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Short Communication

Influence of starch flavour interactions on rheological properties of low concentration starch systems

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Interactions between starch and the complex forming flavour substances decanal and (−)fenchone were studied in low concentration starch systems. Rheological changes were determined with dynamic measurements, the formation of complexes by measuring the iodine binding capacity of starch and by X-ray diffractometry. Decanal and (−)fenchone led to the formation of amylose helices with 6 and 7 D-glycosyl units per turn, respectively, and induced the gelation of low concentration starch systems.

INTRODUCTION

Starch, in particular amylose as linear fraction, is able to form complexes or inclusion compounds with a variety of ligands which are of importance as volatile flavour compounds in foods (Kuge & Takeo, 1968; Osman-Ismail & Solms, 1973; Rutschmann & Solms, 1990*a*). Starch complexation with such molecules is thought to be one of the mechanisms of flavour retention in starch containing food systems (Solms & Guggenbuehl, 1990). So far, most flavour binding studies have been carried out in low concentration starch dispersions. No information has been obtained on the rheological properties of these dispersions. Conde-Petit and Escher (1992, 1994) were able to show that gelation of low concentration starch dispersions is induced by emulsifiers which form complexes with amylose. Gelation may be observed particularly when the structure of starch granules has not totally disintegrated. Gelation as a result of complex formation has been observed with menthone as ligand, whereby the water insoluble menthone has been introduced with the help of lecithin as emulsifier which does not form a complex with amylose (Conde-Petit & Escher, 1995).

This paper reports on rheological changes in starch dispersions induced by complex formation as a result of the addition of decanal and (−)fenchone. These two ligands form two different types of helical V-amylose, i.e. with 6 D-glycosyl residues (decanal) and 7 D-glycosyl residues ((−)fenchone). Rheological changes were followed by dynamic measurements, the formation of complexes by measuring the iodine binding capacity of starch and by X-ray diffractometry.

MATERIALS AND METHODS

Native potato starch was purchased from Blattmann and Co. (Wädenswil, Switzerland). Decanal and (−)fenchone (purum) were supplied by Fluka (Buchs, Switzerland). Lecithin (Phospholipon 90H) was obtained from Nattermann Phospholipid GmbH (Köln, Germany).

The aqueous starch flavour dispersions were prepared as summarized in Fig. 1. Details of the preparation steps are as follows:

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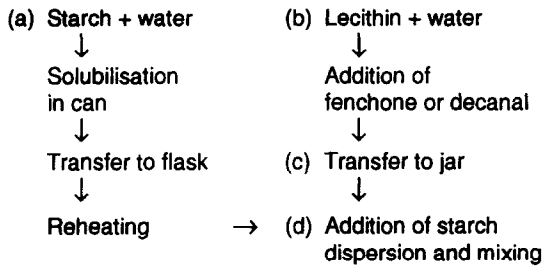

Fig. 1. Schematic presentation of the preparation of potato starch dispersions complexed with flavour (letters a, b, c, d refer to the text).

(a) Aqueous potato starch dispersions (2 g starch/100 g) were prepared by heating suspensions of native starch in sealed cans (380 g). Heat treatment was carried out in a retort (Berlin Chapman, WI, USA) at 1 bar overpressure (121°C) for 30 min. Cans were rotated end over end at 0.2 Hz. The cans were cooled with water to 60°C within 10 min. Immediately thereafter, the dispersion was transferred to 500 ml flasks and reheated in a microwave oven (750 W) for 1 min to 95°C. This hot dispersion was used without delay for further experiments.

(b) Dispersions of decanal and (−)fenchone were prepared by first dispersing lecithin in water (1.15 g/100 g) at 60°C, stirring for 10 min at 60°C and cooling this lecithin dispersion to room temperature. 0.65 g decanal and (−)fenchone, respectively, was added to 4.35 g lecithin dispersion and the resulting mixture shaken vigorously.

(c) The flavour dispersions were weighed into 50 ml sealable jars. The quantity was adjusted in such a way that final flavour concentrations based on starch were obtained between 0 and 200 mmol per mole glucose. 20 g starch/l corresponds to 122.6 mmol glucose/l. Lecithin concentration in the starch system increased with increasing concentration of added flavour. The maximal added amount of lecithin in the starch flavour systems was 3 mmol per mole glucose.

(d) Thereafter, 35 g starch dispersion at 95°C was added to the flavour dispersion. After closing the jars with screw caps the mixture was shaken for 10 s and cooled in a water bath at 25°C. By combining flavour dispersions with the starch dispersions, the starch concentration was slightly reduced to 1.95 g/100 g, which had a negligible effect on the rheological properties of the systems. Rheological and analytical measurements were carried out 1 and 30 h after sample preparation.

Rheological measurements were performed with a Carri-Med controlled stress rheometer (CS 100, Carri-Med Ltd., Surrey, UK) using a cone-plate geometry with a diameter of 6 cm and an angle of 1°59′. The viscoelastic properties of the starch samples were determined at 25°C with oscillation measurements at a constant frequency of 1 Hz and in a shear stress range between 0.01 and 5 Nm^{-2}. The storage modulus, G′, and the loss modulus, G″, were recorded in the linear viscoelastic region.

The iodine binding capacity (IBC) was determined by amperometric titration using a Polarizer E585, Potentiograph E567 and Dosimat 655 from Methrom (Herisau, Switzerland). The voltage of polarization was set to 140 mV and the attenuation of the polarizer to 5 mA. A 30 g sample containing 100 mg starch (S_{tot}), 1 ml 1 mol/l HCl and deionized water was stirred constantly in a glass vessel during titration. The titration was carried out with 0.005 mol/l iodine solution (Titrisol, Merck) and with a titration rate of 1 ml/min. The amount of the bound iodine (I_b) was evaluated graphically and the IBC was calculated as follows:

$$IBC = \frac{I_b}{S_{tot}} .100\,[\%]$$

For the X-ray diffraction measurements, liquid samples were frozen, freeze-dried and the freeze-dried material compressed into disks of 13 mm diameter and a thickness of 1–2 mm. The disks were mounted on a sample holder. The measurements were carried out in the transmission mode at room temperature using a Siemens Kristalloflex D500 diffractometer (Siemens, Karlsruhe, Germany) with a crystal monochromator with CuK_α radiation (1.54 Å) at 40 kV and 35 mA. A divergence slit of 2 mm and a receiving slit of 1 degree were selected. X-ray intensity was recorded with a scintillation counter in a scattering angle range (2θ) of 5–30 degrees with a scanning speed of 0.04 degrees/min. A freeze-dried starch dispersion without addition of ligands was used as amorphous reference sample (halo). Diffractograms of samples with a V-amylose pattern were reduced by using the Fourier filtered curve of the amorphous reference sample.

RESULTS AND DISCUSSION

The present investigations were carried out using potato starch which contains practically no internal lipids and, therefore, no pre-existing inclusion compounds. At low concentration potato starch shows only a slight tendency to retrograde, and dispersions are fairly stable.

The solubilisation process by heat treatment at low shear ensured that a maximum of amylose was leached out from the granules without total disintegration of the granular structure. Inspection of starch dispersions by light microscopy confirmed that fragments of starch granules were still present.

Lecithin was used for preparing the flavour dispersions in order to obtain a better distribution of

flavours in the final starch dispersions. Complexation-induced gelation was also observed by addition of flavour substances alone, but the resulting gels were less homogeneous.

Lecithins of technical grade always contain small amounts of lysolecithin, which is able to form inclusion compounds (Acker & Becker, 1972). Therefore, the potential interference of lysolecithin had to be evaluated by measuring IBC and viscoelastic properties of starch dispersions with increasing concentrations of lecithin. Figure 2 shows that the addition of emulsifier caused only a slight decrease in IBC while the rheological behaviour remained virtually unchanged. Obviously, the lecithin preparation used in these experiments contained a negligible fraction of lysolecithin. The maximum concentration of lecithin used in combination with flavour substances was 3 mmol/mol glucose. Retrogradation of amylose and amylopectin could be excluded because the reference without flavour remained stable over a period of several days. Therefore, any changes of rheological properties in the starch systems with the addition of decanal and (−)fenchone would originate from interactions between starch and flavour.

Figure 3 shows the influence of increasing concentrations of decanal on the IBC and the storage and loss modulus of starch dispersions. The measurements were carried out 1 and 30 h after sample preparation. After 1 h the system had not yet reached equilibrium. In particular, the storage modulus G′ for samples with flavour concentrations in the range 25–75 mmol/mol glucose was changing until the system reached equilibrium after 30 h. Likewise, the IBC was decreasing during this period of time. It is suggested that for certain decanal concentrations, the distribution of decanal in the initial dispersion is critical for complex formation. At higher concentrations, enough decanal molecules were present to induce an immeadiate gelation. Nevertheless, Fig. 3 clearly shows that the storage modulus G′ reached its maximum value when the IBC approached zero, i.e. when the amylose fraction was fully saturated with decanal. Therefore, it can be concluded that gelation is induced by complex formation in the same manner as with complexing emulsifiers (Conde-Petit & Escher, 1992). The gels induced by decanal were softer than those induced by emulsifers. Possible reasons could be the lower molecular weight of decanal and/ or weaker binding forces of decanal to amylose.

Figure 4 shows the IBC and the storage and loss moduli G′ and G″ of potato starch dispersion as a function of (−)fenchone concentration 30 h after sample preparation, i.e. at full equilibrium. (−)Fenchone also induced the gelation of starch when amylose reached saturation, as already observed for decanal. Again, gels were softer than those formed with emulsifiers. For saturating the amylose and for complexation-induced

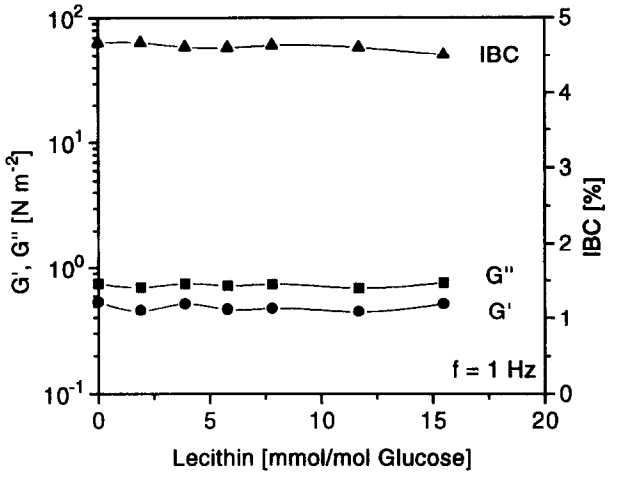

Fig. 2. Influence of lecithin concentration on the IBC and the storage modulus, G′, and loss modulus, G″, of potato starch dispersion (2 g/100 g).

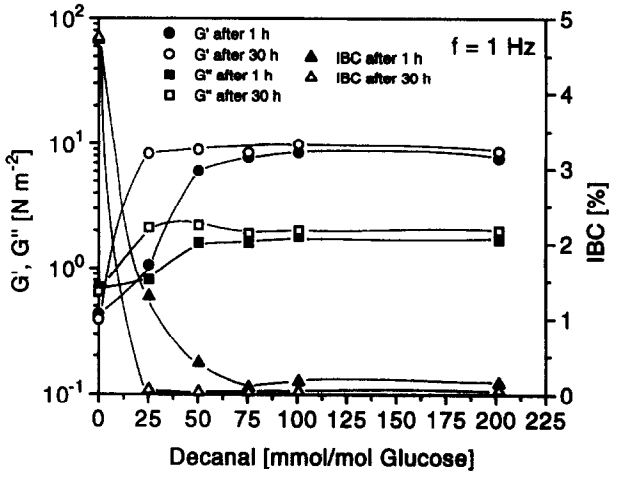

Fig. 3. Influence of decanal concentration on the IBC and the storage modulus, G′, and loss modulus, G″, of potato starch dispersion (2 g/100 g) after 1 and 30 h, respectively.

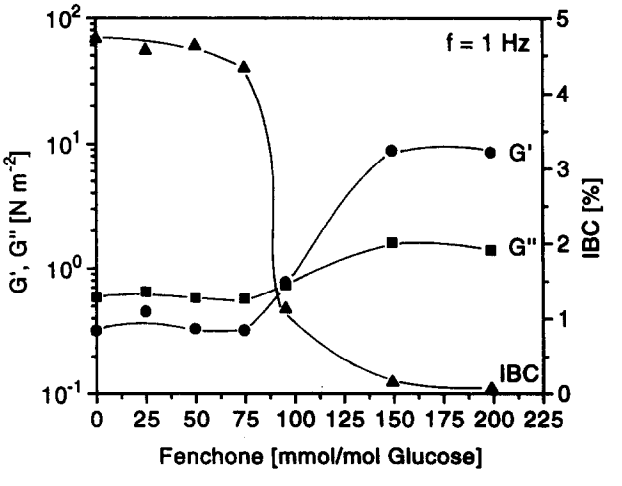

Fig. 4. Influence of (−)fenchone concentration on the IBC and the storage modulus, G′, and loss modulus, G″, of potato starch dispersion (2 g/100 g) after 30 h.

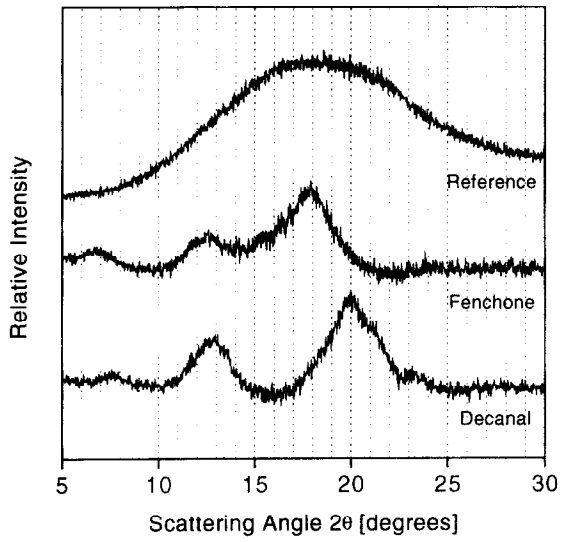

Fig. 5. X-ray diffractograms of freeze-dried potato starch dispersion (2 g/100 g) without addition of ligands (reference) and with addition of decanal and (−)fenchone, respectively.

gelation, a much higher concentration of (−)fenchone than of decanal was necessary (150 mmol/mol glucose vs 25 mmol/mol glucose). Decanal forms helices with 6 glucose residues per turn, while (−)fenchone induces a helix formation with 7 glucose residues per turn. Consequently, more binding sites are available for the complexation with the flavour molecules (Rutschmann & Solms, 1990*b*). Menthone also forms helices with 7 glucose residues per turn, and the concentration necessary for gelation (50 mmol/mol glucose) is rather high (Conde-Petit & Escher, 1995).

Addition of ligands to a starch system leads to the formation of single left-handed helices of amylose. The V-amylose can be obtained with 6, 7 or 8 D-glycosyl residues per turn (Yamashita, 1965; Yamashita & Hirai, 1966; Yamashita & Monobe, 1971). In Fig. 5, the X-ray diffractograms of a reference sample without emulsifier or flavour addition, and of samples with decanal and (−)fenchone addition are presented. The pattern of the reference shows an amorphous halo. No indication of crystallisation or retrogradation effects was found. The samples with decanal and (−)fenchone exhibited V-amylose patterns indicating the formation of single amylose helices. The size of the crystallites formed was very small. The 2θ-values of 7.5, 13 and 20° for decanal agree well with the values 7.5, 13 and 20.6° measured by Osman-Ismail and Solms (1972) and 7.4, 13 and 20.2° obtained by Rutschmann and Solms (1990*b*), respectively. The X-ray diffractogram of decanal confirms the formation of a V-amylose with 6 glucose residues per turn. The 2θ-values 7, 12.5 and 18° result from the complexation with (−)fenchone, showing a V-amylose with 7 glucose residues per turn. These values are comparable to those found for menthone (Osman-Ismail & Solms, 1972; Rutschmann & Solms, 1990*b*).

It may be concluded that complexation of amylose by volatile flavour substances leads to gelation-like changes of low concentration starch dispersions. According to the model proposed by Conde-Petit and Escher (1992) the gelation is caused by physical aggregation of the insoluble amylose ligand complexes.

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