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Note

A Fourier-transform infrared study of the gelation and retrogradation of waxy-maize starch

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Previous studies of the Fourier transform (F.t.)-i.r. spectra of aqueous solutions of polysaccharides showed that the region 1400–800 cm^{-1} is sensitive to polymer conformation[1]. Most bands in this region arise from highly coupled C–O and C–C stretching modes of the polysaccharide backbone[2], but many of the bands are difficult to assign.

The retrogradation and gelation of starch and starch components has been studied widely by using X-ray diffraction, differential scanning calorimetry, and rheological methods. Recent studies[3,4] showed that amylopectin partially crystallises during gelation and retrogradation. We now report on the F.t.-i.r. spectra of aqueous solutions of waxy-maize starch (>98% amylopectin) before and after gelatinisation and during retrogradation. Measurements of shear modulus have also been made.

The changes in the F.t.-i.r. spectra during the retrogradation are illustrated in Fig. 1. The spectrum of freshly gelatinised starch shows several bands in the region 1200–850 cm^{-1}. The most intense band is broad with a maximum intensity at 1022 cm^{-1} and a noticeable shoulder on the high-frequency side. After retrogradation for 22 days, this broad line has become resolved into two distinct bands with maxima at 1019 and 1046 cm^{-1} (minimum of the intervening valley at 1037 cm^{-1}). During retrogradation, the band at 1046 cm^{-1} gradually appears as the valley forms. This apparent separation occurs mainly by a line-narrowing process involving the bands at 1046 and 1019 cm^{-1}. Other bands also showed some change during retrogradation, but they were less pronounced and less easily quantified.

The extent of apparent line separation during retrogradation was quantified by taking the ratio (*R*) of the absorbances at 1019 and 1037 cm^{-1} (the valley minimum in the fully retrograded material) as a function of time (Fig. 2). Also shown in Fig. 2 is the plot of shear modulus (G') against time for a similar sample of waxy-maize gel. The shapes of these two curves are similar.

The shear modulus results were similar to those obtained[3] for amylopectin,

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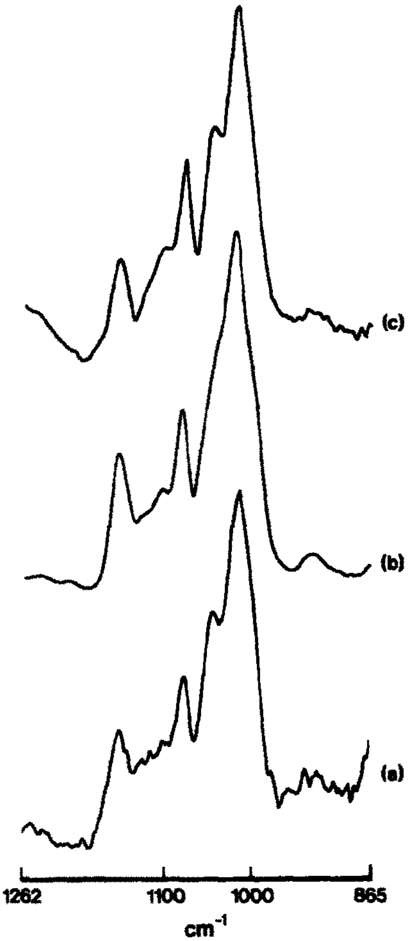

Fig. 1. F.t.-i.r. spectra of waxy-maize starch with the contribution of water substracted digitally: 20% native waxy-maize starch (a) in water, (b) immediately after gelatinisation, (c) retrograded at 1° for 22 days. Vertical scale in absorbance units.

and the general shape is similar to those for the time course of such other parameters as crystallinity, isothermal volume change, and enthalpy of dissolution. The correlation between crystallinity and the F.t.-i.r. spectra is reinforced by the fact that the spectrum of a highly crystalline short-chain amylose[5] (DP22) exhibits a deep valley at 1037 cm^{-1} and even sharper bands at 1046 and 1019 cm^{-1}. Furthermore, the addition of water, which increases the crystallinity of starches[6], also enhances the resolution in this region.

The spectrum (Fig. 1) of ungelatinised, native waxy-maize starch is similar to that of the retrograded material and exhibits the bands at 1019 and 1046 cm^{-1} and the weak shoulder at lower frequency (<1000 cm^{-1}). After gelatinisation, the bands

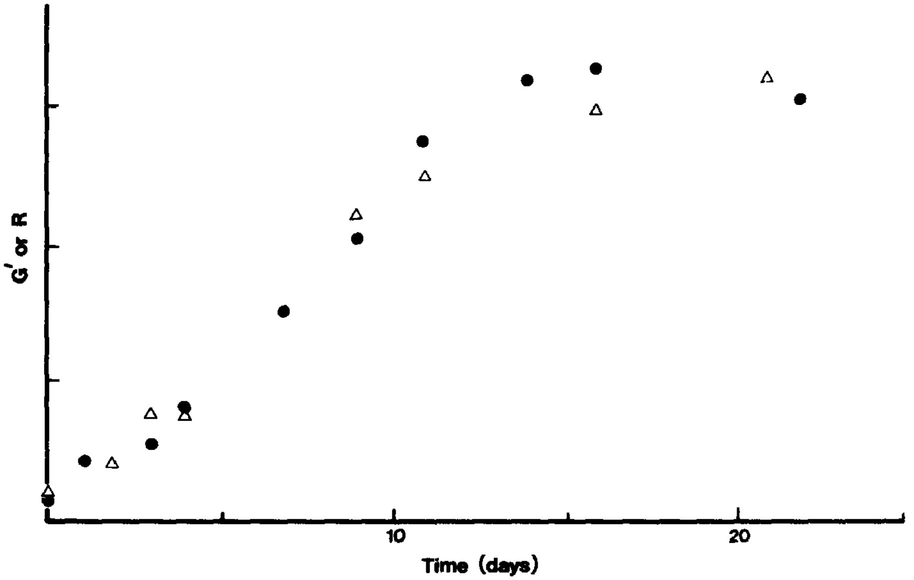

Fig. 2. Change in shear modulus (G', △) and F.t.-i.r. band ratio (R, ●) with time during the retrogradation of waxy-maize starch. Vertical scale: F.t.-i.r., 2 units per division; shear modulus, 8×10^{-3} N.m.$^{-2}$ per division.

at 1046 and 1019 cm^{-1} are broadened and merged consistent with the loss of native crystallinity during gelatinisation. During retrogradation in a sealed cell, there was no apparent change at <1000 cm^{-1}, although a strong band was observed at ~996 cm^{-1} in samples that had been allowed to lose water during storage. This band was also seen in the spectrum of dry native starch.

The above results demonstrate a direct correlation between a spectroscopic measurement and a rheological property. The spectroscopic change arises from a narrowing of vibrational bands associated with helix formation. The polymer in the gel state can have a wide distribution of conformational states and associated hydrogen-bond energies that give rise to broad lines. When extensive helix formation occurs, line-narrowing results as the number of conformational states is reduced and there is a narrower distribution of hydrogen-bond energies. Therefore, the i.r. spectra reflect differences in short-range order only, and consequently A and B type starches are indistinguishable in this region. The different X-ray patterns produced by these types arise from long-range differences associated with the different packing in the hexagonal array.

EXPERIMENTAL

Preparation of gels. — For the studies of retrogradation, a 20% gel of waxy-maize starch (var. Amioca obtained from Laing National) was prepared by dispersing the starch with gentle agitation in boiling, oxygen-free water containing 0.02% of sodium azide as preservative. The hot solution was poured into the F.t.-i.r. cell and cooled rapidly to 1° to initiate gelation. A sample, in slurry form, was also prepared for F.t.-i.r. analysis before gelatinisation.

F.t.-i.r. measurements. — All measurements were carried out on a Digilab FTS60 spectrometer operating at 4 cm^{-1} resolution using a TGS detector; 64 or 256 interferograms were co-added before Fourier transformation. Triangular apodisation was employed. Retrogradation was studied by using a cylindrical internal reflectance (CIR) cell (Spectra-Tech Inc.) with a ZnSe crystal. The gel was sealed into the CIR cell in order to prevent loss of water, and the cell was stored at 1°. At regular intervals, the cell was allowed to reach room temperature before F.t.-i.r. measurements were made using 64 scans. A background for the empty CIR cell was obtained and used for all subsequent samples; its validity was demonstrated by the flat baselines obtained in spectra acquired even after 22 days. The spectrum for water was subtracted from all starch spectra in order to eliminate the distorting effect of water in the region 1100–800 cm^{-1}.

The spectrum of the material before gelatinisation was acquired by using a Spectra-Tech continuously variable angle, attenuated total reflectance (ATR) attachment. A ZnSe parallelogram crystal (50 × 20 × 3 mm, 45°) was used, and the incident angle was set at 45°. The sample was spread onto the crystal as a slurry and then clamped to ensure a good optical contact. A spectrum of water, for subtraction purposes, was obtained in the same way.

Measurements of shear modulus. — The formation of networks was monitored by following the development of the shar modulus G', using[7] a Rank Brother's pulse shearometer. Samples of gel were stored under conditions identical to those used for F.t.-i.r., and measurements were made at the same intervals where possible.

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