measurements were carried out with a Seiko differential scanning calorimeter 120C, cooled with liquid N_2 and flushed with a constant flow of N_2 (40 mL min^{-1}) to obtain an inert atmosphere. An empty pan was used as a reference. The heating rate was 5°C per min. The instrument calibration was performed with indium [$\Delta H_{fusion} = 28.59$ J g^{-1}, melting point (T_{onset}) = 156.60°C] and gallium [$\Delta H_{fusion} = 79.91$ J g^{-1}, melting point (T_{onset}) = 29.78°C].

The DSC samples were mixed with an accurately pre-weighed amount of water. The mixtures were pre-mixed and equilibrated overnight under parafilm at room temperature. The starch mixtures (approximately 10–20 mg) were weighed into silver or stainless steel pans (15 μL) and the pans were hermetically sealed.

Wide-angle X-ray diffractometry.—Diffractograms were recorded on a Philips PC-APD diffractometer in the reflection geometry in the angular range 10–30 (2θ). The Cu-K_α radiation from the anode operating at 40 kV and 50 mA was monochromated using a 15-μm Ni foil. The scattered radiation was detected using a proportional detector. Crystallinity was measured according to the methods of Hermans and Weidinger [15]. Diffractograms were smoothed (Savitsky–Golay, polynome = 2, points = 15) and baseline-corrected by drawing a straight line at an angle of 7°. The height (H_c at 17.3°) and the area (A_c between 16–18.5°) of the crystalline diffraction were measured relative to the height (H_t) and area of the total diffraction (A_t) of the peak measured from the baseline. The ratios $R(X_H) = H_c/H_t$ and $R(X_A) = A_c/A_t$ are related to X [which is defined as the relative crystallinity in comparison with native potato starch ($X_{XRD} = 1.0$ or $\%X_{XRD} = 100\%$)] by the relations:

$$\%X_{XRD} = [R(X_A) - 0.0090]/0.0040$$

$$\%X_{XRD} = [R(X_H) - 0.095]/0.0055$$

FTIR.—Absorbance spectra were recorded on a BioRad FTS-60A spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector using the Digilab attenuated total reflectance (ATR) accessory with a ZnSe crystal at an angle of incidence of 45°. Samples, of particle sizes below 125 μm, were measured directly after pressing the samples on the crystal. The spectra, obtained at a resolution of 4 cm^{-1}, were averages of 400 scans, and were recorded against an empty cell as background. Spectra were baseline-corrected at 1200 and 800 cm^{-1} by drawing a straight line. All spectra were deconvoluted using techniques described by Cameron and Moffat [31] and modified for use on the FTS-60A. A half-bandwidth of 15 cm^{-1} and an enhancement factor of 1.5 with triangular apodization were employed. Intensity measurements were performed on the deconvoluted spectra by recording the height of the absorbance bands from the baseline. Instead of single-intensity measurements, ratios of absorbance intensities were used to compensate for path-length differences between samples that might arise from incomplete coverage of the ATR crystal.

3. Results and discussion

Influence of crystallinity.—In Fig. 1 the wide-angle X-ray diffractometry diffractograms are shown for the samples of native starch with Paselli starch mixed in the range 0–100%. Native potato starch shows the typical B-type diffraction pattern. The diffractograms of 100% Paselli starch show no discrete diffractions. This type of starch sample can be assumed to be totally amorphous according to wide-angle X-ray diffractometry.

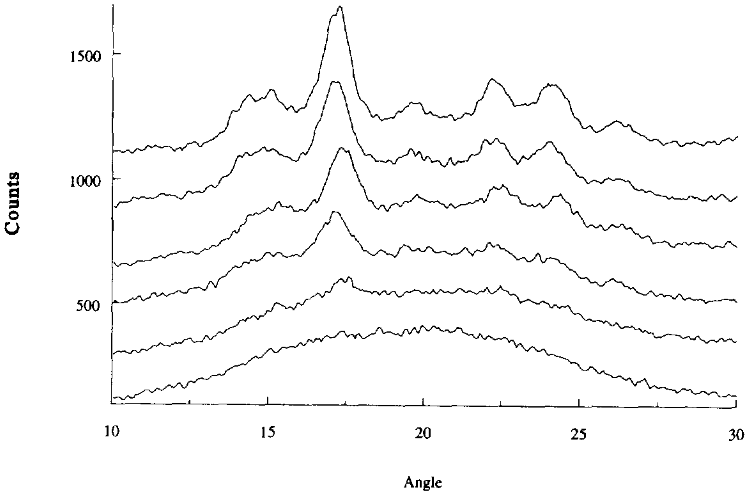

Fig. 1. Wide-angle X-ray diffractograms of the mixtures of native potato starch with 0, 20, 40, 60, and 100% Paselli starch (top to bottom).

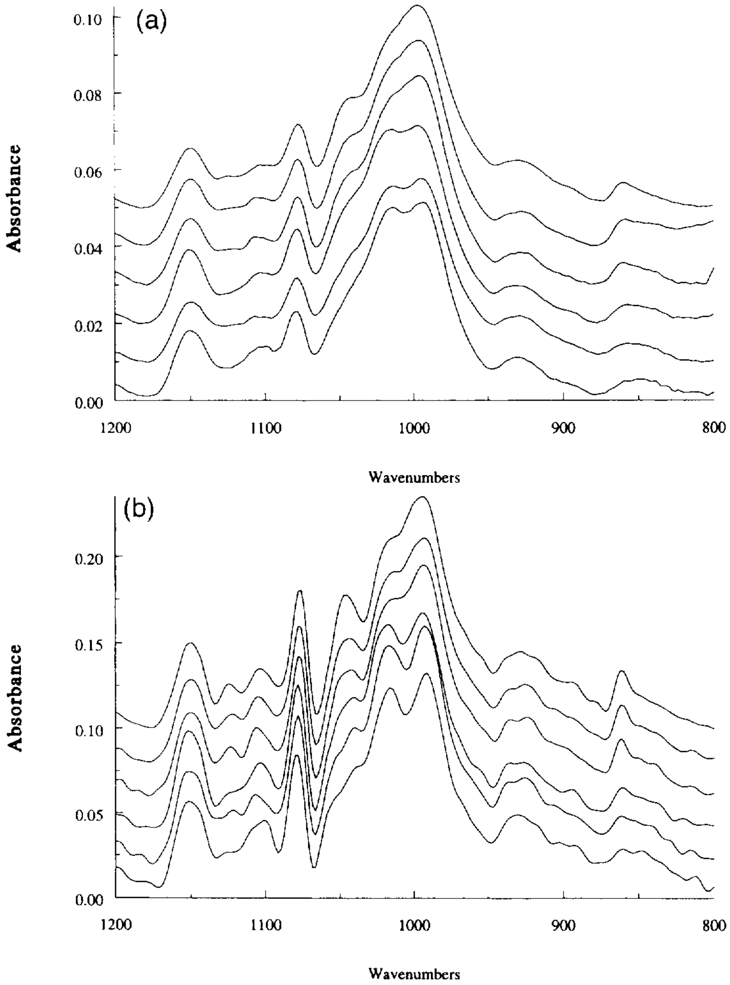

Fig. 2. Original (a) and deconvoluted (b) ATR spectra of the mixtures of native potato starch with 0, 20, 40, 60, and 100% Paselli starch (top to bottom).

In Fig. 2 the original and deconvoluted ATR spectra in the range 800–1200 cm^{-1} of the mixtures of native and Paselli starch samples are given. A similar result is obtained for the spectra and the diffractograms of the mixtures composed of native and pregelatinized starch. When changing from semi-crystalline to amorphous starch, the specific molecular surroundings, as present in the starch B-type lattice, become lost and as a result the spectra of amorphous starches show changes in band shape and intensity. The IR bands at 1077 and 994 cm^{-1} do not show significant changes with decreasing crystallinity. The bands at 1047, 1022, and 861 cm^{-1} are sensitive to changes in crystallinity. The band at 1022 cm^{-1} increases with decreasing crystallinity and has been shown to be characteristic of freshly prepared, hot starch-gel systems [23–28]. The band at 1047 cm^{-1} appears to be composed of two overlapping bands at 1040 and 1053 cm^{-1}. Neither of these bands is observed in freshly prepared hot starch gels. During retrogradation the band at 1040 cm^{-1} develops within several hours, whereas the absorbance at 1053 cm^{-1} increases over longer periods. The slower process is assigned to aggregation and crystallization processes of starch, for example, in gels and bread [23–28]. Thus, the broad band at 1047 cm^{-1} in the spectrum of starch is related to starch crystallinity because the band increases with increasing crystallinity. The bands at 1047 and 1022 cm^{-1} can be used for the determination of starch B-type crystallinity. The amount of short-range ordering of the starch samples can be expressed, by using the intensity of the bands most characteristic of crystalline and amorphous starch, by the ratio $R(1047/1022)$ or by using the intensity of the band characteristic of crystalline starch at 1047 cm^{-1} expressed as the ratio $R(1047/1035)$. Instead of the areas, the heights of the bands measured from the baseline are taken because the bands at 1047 and 1022 cm^{-1} showed an increasing asymmetrical shape with changing crystallinity due to the overlap of both bands and interference with the band at 994 cm^{-1}. The calculated R-values are plotted in Fig. 3 vs. the amount of native potato starch (with a $\%X_{\mathrm{XRD}} = 100\%$), $\%PN$. No significant differences were observed between the Paselli and pre-gelatinized starch series. The function of the ratio of the heights of the bands (R) against $\%X_{\mathrm{XRD}}$ have been fitted with linear regression. From the lines of linear regression depicted in Fig. 3, it was deduced that R is related to the amount of potato starch with $\%X_{\mathrm{XRD}} = 100\%$ B-type crystallinity, $\%PN$, following the equation:

$$\%PN = (R - a_0)/(a_1) \tag{1}$$

where R = the ratio, a_0 = intercept at $\%PN = 0$, a_1 = slope.

The results of the linear regression fits are summarized in Table 1.

Influence of water content.—The deconvoluted spectra of native and amorphous potato starch with various amounts of water (0–50%) are shown in Fig. 4. Band-narrowing is observed for the bands at 1047, 1022, and 994 cm^{-1}. The positions of the bands at 1047 and 1022 cm^{-1} and the valley at 1035 cm^{-1} are not shifted by the addition of water, although their ratios have changed. The ratio $R(1047/1035)$ is very sensitive to water content as shown in Fig. 5. The change in the ratio shows a good linear regression within the range 0–50% water:

$$R(1047/1035) = 0.017 \times (\%W) + 0.89(R_{\mathrm{val}} = 0.98,\ n = 9),$$

where $\%W$ = percentage water on basis of total mass.

The position of the band at 994 cm^{-1} is also sensitive to water and shifts from 991 (0% water) to 1003 cm^{-1} (50% water). The absorbance has an asymmetrical shape and seems to be composed of two highly overlapping bands at ca. 991 and 1003 cm^{-1}. Above 50% water no changes are observed in the spectrum.

The deconvoluted spectra of pre-gelatinized starch with various amounts of water (0–40%) are shown in Fig. 4. A band-narrowing process is observed. Dry, amorphous starch shows very broad lines. Adding water results in the development of a valley at 1035 cm^{-1} and a band at 1047 cm^{-1}, characteristic of amorphous starch with water contents above 10%. The position and ratio of these bands do not change by adding more water. The position of the band at 1022 cm^{-1} shifts to ca. 1015 cm^{-1}. The ratio

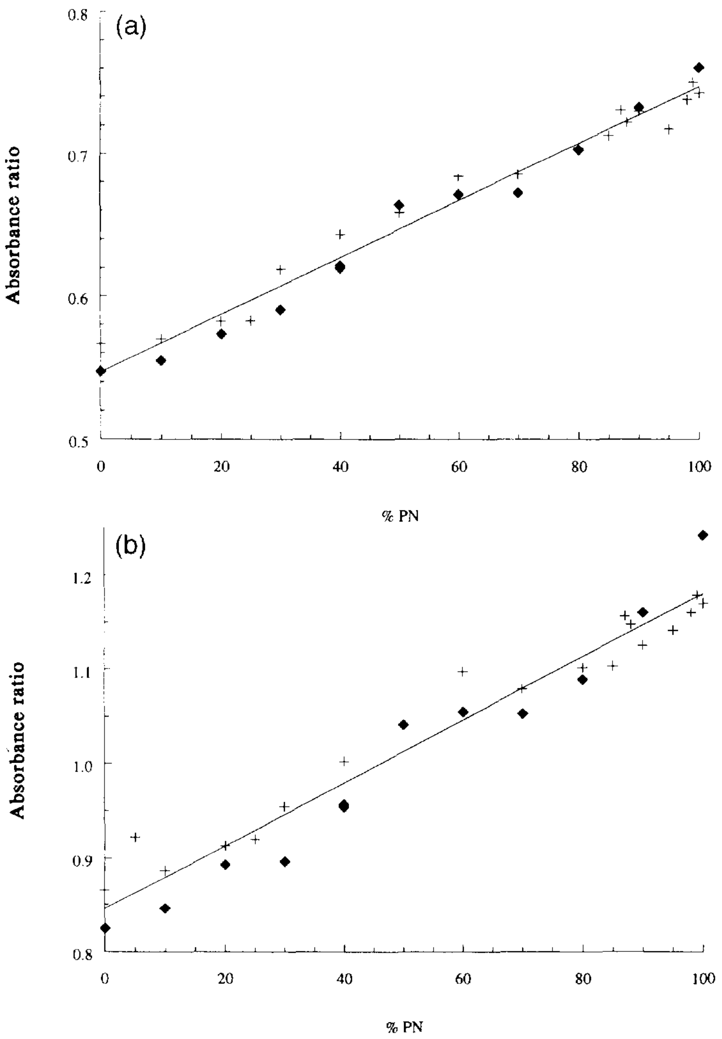

Fig. 3. *R*(1047/1022) (a) and *R*(1047/1035) (b) vs. %PN.

1047/1022 is influenced by the changes in band position and band shape. The changes in band shape at 1022 cm^{-1} are probably due to changes of the band at 992 cm^{-1}, which is highly overlapping. This band is sensitive to changes in water content. The band shifts from 992 (at 0% water) to 1004 cm^{-1} (at 40% water). At low water content the band half-width is ca. 20 cm^{-1} and at 40% water the band is decreased to a shoulder of the band at 1022 cm^{-1}. The ratio 1047/1035 is not changed within the range of 10–40% water for amorphous starch.

Thus, water has a large influence on the CO and CC stretching and COH bending vibrations for both crystalline and amorphous starch. Band-narrowing is observed in this region and several bands are changed in intensity. The band at 994 cm^{-1}, which is

Table 1
The results of the fits of the linear regression

R	a_1	a_0	R_{val},[a] $n=30$
1047/1022	0.0020	0.55	0.99
1047/1035	0.0033	0.85	0.97

[a] R_{val} is the variance accounted for.

mainly due to COH bending vibrations, is especially sensitive to the water content and these vibrations must involve water–starch interaction by, for example, hydrogen bonding, which will influence the COH bending modes. Changes of this band have been

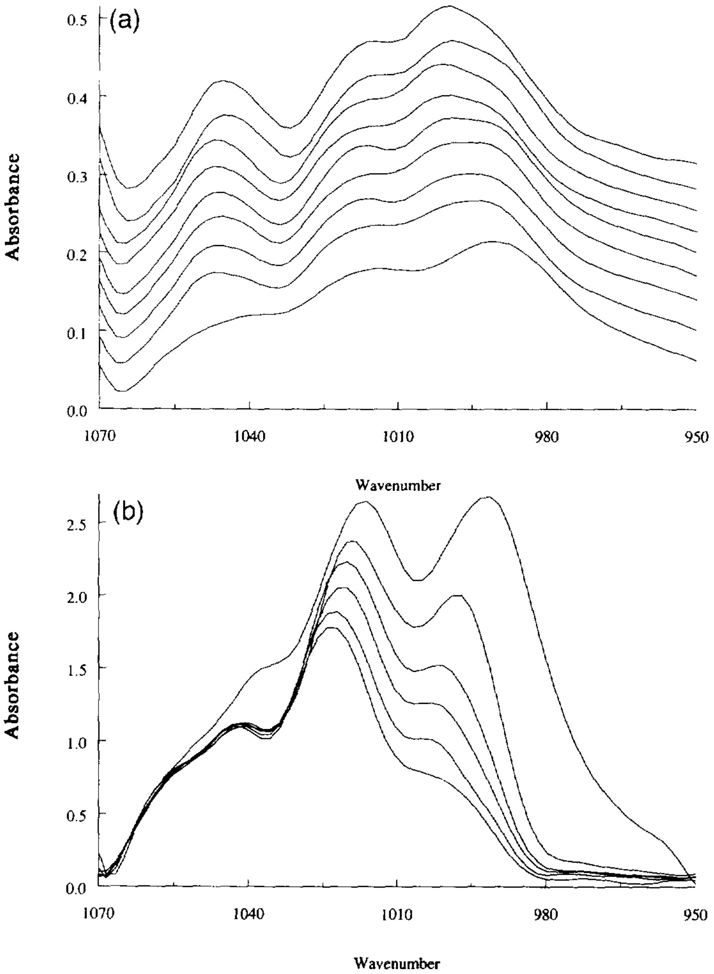

Fig. 4. Influence of water content [0% (bottom)–50%] on the deconvoluted spectra of native potato starch (a) and on the deconvoluted spectra of amorphous potato starch (b).

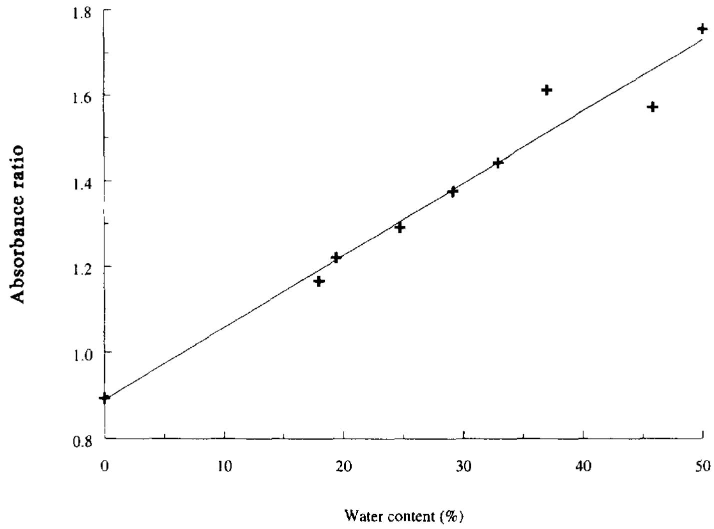

Fig. 5. Water content vs. $R(1047/1035)$ for native potato starch.

ascribed to changes in the molecular environment of the primary hydroxyl group in V-type amylose, due to changes in intramolecular hydrogen bonding [32]. The band at 1022 cm^{-1} is influenced slightly by water, mainly because of the overlap with the band at 994 cm^{-1}. The band at 1047 cm^{-1}, which is sensitive to crystallinity, is not very sensitive to water content. For amorphous starch no change in shape is observed above 10% water. For crystalline starch the band increases. Below 10% water the spectrum of both amorphous and crystalline starch shows a strong band broadening. Line broadening as a result of loss of water is observed in the diffractograms of native starches (Fig. 6). The crystal lattice is distorted by removing water. As a result the crystalline and molecular order is lost. At low water content there is a wide distribution of possible molecular conformations and bond energies. Thus, upon the addition of water a more ordered starch is obtained. This is in agreement with line-narrowing effects observed in solid-state ^{13}C NMR spectra [33] and Raman spectra [34], and explained by a reduction in possible conformations.

Expressing short-range ordering in terms of crystallinity corrected for various water contents.—Short-range structure is related to the amount of native crystalline starch and long-range structure as expressed in eq (1) and to changes in water content by eq (2). The changes in short-range structure can thus be expressed at various water contents in the range of 10–50% water by combining eqs (1) and (2):

$$\%S_{\mathrm{IR}} = \{[R(1047/1035) - a_0]/(0.017 \times \%W + 0.89 - a_0)\} \times 100\% \qquad (3)$$

$\%S_{\mathrm{IR}}$ is an expression for the amount of short-range order in partially crystalline starch at a specific water content in the range 10–50% and can be applied to follow quantitatively the changes in short-range order in starch.

Changes in short-range ordering and crystallinity during melting of potato starch.—The DSC results of the melting of native potato starch samples with 18 or 26% water are shown in Table 2. Three groups of transitions were identified, namely, the melting

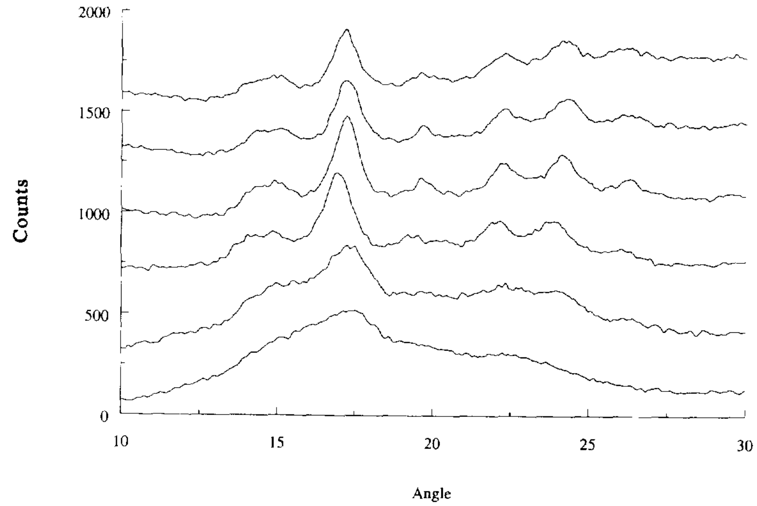

Fig. 6. Wide-angle X-ray diffractograms of native potato starch with 0, 10, 20, 30, and 40% water (bottom to top).

transitions, M1 and M2, between 100–175°C and the high-temperature transition, H, between 165–190°C [35–37]. The last transition is not related to the melting of crystallites nor to the degradation of helical conformations [37].

The diffractograms and the deconvoluted IR spectra of the melting of potato starch with 18% water are shown in Fig. 7. The B-type crystallinity is lost during melting. A decrease in the intensity of the band at 1047 cm^{-1} is observed due to a loss in short-range order during melting. The diffractograms of the melting of potato starch with 26% water also show a loss in crystallinity and thus in long-range ordering. The spectra of the melting of potato starch with 26% water show a similar decreasing intensity of the band at 1047 cm^{-1}.

The changes in long-range ordering are calculated as $\%X_{\mathrm{XRD}}$ relative to native potato starch with a water content of 18%, using the area and intensity of the peak at 17.3°. The changes in short-range ordering are expressed in terms of $\%S_{\mathrm{IR}}$ by using the band ratio $R(1047/1035)$ and eq (3). The changes in short-range and long-range order are shown in Fig. 8 for the melting of potato starch containing 18 or 26% water. The results of the changes in crystallinity and short-range order during melting for the two water contents are summarized in Table 3 in terms of relative crystallinity ($\%X_{\mathrm{XRD}}$) and short-range order ($\%S_{\mathrm{IR}}$).

Table 2
The melting temperatures determined with differential scanning calorimetry

% Water (w/w)	T^{o} (°C)	T^{pM1} (°C)	T^{pM2} (°C)	T^{pH} (°C)	T^{c} (°C)
18	105	115	150	180	190
26	91	104	167	178	187

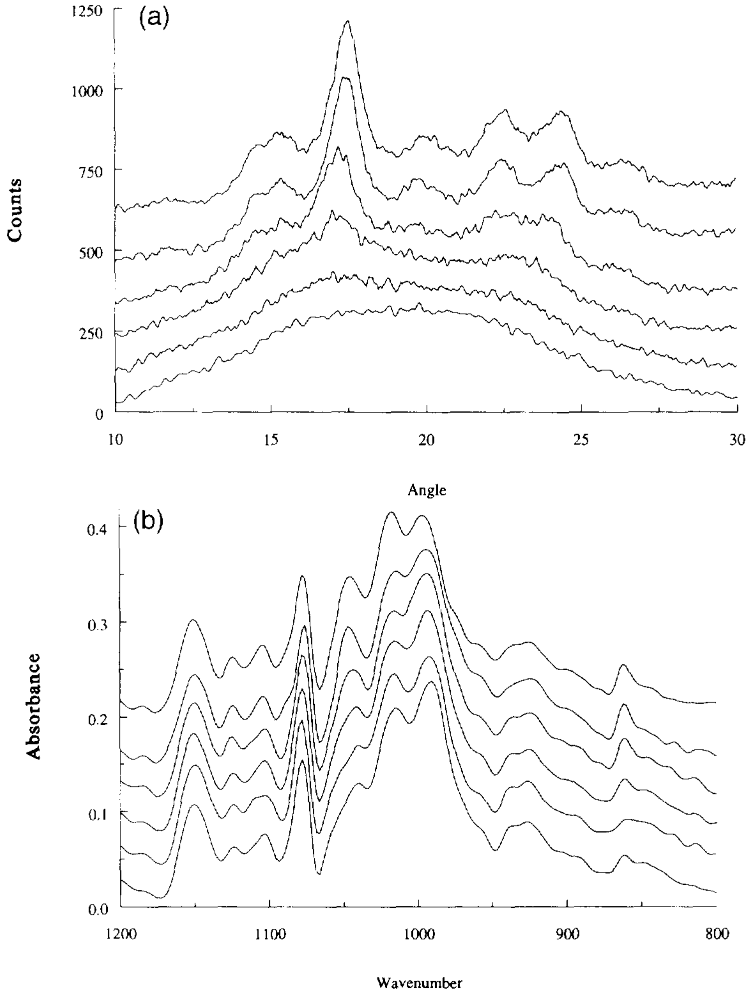

Fig. 7. (a) Wide-angle X-ray diffractograms of the melting of native potato starch at various temperatures (90, 110, 130, 150, 170, 195°C, respectively, top to bottom). (b) Deconvoluted ATR spectra of the melting of native potato starch at various temperatures (90, 110, 130, 150, 170, 195°C, respectively, top to bottom).

The crystallinity is increased for the melting of potato starch with 26% water in going from 25 to 90°C. For the melting of potato starch with 18% water the crystallinity is not increased in going from 25 to 90°C, as is also observed for the amount of short-range order. The increasing order just below the melting temperature can be explained by annealing of the starch crystalline domains at higher water contents [38]. Above 90°C, melting of the crystallites for both mixtures occurs and both long- and short-range order are lost. This is in agreement with the observed onset temperatures as measured with DSC. The onset temperature of melting of potato starch with 18% water is 105°C and with 26% water is 91°C. The experiments show that after the M1 transition has been

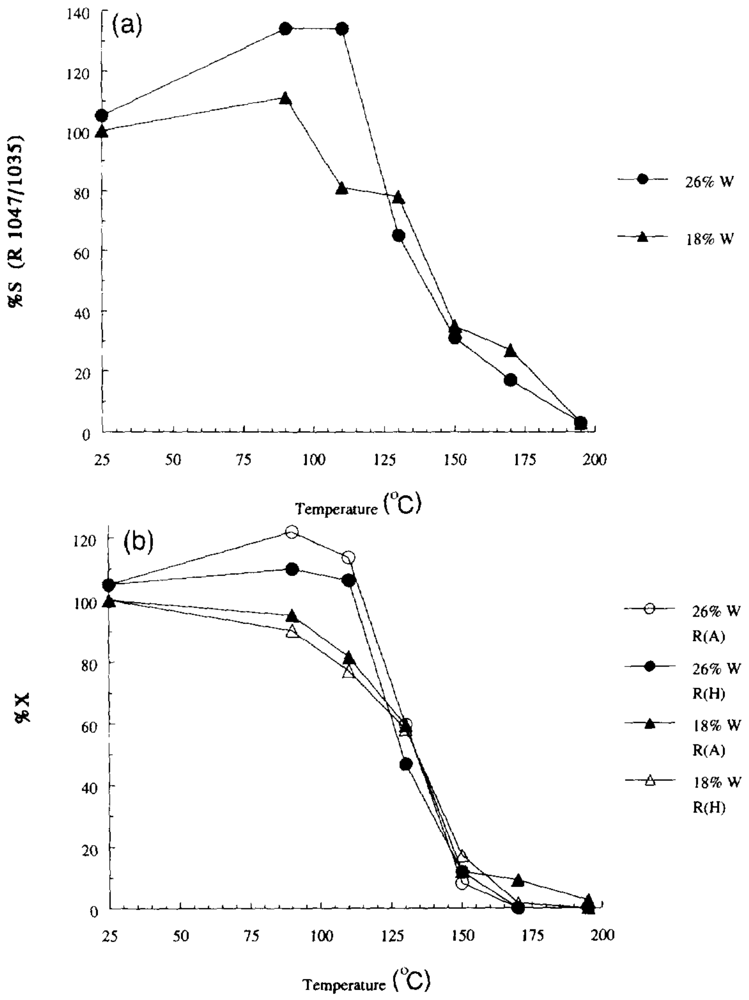

Fig. 8. The changes in (a) short- and (b) long-range order during the melting of native potato starch with 18 and 26% water.

passed ca. 40–60% of the long- and short-range order is destroyed. By heating above M1 the residual crystalline and short-range order are successively lost. The changes in short-range order are in agreement with solid-state NMR experiments [37], which have shown that ca. 50% of all helical conformations have disappeared after transition M1. During melting the amount of short-range order expressed in terms of %*S* on the basis of IR data is somewhat higher. This suggests that long-range order is lost before short-range order. For the mixtures with 18 or 26% water, both the short-range and the long-range order are lost at 195°C.

Table 3
Changes in short- and long-range structure during the melting of potato starch

Water (%)	Temp. (°C)	%X_{XRD} (A_c/A_t)	%X_{XRD} (H_c/H_t)	%S_{IR} (R 1047/1035)	R (1047/1035)
18	25	100	100	100	1.19
	90	95	90	111	1.23
	110	81	77	81	1.13
	130	59	58	78	1.12
	150	12	17	35	0.97
	170	9	2	27	0.94
	195	3	0	3	0.85
26	25	105	105	105	1.36
	90	122	110	134	1.50
	110	114	106	134	1.50
	130	59	47	65	1.16
	150	8	12	31	1.00
	170	0	0	13	0.91
	195	0	0	3	0.86

4. Conclusions

A direct method based on IR spectroscopy for the quantification of short-range structure has been developed. The absorbance bands at 1047, 1022, and 994 cm^{-1}, respectively, are sensitive to changes in short-range order and, indirectly, to crystallinity, for the amount of amorphous starch, and for the influence of water content on the intramolecular hydrogen bonding. The changes in intensity of the bands at 1047 and 1022 cm^{-1} show a first-order relationship with the amount of native potato starch and with B-type crystallinity (%X) as determined by wide-angle X-ray diffractometry. The IR spectrum, and thus the short-range order in starch, is sensitive to changes in water content. With this method it is possible to measure samples with different water contents. The IR spectroscopic data have been expressed in terms of short-range order over a range of 10–50% water for partially destructured starch.

The changes in short-range order during the melting of native B-type potato starch, with two different water contents, have been expressed in terms of IR data. The changes in short-range structure concur with structural changes as measured by DSC and wide-angle X-ray diffractometry.

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