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Structure and thermomechanical properties of extruded amylopectin–sucrose systems

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Abstract

The degree of heterogeneity in three non-expanded amylopectin–sucrose (88:12, 68:32 and 57:43) systems prepared by twin-screw extrusion was studied using FTIR microspectroscopy. The results obtained with a spatial resolution of 30 μm suggested a fluctuation in the compositions of these blends. As expected, the heterogeneous character of these blends was reflected in their thermomechanical behaviour as studied by DMTA. The thermograms of the blends containing 27–29% water (db) exhibited typically four transitions (tan δ peaks) which were assigned to a β-relaxation process, T_1 (−44 to −24 °C), a glass-transition of a sucrose-rich phase, T_2 (−20 to −6 °C), an ice-melting transition of the sugar-rich phase, T_3 (−10 to −2 °C) and a glass-transition of an amylopectin-rich phase, T_4 (3 to 22 °C) depending on the blends composition. The reduction of the water content by dehydration of these blends down to 9–13% (db) resulted in the expected disappearance of the ice-melting transition and the shift of the temperatures of the glass–rubber transitions to 11–23 °C for the sucrose-rich phase (T_2) and to 58–87 °C for the amylopectin-rich phase (T_4). Wide angle X-ray diffraction was used to monitor the degree of order particularly to verify the amorphous state of sucrose in the blends over the sugar and water content ranges of interest.

Keywords: Starch; Amylopectin–sugar; Extrusion; Glass-transition; DMTA

1. Introduction

The ability of small and intermediate sized molecules to modify the properties of biopolymers is of considerable scientific and technological importance. Of particular interest is the plasticisation of macromolecules such as proteins and starch polysaccharides by water and sugars (Kalichevsky, Jaroszkiewicz, & Blanshard, 1993a; Lourdin, Bizot, & Colonna, 1997a,b; Lourdin, Coignard, Bizot, & Colonna, 1997c; Orford, Parker, Ring, & Smith, 1989; Slade & Levine, 1991, 1993). The food polymer science approach based on understanding and exploiting the degree of molecular mobility and its impact on the rate of chemical and physical changes in relation to the glass–rubber transition offers the opportunity to rationalise the effect of formulation and processing/storage conditions on the processability and the stability of foods as proposed by Slade and Levine (Slade & Levine, 1991, 1993). For example, the impacts of water content, sugars and storage temperature on starch retrogradation, an area where conflicting reports can be found in the literature can be systematically understood within the framework of this approach (Farhat, Blanshard, & Mitchell, 2000a; Farhat, Descamps, Blanshard, & Mitchell, 2000b).

The cornerstone of the plasticisation theory is the assumption that the plasticiser(s) and the macromolecule form a homogeneous system. If this condition is fulfilled, the glass-transition temperature can be readily predicted by extending equations developed for synthetic polymers such as those proposed by Couchman and Karasz (1978), Gordon and Taylor (1952), and Ten Brinke, Karasz, and Ellis (1983), etc. to multi-component systems as demonstrated, e.g. by Kalichevsky et al. (1993a). However, very often, mixed systems do not form homogeneous blends leading to the observation of multiple transitions (Forssell, Mikkila, Moates, & Parker, 1997; Kalichevsky et al., 1993a; Moates, Noel, Parker, & Ring, 2001; Mousia, Farhat, Blachot, & Mitchell, 2000). This heterogeneity can be due to phase separation due to low miscibility, e.g. during film casting from solutions (Forssell et al., 1997;

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Gaudin, Lourdin, Forssell, & Colonna, 2000; Gaudin et al., 1999a; Gaudin, Lourdin, Le Boltan, Ilari, & Colonna, 1999b; Lourdin et al., 1997a–c; Lourdin, Ring, & Colonna, 1998; Moates et al., 2001) and/or the lack of efficient mixing (Kalichevsky et al., 1993a) leads to departures from the anticipated behaviour, a departure that, in many cases can be qualitatively or quantitatively accounted for (Farhat, Hill, Mitchell, Blanshard, & Blachot, 1998; Farhat, Mitchell, Blanshard, & Derbyshire, 1996; Mousia et al., 2000).

The aim of this study is to quantify the extent of concentration variations in biopolymer–plasticisers mixed systems and assess the effect of the structure on the mechanical properties. For this, the degree of molecular order (crystallisation) and the extent of homogeneity of non-expanded amylopectin–sucrose extruded mixtures at intermediate and low water contents were studied and the impact of the fluctuations of the sucrose concentration within the mixed system on its thermomechanical properties were investigated.

2. Materials and methods

2.1. Materials

Amylopectin as pregelatinised waxy maize starch was supplied by National Starch and Chemical Corp. (Manchester, UK). Fine, free flowing milled sugar powder with a 19–26 μm mean particle size was kindly donated by British Sugar Plc. (Peterborough, UK).

2.2. Sample preparation

Amylopectin and sucrose were mixed in different ratios using a Kenwood Peerless mixer for 90 min. The mixtures were extruded through the 1 mm × 30 mm slit die of a Clextral BC-21 co-rotating, intermeshing, twin-screw extruder. The 40 cm long extruder barrel was composed of four temperature zones (40, 90, 110 and 80 °C). The screw speed was 200 rpm and the solids feed rate was 5 kg/h. Distilled water was introduced into the extruder barrel using a piston pump to achieve water contents between 27 and 29% dry solid weight basis (db) in the final non-expanded extruded ribbons. The water flow rate was calculated to achieve the desired water content taking into account the original moisture content of the ingredients (11% db for pregelatinised waxy maize starch and less than 1% for crystalline sucrose), the composition of the solids feed and the solids feed rate. The moisture contents were determined by vacuum drying at 70 °C for 24 h. The samples were studied either shortly after extrusion or after storage for 15 days at 5 °C and 23% RH (over a saturated CH_3COOK solution) in order to decrease the water content to 9–13% db.

2.3. Wide angle X-ray diffraction

X-ray spectra were recorded on the extruded ribbons for 2θ between 4 and 32° at 0.05° (1 s exposure) intervals using a Bruker D5005 (Bruker AXS, UK) diffractometer equipped with a copper tube operating at 40 kV and 50 mA producing Cu Kα radiation of 1.54 Å wavelength.

2.4. FTIR microspectroscopy

Thin films (5–10 μm thick) were obtained by cryo-microtoming the extruded ribbons parallel to the surface and placed on ZnSe windows. Transmission FTIR measurements were performed using a Bruker IFS 48 (Bruker, UK) spectrometer operating with an IRscope-1 infrared microscope equipped with a 100 μm, liquid N_2 cooled MCT detector. The computer-control motorised microscope stage was programmed in order to acquire 17 × 17 spectra with a 30 μm diameter circular aperture and a step of 30 μm. A spectral resolution of 8 cm^{-1} was used and 128 scans were acquired for each spectrum. Air, humidified by bubbling in distilled water, was circulated above the sample to avoid drying of the films during the analysis.

2.5. DMTA measurements

A Rheometrics Scientific (Mark III) dynamic mechanical thermal analyser operating in bending mode was used. Rectangular strips (approximately 5 mm × 14 mm × 1 mm) were cut from the extruded ribbons and clamped in single cantilever geometry. DMTA thermograms were acquired at 2 °C/min at two frequencies (1 and 5 Hz). The samples were covered with silicone oil in order to alleviate the problem of water loss at high temperatures.

3. Results and discussion

X-ray diffraction analysis was performed to investigate (i) the degree of molecular order post-processing and (ii) the occurrence of any change in order, such as sucrose crystallisation, of the samples occurred during the storage/dehydration process. The diffractograms acquired on the amylopectin–sucrose extrudates shortly after extrusion were typical of amorphous systems exhibiting a broad pattern regardless of their sucrose content (Fig. 1). The feature centred at approximately $2\theta = 12–13°$ results from the contribution of amorphous sucrose (Mathlouthi, 1995). As expected the contribution of this peak to the total spectrum increased with increasing sucrose content.

Similarly, the samples retained their amorphous character when they were dried down to 9–13% db water content, through storage at 5 °C and 23% RH. This analysis was performed to verify whether sucrose had crystallised as a result of the decrease of the water content of the samples, particularly for the samples with high sugar contents.

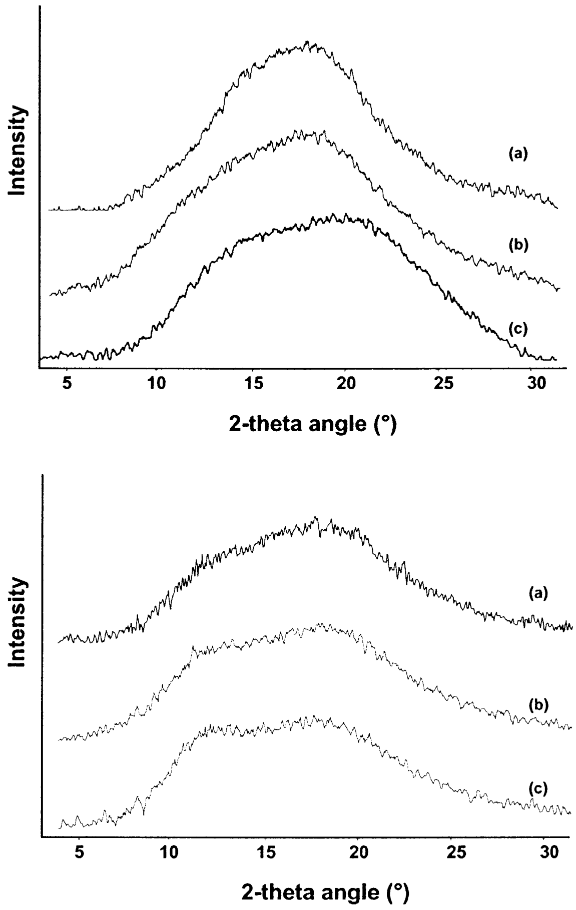

Fig. 1. X-ray diffractograms of the amylopectin/sucrose extrudates recorded shortly after extrusion, 27–29% water db (top) or after equilibration at 23% RH (9–13% water) (bottom). In each diagram, from top to bottom, amylopectin/sucrose ratio: 88/12 (a), 68/32 (b) and 57/43 (c).

FTIR microspectroscopy has been successfully used to characterise the phase behaviour of dilute amylopectin/gelatin solutions (Durrani & Donald, 1994, 1995). The method was lately applied to study the homogeneity of concentrated amylopectin/gelatin extrudates (Mousia et al., 2000; Mousia, Farhat, Pearson, Chesters, & Mitchell, 2001).

While there are vast differences between the mid-infrared spectrum of amylopectin and that of gelatin, differences that have been exploited to map the distribution of one of these components in a blend (Durrani & Donald, 1994, 1995; Mousia et al., 2000, 2001), the spectra of amylopectin and sucrose are similar due to the similarities in their chemical structures at the distance scale relevant to molecular spectroscopy. The spectra of both carbohydrates (amylopectin and sucrose) have the same characteristic overlapping bands arising from C–O and C–C stretching vibration modes, the 'saccharide band' between 1300 and 900 cm^{-1} (Fig. 2) (Mathlouthi, 1995; Mathlouthi, Cholli, & Koeing, 1986).

The thin film of amorphous sucrose used to acquire the spectrum in Fig. 2 was prepared by freeze-drying a small amount of a 25% (w/w) aqueous solution of sucrose, which was poured onto a ZnSe window. The spectrum is very similar to that reported by Mathlouthi (1995) and Mathlouthi et al. (1986) for amorphous freeze-dried sucrose.

Despite the similarities between the spectra of amylopectin and sucrose, there are several characteristic features, particularly in the band centred at around 925 cm^{-1}, which is much stronger in the spectrum of amorphous sucrose than in that of amorphous amylopectin. The area of this band relative to the total area of the bands between 1190 and 950 cm^{-1} was used as a marker of sucrose concentration. This band was selected as the marker of sucrose since it did not overlap with any other amylopectin or sucrose absorbance and thus the mathematical integration to obtain its peak area can be reliably achieved. A calibration was constructed and used for the quantitative analysis of the composition fluctuations of the extruded blends. Mousia et al. (2001) described two methods for the calibration of the FTIR band ratio results in order to obtain quantitative concentration data: (i) acquiring spectra using the largest aperture available, i.e. the sampling of a 100 μm × 100 μm square area of the sample (limited by the size of the detector) over the range of sample compositions studied, or (ii) averaging of the values obtained from the FTIR spectra

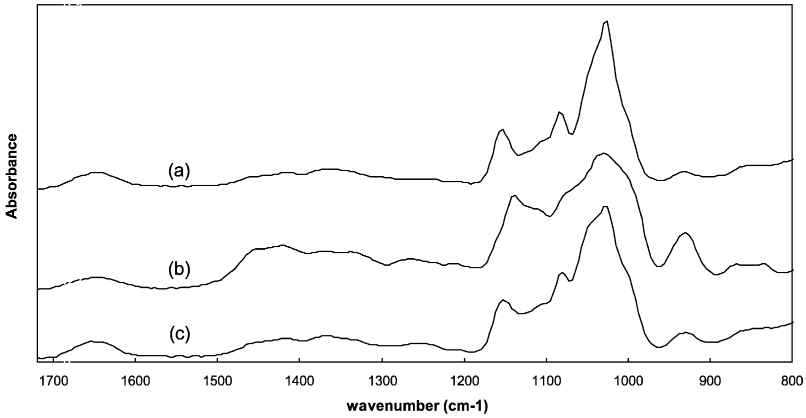

Fig. 2. Typical FTIR transmission spectra of thin films of extruded amylopectin (a), amorphous sucrose (b) and extruded amylopectin/sucrose 68/32 acquired with open aperture (100 μm detector).

making up the 2D microspectroscopy maps acquired using the 30 μm aperture (17 × 17 spectra). The two methods were found to give comparable results (Mousia et al., 2001) with the second method recommended since it samples a wider area of the film (approximately 500 μm × 500 μm). This method was adopted in this study (Fig. 3).

Typical FTIR maps obtained using the 30 μm round aperture describing the variation of sucrose concentration across the sampled area (approximately 500 μm × 500 μm) acquired on the blends shortly after extrusion (water content 27–29% db) are shown in Fig. 4. The results clearly demonstrate the fluctuation in the blend compositions at the spatial resolution used. The concentration ranges obtained for each of the blends are summarised in Table 1.

Although it might be expected that small molecules such as sugars would form homogeneous mixtures with biopolymers and particularly with polysaccharides such as amylopectin, there are clear experimental evidences that there is a considerable degree of heterogeneity in the amylopectin–sugar blends assessed in this study. However, the FTIR sucrose concentration maps revealed that at the distance scale relevant to this technique (30 μm in this study) there are no areas of the sample where only one of the two components of the blend is present.

The effect of the heterogeneity of the blends on their mechanical properties was studied using dynamic mechanical thermal analysis. Like other spectroscopic techniques, mechanical spectroscopy probes molecular relaxation processes by detecting the amount of energy absorbed by a material particularly when the measurement frequency approaches that of a given molecular relaxation process. In the case of mechanical spectroscopy, energy is absorbed as a result of change in viscoelastic properties and damping characteristics. Typical molecular relaxations probed by DMTA include, in order of increasing temperatures, secondary relaxations (typically γ and β) involving small-scale motions such as those of side groups and side-chains, the glass-transition (α) where cooperative movements of molecules and polymer backbones occur and, the melting transition in crystalline and partially crystalline systems. Dynamic mechanical analysis techniques include mechanical analysis over a frequency range at a constant temperature (frequency sweep) or over a temperature range at a given frequency (temperature sweep). Temperature sweeps at two frequencies (1 and 5 Hz) were performed in this study.

The ability of mechanical spectroscopy techniques to probe multi-phase systems such as some block and graft copolymers and mixed systems and to detect the individual glass–rubber relaxations of each phase is widely reported in the areas of synthetic and natural polymers (Blanshard, 1995; Chan, Pathmanathan, & Johari, 1986; Kalichevsky, Blanshard, & Marsh, 1993b; Kalichevsky et al., 1993a; McCrum, Buckley, & Bucknall, 1988; Mousia et al., 2000).

The DMTA thermograms acquired on the various amylopectin and amylopectin–sucrose extrudates showed multiple transitions (Figs. 5 and 6). The following section attempts to assign the various transitions by assessing (i) their frequency dependence: α and β relaxations are expected to shift to higher temperatures as the measurement frequency increases while melting transitions (typically ice-melting in this study) do not exhibit frequency dependence, and (ii) their dependence on water content: α relaxations are expected to shift to lower temperature at high water content (plasticisation) while β relaxations should exhibit little dependence on water levels (Noel, Parker, & Ring, 1996; Noel, Ring, & Whittam, 1992).

The DMTA thermograms acquired on an extruded amylopectin sample containing ~36% water (db) exhibited three transitions which can be clearly identified from their respective tan δ peaks (Fig. 5). The small transition centred around −50 °C is associated with the silicon oil used to coat the sample as moisture barrier and was therefore not accounted for in the analysis of the DMTA results. The transitions at approximately −30 and 10 °C (1 Hz) were assigned to a β-relaxation (secondary relaxation) and an

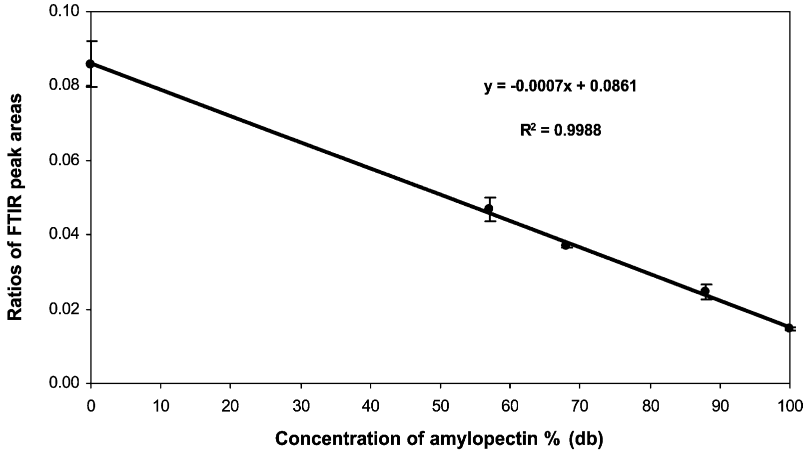

Fig. 3. Calibration of the ratio of the FTIR absorption bands versus the concentration of sucrose in the system (w/w db). Error bars represent one standard deviation of three measurements.

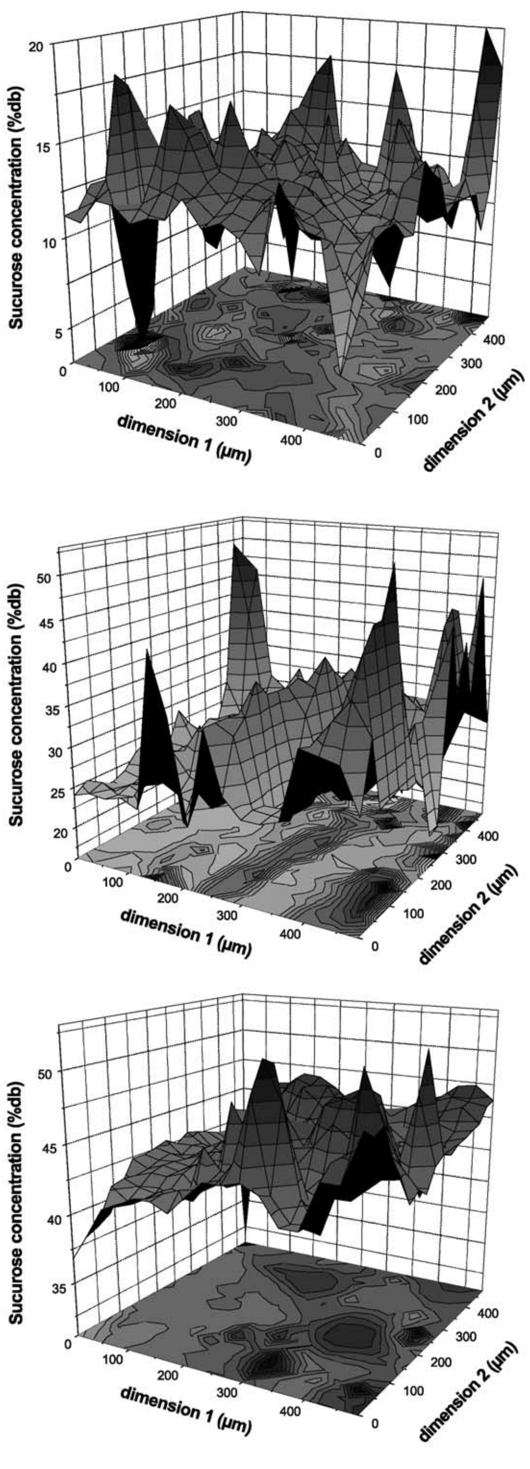

Fig. 4. Sucrose concentration profiles derived by FTIR microspectroscopy. The dry weight basis sucrose concentration in the blends were 12% (top), 32% (middle) and 43% (bottom).

Table 1
The fluctuation of the concentration of sucrose as studied by FTIR microspectroscopy compared to the composition of the blends

	Sucrose concentration (% db)		
Sample formulation	12	32	43
Concentration range from FTIR	3–20	17–53	32–52
Average FTIR concentration	12	29	44

α-relaxation (glass–rubber transition), respectively. These transitions shifted to high temperatures as the frequency increased from 1 to 5 Hz. The measured glass-transition temperature is in agreement with the expected value of 10–15 °C based on studies on similar systems using the same technique (DMTA, tan δ, 1 Hz) reported elsewhere (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992; Mousia et al., 2000).

The thermograms of the amylopectin/sucrose: 57/43 and 68/32 samples showed typically four transitions at 27% db water content—these are referred to as T_1, T_2, T_3 and T_4. When the water content of these samples was reduced to 13% db the transition T_3, which showed no frequency dependency, disappeared. The amylopectin/sucrose: 88/12 system showed three transitions at 29% db water content and only two in the dried state (9% db). These transitions (tan δ) are summarised in Table 2 for the three amylopectin–sucrose blends investigated and at two water contents for each blend.

In contrast with T_3, the T_1, T_2 and T_4 transitions showed frequency dependency with the temperatures at which the transitions were observed increasing when the measurement frequency increased from 1 to 5 Hz.

The transition T_1, was observed in all three amylopectin–sucrose blends and showed no dependency on the water content. This transition was assigned to a β-relaxation process and both the temperature at which it was observed and its behaviour vis-à-vis water content is in agreement with the dielectric data reported on carbohydrate–water glasses (Chan et al., 1986; Noel et al., 1996, 1992).

The transition T_2, which was also observed at all three sucrose concentrations shifted to higher temperatures as the water content of the blend decreased. This transition was believed to describe the glass–rubber transition of a sugar-rich phase.

The T_4 transition was present in the thermograms of all the blends investigated. The temperature of T_4 shifted to higher temperatures when the measurement frequency increased from 1 to 5 Hz. T_4 showed also a strong water content dependency shifting to higher temperatures when the moisture content decreased from 27–29% db down to 9–13% db (Table 2). This transition occurring at the highest temperatures in the thermograms was attributed to the glass-transition of an amylopectin, or an amylopectin-rich phase.

Finally, the transition T_3 was observed in the thermographs of the blends with high sugar concentrations (32 and 43% db) only at high water contents (27% db). As mentioned earlier T_3 showed no frequency dependency. This transition was assigned to an ice-melting transition since it was only observed in the high water content samples. It is believed that T_3 results from the ice formed in the sucrose-rich phase, since this phase had a glass-transition (T'_g) between −20 and −15 °C for the 68/32/27

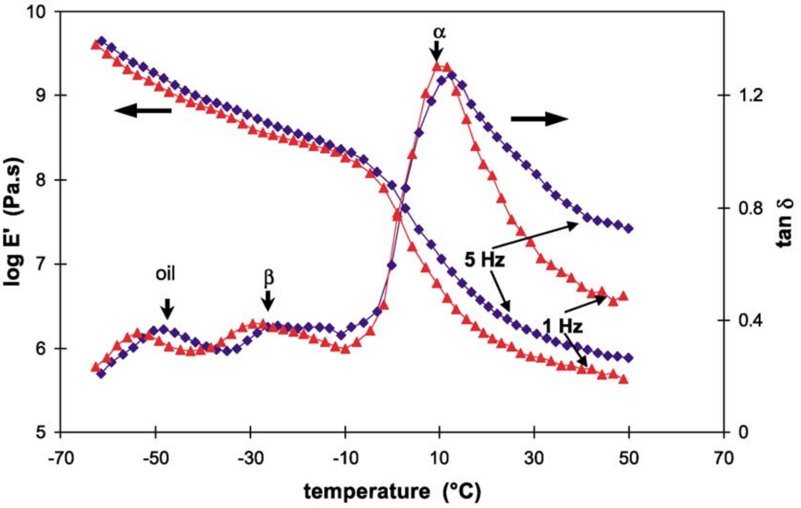

Fig. 5. DMTA thermograms of pregelatinised waxy maize starch extrudates containing 36% water (db) acquired at frequencies of 1 and 5 Hz.

and between −16 and −10 °C for the 57/43/27 amylopectin/sucrose/water blends. This transition was observed as a shoulder on the main tan δ peak. This is not unexpected since ice formation is only expected in the high water content samples. However, these only contained between 27 and 29% water on a dry basis and therefore only a small amount of ice can form particularly that it can only form in the sugar-rich phase which even at the highest sugar content only constitutes less than half of the total sample. Furthermore, the fact that this contribution is 'squeezed' between the two main α-relaxations can contribute to difficulties in observing it. The fact that the T_3 transition was not observed in the amylopectin/sucrose/water 88/12/29 system indicated the absence of ice formation during the cooling of this sample in the DMTA apparatus. This is in agreement with the observed higher glass-transition temperatures of the sugar-rich phase (T_2). It is therefore suggested that the transition temperature of T_2 is the T_g of this sugar-rich phase rather than a T'_g of a freeze concentrated sugar-rich phase as is the case for the higher sugar content blends. An alternative raison for the absence of T_3 from the thermogram of the 88/12/29 amylopectin/sucrose/water blend is the limited sensitivity of the DMTA technique in detecting a small ice-melting contribution resulting from the smaller amount of the sucrose-rich phase in the sample due to the blend composition as discussed above (sucrose content = 9.3% of the total sample weight).

T_3 occurred at temperatures (tan δ) between −10 and −6 °C for the 68/32/27 blend and between −4 and −2 °C for the 57/43/27 amylopectin/sucrose/water system. These values are higher than those reported for the T'_m of sucrose–water systems measured by DSC (1). This can be understood in terms of (i) the fact that transitions measured by the tan δ peak (1 Hz) are approximately 5–10 K higher than their equivalent measured by DSC (Kalichevsky et al., 1992) and (ii) the phase responsible for this transition may contain some amylopectin and would therefore be expected to have a T'_m higher than that pure sucrose/water phase.

It is worth noting that except for the β transition temperature, the repeatability of two or four replicates (depending on the sample), within six degrees in the worth case for all other transitions, was very satisfactory considering the nature of the DMTA measurement and sample variability. The temperature of the β-relaxation is difficult to determine accurately for several raisons such as the relatively low temperature at which it occurs, the width of the transition and the subsequent difficulty in defining the temperature of maximum tan δ, the overlap with the transition from the oil used to alleviate moisture loss since water content is the defining factor for the temperature of the α-relaxation, etc.

In order to assess the role of sucrose in plasticising amylopectin in the amylopectin-rich phase, the temperature of the T_4 transition was compared to the T_g expected for amylopectin–water systems based on the results reported elsewhere on similar systems using the same technique (DMTA, tan δ, 1 Hz) (Kalichevsky et al., 1992; Mousia et al., 2000). The glass-transition temperatures measured on the amylopectin–sucrose blends are lower than those predicted for the equivalent amylopectin–water systems suggesting a degree of plasticisation of the biopolymer by sucrose. While increasing the sucrose concentration from 12 to 32% (db) decreased the T_4 transition temperature relative to the expected T_g of the equivalent amylopectin–water system by 6–8 and 27–32 °C, respectively, reflecting the increased plasticisation as an increasing fraction of the biopolymer was replaced by sucrose, the further sucrose concentration increase to 43% db had the opposite effect. These results are in agreement with the findings of Kalichevsky et al. (1993a) where sugars were found to plasticise amylopectin when used in small concentrations but at higher sugar contents amylopectin–sugar mixtures behave as non-homogeneous two-phase systems.

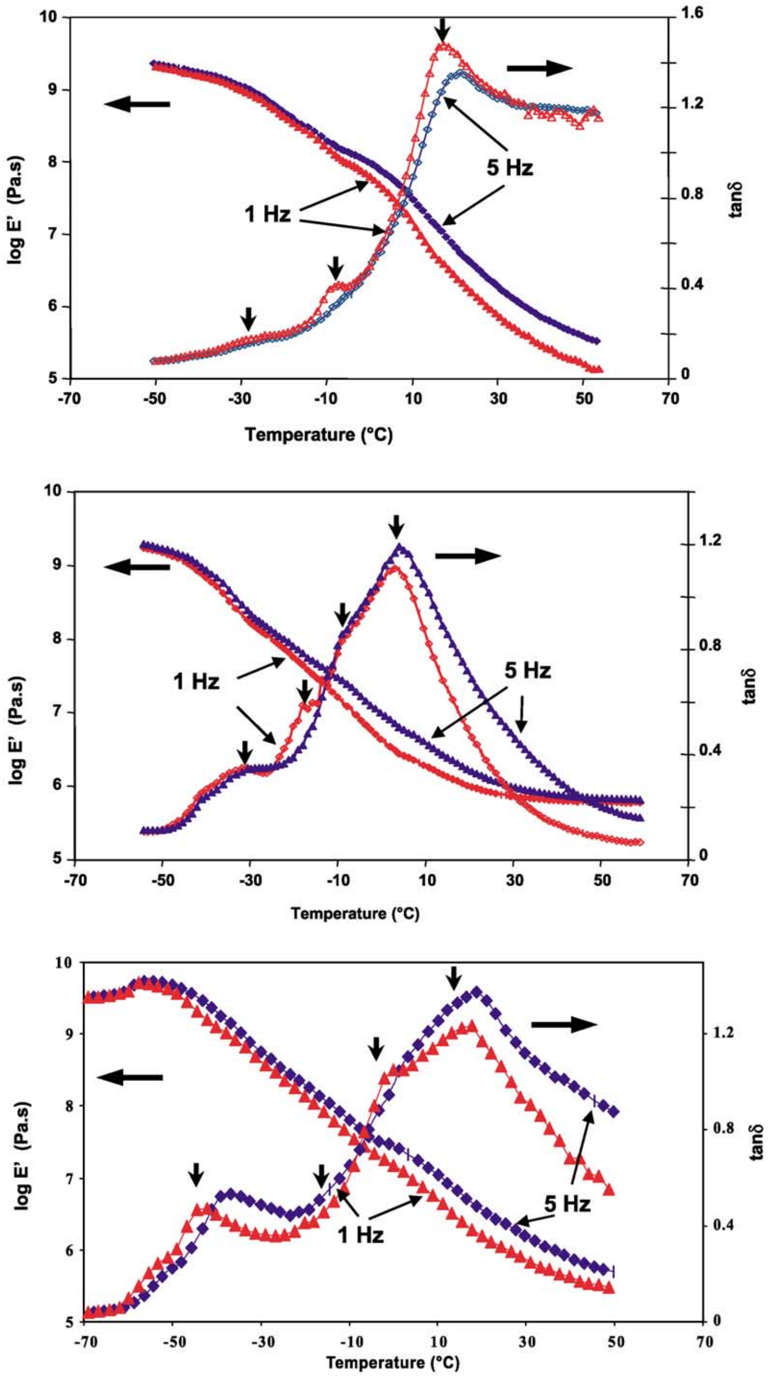

Fig. 6. DMTA thermograms of the extruded amylopectin/sucrose blends. From top to bottom, amylopectin/sucrose/water: 88/12/29, 68/32/27 and 57/43/27.

While the observations of Kalichevsky et al. (1993a) are somehow expected in the light of the sample preparation method adopted by these authors, namely hot pressing of powder mixtures of amylopectin as pregelatinised waxy maize starch and frozen sugar–water solutions, a better degree of mixing by the twin-screw extrusion process was expected. A fundamental question remains regarding whether amylopectin and sucrose are thermodynamically compatible at these low water contents. It is however believed that, at low water content, restricted molecular mobility would increase the time scale of long range, microscopic phase separation processes considerably compared to the experimental time scale. Starch retrogradation and other crystallisation processes could lead to range phase separation. The X-ray diffraction results suggested however that sugar crystallisation and amylopectin retrogradation did not occur in this study.

In studies where starch/co-plasticiser samples in the form of films are prepared by casting from solution, e.g. in the studies of Lourdin, Forssell, Ring and co-workers (e.g.

Table 2
Summary of the temperatures of the transitions measured by DMTA (tan δ) on the amylopectin/sucrose extrudates in relation to the anticipated T_g values for the equivalent amylopectin–water systems. All the measurements obtained at a given water content are reported

Amylopectin/sucrose ratio	Water content (% db)	Predicted amylopectin T_g (°C)	Measured transition temperatures (°C)			
			T_1	T_2	T_3	T_4
88/12	29	28	−41	−8		22
			−38	−6		21
			−35	−12		20
			−24	−7		18
	9	121	−33			83
			−34			87
68/32	27	35	−36	−20	−7	8
			−37	−19	−10	7
			−33	−15	−6	4
			−31	−18	−9	3
	13	99	−36	16		60
			−43	11		58
57/43	27	35	−42	−16	−4	18
			−42	−13	−2	16
			−29	−16	−3	17
	13	99	−44	23		>60[a]
			−42	14		>60[a]

[a] Due to sample brittleness, only the onset of the tan δ peak was measured for these samples and therefore the onset of the tan δ peak temperature is reported.

Forssell et al., 1997; Gaudin et al., 1999a,b, 2000; Lourdin et al., 1997a–c, 1998; Moates et al., 2001), etc. phase separation is likely to occur in the solution state and during cooling/concentration if thermodynamic incompatibilities between the components exist and through retrogradation of amylose and subsequently amylopectin on storage. Some of the questions relating to these types of systems and preparation methods may be addressed through studying mixtures prepared by different drying regimes (time/temperature/concentration) from a high water system and through a careful choice of the polymer (e.g. amylopectin versus amylose) and co-plasticiser components.

4. Conclusions

This study clearly demonstrated that blends of amylopectin and sucrose produced by extrusion at relatively low specific mechanical energy (typically ≤150 W h/kg in this study) and temperature (≤110 °C in this study) are often non-homogeneous despite the thorough mixing conveyed by the twin-screw extrusion process. Such conditions are common in some breakfast cereal and third generation snacks manufacturing.

The extent of heterogeneity can be monitored using FTIR microspectroscopy, which despite its limited spatial resolution (30 μm in this study) revealed fluctuations in the sucrose content across the samples. The spatial resolution of the technique could be improved up to typically 10 μm (diffraction limit of the relevant mid-infrared spectral range of interest) (18) at the expense of measurement times (several hours). Furthermore, in practice low signal/noise ratios limit the achievement of high resolutions. These problems can now be addressed in the light of new development in array infrared imaging techniques where typically 64 × 64 MCT detectors are used to acquire simultaneously 4096 spectra mapping a 400 μm × 400 μm area with a resolution of 4 μm × 4 μm (Bhargava, Wall, & Koenig, 2000).

As expected, the thermomechanical properties of these blends reflected their heterogeneous character with the appearance of multiple transitions in their DMTA thermograms. Four main transitions were identified and assigned, in order of increasing temperature, to a β-relaxation (T_1) process, the glass-transition of a sucrose-rich phase or a freeze concentrated sucrose-rich phase (T_2), the melting of ice of the sucrose-rich phase and finally to the glass-transition of the amylopectin-rich phase (T_4). The results suggested that a fraction of sucrose plasticises the amylopectin in an amylopectin-rich phase.

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