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FTIR study of state and phase transitions of low moisture sucrose and lactose

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Abstract

Mid-infrared spectra of freeze-dried sucrose and lactose systems were acquired over a range of temperatures (30–200 °C) and water contents (0–6.3%). Starting from the glassy state, the experimental conditions were selected to cover the main thermal transitions: the glass–rubber transition, the crystallisation and, for some samples, the subsequent melting. The FTIR spectra were very sensitive to the physical state. While subtle but systematic spectral differences between the glassy and rubbery states were detectable throughout the spectrum, a very pronounced increase in spectral resolution was observed as crystallisation occurred and was followed by the expected spectral broadening during melting. The temperatures at which these changes occurred were in satisfactory agreement with the transition temperatures measured by differential scanning calorimetry (DSC). The increase in molecular mobility as a result of increasing temperature or plasticisation by water led to a significant shift of the O–H stretching band to higher wavenumbers indicating a weakening of hydrogen bonding. This shift reached a maximum as the DSC measured crystallisation temperature range was approached. As expected, the crystallisation led to a highly effective hydrogen bonding network. This was more significant for lactose than for sucrose. No significant step change in hydrogen bonding was observed at Tg. As anticipated, the temperature at which these transitions occurred decreased with increasing water content but overlapped when observed in the context of the shifted temperature ($T-\mathrm{Tg}$).

Keywords: Sucrose; Lactose; Glass-transition; Crystallisation; Hydrogen bond

1. Introduction

When a liquid is cooled below its melting point (Tm), the occurrence of a 'true' solid (i.e., crystalline) is only possible if the cooling rate is sufficiently slow to allow for nucleation and subsequent crystallisation. Rapid cooling however leads to the occurrence of the rubbery state, a supercooled liquid with relatively high viscosity as defined by its resistance to flow. On further cooling, the glassy state, a solid-like supercooled liquid is achieved[1,2] (Fig. 1). The importance of these phase and state transitions that a food or its components undergo during processing (heating, hydration/drying, etc.) and storage is now well acknowledged and has been the subject of many reviews and books.[3–5]

Both the glassy and rubbery states possess higher chemical potential and free energy than the crystalline solid and are therefore kinetic states, which are not at a thermodynamic equilibrium.[5,6] While the significantly reduced molecular mobility in the glassy state leads to its relative stability, in particular towards crystallisation, the rubbery state is physically unstable and prone to crystallisation. The effect of temperature on the kinetics of crystallisation was described in detail by Roos.[5] It is understood in terms of the dependence of the nucleation and growth rates on temperature. This yields a bell-shaped relationship between crystallisation rate and temperature, where a maximum rate of crystallization is reached approximately halfway between Tg and Tm (Fig. 1, insert). For many systems, such as some synthetic polymers, mono- and disaccharides, etc., when a glassy material is heated beyond its Tg, crystal-

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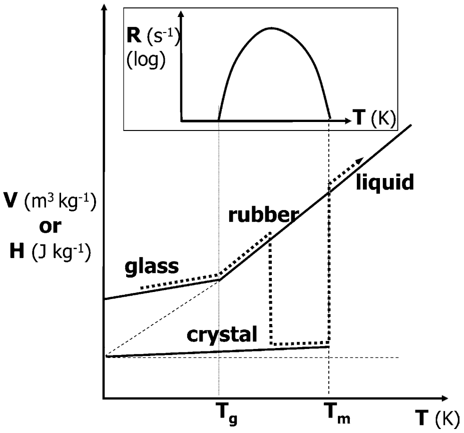


Fig. 1. Phase/state transitions monitored through the dependence of the specific volume (V) and enthalpy (H) on temperature (T). The insert depicts the effect of temperature on the rate of crystallisation (R). The thick dotted line depicts the typical behaviour observed when a low molecular weight carbohydrate (typically mono- or disaccharide) is heated from the glassy state.

lisation can occur within the experimental time scale set by the heating rate as a result of the significantly high rate of molecular mobility in the rubbery state (Fig. 1). Continued increases in temperature would eventually lead to the melting of the crystalline solid.

In the case of carbohydrates, this approach led to significant progress in understanding the crystallisation of sugars[7,8] and starch retrogradation[9–11] and is behind many food and pharmaceutical encapsulation and delivery systems.

A range of techniques for monitoring such transitions is available. The choice of a particular technique is often guided by fundamental (physical property studied, time and distance scales probed, etc.) and practical (availability, sampling requirements, measurement time, sensitivity, etc.) criteria. While the crystalline state lends itself to a range of analytical tools (X-ray diffraction, microscopy, solid state NMR, etc.) which enable full 3D characterisation, studying the amorphous state, and particularly the glassy and rubbery states, often relies on monitoring the changes of a given physical property (heat capacity, modulus, molecular mobility and correlation time, dielectric permitivity, etc.) as the temperature is changed over a range that encompasses the glass–rubber transition temperature.[5]

Differential scanning calorimetry (DSC) is by far the most widely used technique for studying crystallisation, melting, glass–rubber transition, and physical ageing phenomena, in particular for carbohydrate systems. This technique offers many advantages, not the least of which are: direct access to thermodynamic properties e.g., heat capacity, latent heat of phase transitions, the temperature of the glass transition (Tg), crystallisation (Tc) and melting (Tm), sensitivity, control of temperature and moisture content, speed of analysis and the relatively new temperature modulated methods. A major limitation of this, and several other widely used techniques such as dynamic mechanical thermal analysis (DMTA) and dielectric thermal analysis (DETA), is that the thermogram does not directly contain chemical information enabling the unequivocal assignment of the thermal transitions to specific molecular processes (e.g., motion of the polymer side chain versus that of the backbone) or a particular component in a mixed system.[12]

In this study, the transitions occurring during the heating of glassy carbohydrates at different water contents were monitored by DSC in conjunction with FTIR spectroscopy in an attempt to study the molecular origin/fingerprint of the main thermodynamic transitions. Two disaccharides, sucrose and lactose, were selected for this study.

2. Experimental

Sucrose (Lot No. 44H06512) and β lactose (Lot. No. 73H0314) were purchased from Sigma (UK).

2.1. Sample preparation

Amorphous carbohydrate systems were prepared by freeze-drying 10% (w/w) sugar solutions in distilled water using an Edwards Super Modulyo Freeze Drier (Edwards High Vacuum). During the freeze-drying process, the pressure was maintained below 0.1 mbar and the condenser temperature below −45 °C for a period of 5 days. To ensure the removal of the residual 1–2% moisture present after freeze-drying, the samples were stored under vacuum in a desiccator over P_2O_5 for at least 2 days before subsequent analysis.

A range of moisture contents were achieved by hydrating (7 days at 20 ± 2 °C) the freeze-dried samples over saturated salt solutions providing a range of relative humidities. The salts were LiCl (RH = 11%), CH_3COOK (22%) and $MgCl_2$ (33%).[13]

X-ray powder diffraction analysis on the samples post-hydration confirmed that, except for sucrose stored at 33% RH, the sugar remained in the amorphous state for both lactose and sucrose over the moisture content range relevant to this study (results not shown). Hence the sucrose sample stored at 33% RH was excluded from the study.

2.2. Moisture analysis

The moisture contents of the freeze-dried sugar samples were measured using the Karl Fischer coulometric titration. A Mitsubishi CA-05 Moisture Meter was used for the measurement. For each sample analysed,

~0.1 g was left in 3 mL of formamide (Fisons) for an hour in a sealed vial to extract the water present. For each sample, a formamide blank was prepared and the experiments were performed in quadruplicate.

2.3. DSC measurements

Approximately 10 mg of sample were hermetically sealed in a DSC stainless steel pan and analysed using a Perkin–Elmer DSC-7 calibrated for temperature and heat flow using indium and cyclohexane. An empty pan was used as a reference. In order to match the heating rate achieved by the FTIR methodology, a heating rate of 3 °C/min was used.

2.4. FTIR measurements

Attenuated total reflectance (ATR) mid-infrared spectra were acquired using an IFS48 (Bruker Optics) spectrometer equipped with a DTGS detector and a heated single reflectance diamond ATR accessory (Graseby Specac) with a sealed sapphire anvil.

Spectra (32 scans, of 4 cm^{-1} resolution) were acquired at temperatures between 30 and 200 °C at 5 °C intervals. At each temperature, the sample (~2 mg) was allowed to achieve thermal equilibrium by waiting for 1 min before acquiring any data. The overall underlying heating rate was approximately 3 °C/min.

The spectra were vector normalised over the wavelength ranges of interest: 3500–3000 and 1200–800 cm^{-1}. All measurements were performed in duplicate.

3. Results and discussion

3.1. Characterising state/phase transitions by DSC

The state and phase transitions of the two glassy sugars (sucrose and lactose) hydrated to different extents were studied using DSC. Fig. 2 shows a typical DSC thermogram obtained for freeze-dried sucrose sample stored at 11% RH and containing 3.3% water (w.b.). The thermogram displays the three transitions expected in this temperature range: (i) the glass transition reflecting the step change of the specific heat capacity (c_p) at the glass transition temperature (Tg); (ii) the exothermic crystallisation of sucrose from the rubbery state at the temperature Tc; followed by (iii) the melting endotherm at Tm.

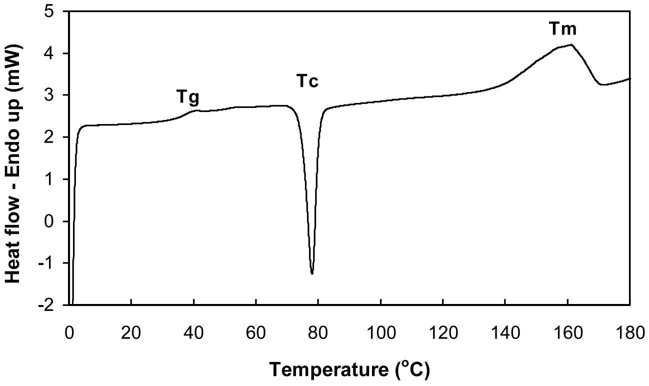


Fig. 2. Typical DSC thermogram for freeze-dried sucrose. Shown is the thermogram of a sample containing 3.3% water (w.b.) (RH = 11%).

The relative humidity, moisture contents and the results of the DSC analysis for all the samples of this study are summarised in Table 1.

As expected, effective plasticisation of the carbohydrate materials by water was observed leading to a significant decrease of Tg and Tc (and Tm for sucrose) as the moisture content increased. This phenomenon has been widely reported[3,14,15] and will not be discussed here as it is not the main aim of this study.

The transition temperatures are in good agreement with those reported by Roos and Karel.[15] These values will be used in the rest of the paper to rationalise the differences observed in the FTIR spectra of these carbohydrates acquired over a range of temperatures. The FTIR results will be viewed in the context of the 'shifted' temperature parameter ($T-\mathrm{Tg}$) where T is the experimental temperature and Tg refers to the temperature at which the DSC measured c_p change, associated with the glass-transition, is complete ($\mathrm{Tg_{end}}$). ($T-\mathrm{Tg}$) provides a useful framework for examining the dependence of physical properties such as molecular mobility,[16] sugar crystallisation,[15] starch retrogradation,[17] etc.) on temperature, in the glassy and rubbery states.

3.2. Effect of state/phase transitions on the FTIR spectrum

Fig. 3 shows typical FTIR spectra (1200–800 cm^{-1}) of a freeze-dried sucrose glass, which was hydrated over LiCl (RH = 11%) to a moisture content of 3.3% (w.b.) acquired over the temperature range 30–200 °C. The spectral region between 1200–800 cm^{-1} comprises a series of overlapping bands, mostly resulting from C–O and C–C stretching vibrations.[18,19] The precise assignment of these bands is not unequivocal.

The lineshape of the mid-infrared spectra acquired on both sugars depended on temperature, with dramatic changes when the temperature approached the DSC measured crystallisation and subsequent melting temperatures. At very high temperatures (typically ≥ 185 °C for sucrose), the FTIR spectrum changed dramatically suggesting the occurrence of degradation of the sugar and the modification of its chemical structure.

Crystallisation led to a pronounced increase in spectral resolution reflecting the three-dimensional re-

Table 1
Tg, Tc and Tm as measured using DSC

	RH (%)	Water content (% w.b.)	Tg onset (°C)	Tg end (°C)	Tc onset (°C)	Tc end (°C)	Tm onset (°C)	Tm end (°C)
Sucrose	0	0.5 ± 0.01	58.6	63.9	101.1	106.6	157.0	181.9
	11	3.3 ± 0.01	33.2	39.0	74.6	80.3	140.6	169.7
	22	4.7 ± 0.2	21.8	27.5	61.9	72.2	133.0	163.2
Lactose	0	0.4 ± 0.05	93.2	97.3	154.0	162.6	ND	ND
	11	4.4 ± 0.1	49.4	54.2	97.7	98.5	ND	ND
	22	5.7 ± 0.02	32.3	39.7	76.5	83.4	ND	ND
	33	6.3 ± 0.2	26.8	33.8	72.3	78.8	ND	ND

peated structure of the crystalline system, which yields discrete distribution of bond environments with defined vibrational frequencies. This observation is similar to early reports by Mathlouthi and coworkers[20] where they compared the FTIR spectra of sucrose as a crystal, a freeze-dried amorphous 'solid' and in solution. The observation of crystallisation by molecular spectroscopy does not however yield information on the quality of the crystals formed. This would be ultimately determined using X-ray powder diffraction. Unfortunately, the sample was too small to recover at the end of the FTIR experiment and characterise by XRD. It is however likely that the crystals formed during the so-called cold crystallisation (i.e., from rubbery state) under dynamic heating conditions are not as perfected as those formed by crystallisation from solution.

Melting led to the expected broadening of the resolved FTIR spectrum reflecting the amorphous nature of the liquid melt. The spectral changes as the material underwent its glass to rubber transition were less pronounced but can be clearly seen (Fig. 4(a)). They included some small shifts in wavenumber but more clearly, changes in the relative absorbances. For sucrose the most noticeable was the decrease of the absorbance at ~1033 cm^{-1} and the increase of the intensity of the band at ~979 cm^{-1}. The contrasts between the characteristics of the infrared spectra in this 'structural' spectral region of the amorphous glassy and rubbery states, and in the liquid in comparison to that of the crystalline solid, were essentially similar for both sugars (Fig. 4).

The comparison of the FTIR spectra of lactose post-crystallisation to those of commercial α and β lactose suggested that all the studied lactose samples crystallised into the β form, which is accepted to have an anhydrous crystal lattice.

In an attempt to quantify these changes, the ratio of the absorbance at 979 cm^{-1} for sucrose or 987 cm^{-1} for lactose, believed to be associated mostly with ring C–C stretching vibrations, to that at ~1034 cm^{-1}, believed to result from C–O stretching vibration of the CH_2–OH (as the other C–O stretching vibrations, such as the ring CH–OH and C–O, would be expected to contribute at higher wavenumbers) was calculated.

The plot of this intensity ratio versus (T − Tg) for both sucrose and lactose showed the following general

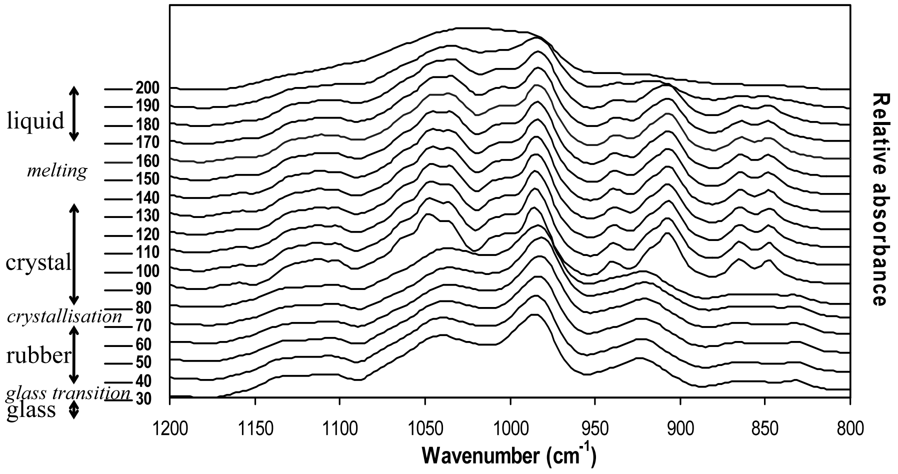
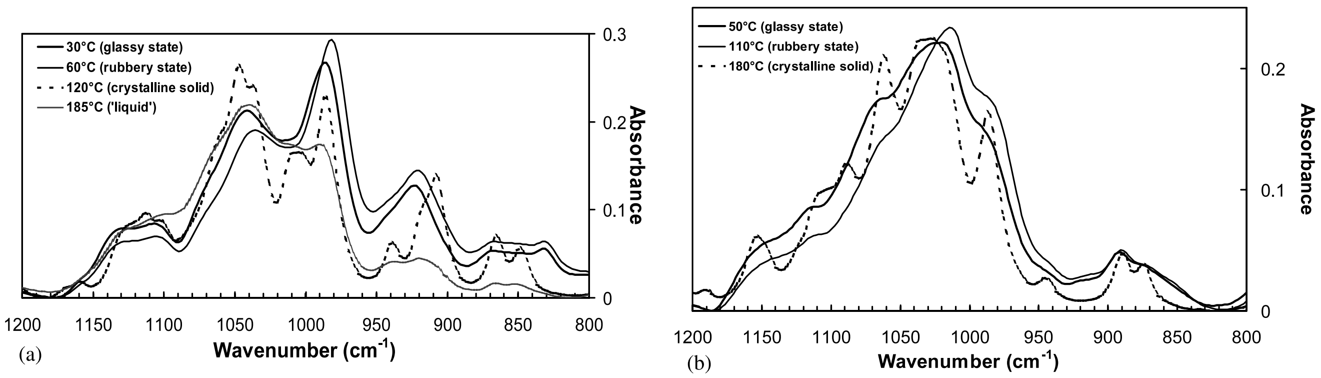


Fig. 3. Effect of temperature on the mid-infrared spectra (1200–800 cm^{-1}) of freeze-dried sucrose containing 3.3% water (w.b.) (RH = 11%). Spectra acquired between 30 (bottom) and 200 °C (top) in steps of 5 °C. For clarity, the spectra were stacked and only half of the available data (10 °C steps) is displayed. The spectra are examined in the context of the DSC measured transitions (left).



(a) (b)

Fig. 4. (A) Typical mid-infrared spectra (1200–800 cm^{-1}) of glassy, rubbery, solid and liquid sucrose (a) and lactose (b) containing 3.3 and 4.4% water (w.b.) (RH = 11%), respectively. (B) Typical mid-infrared spectra (1200–800 cm^{-1}) of glassy, rubber, solid and liquid sucrose (a) and lactose (b) containing 3.3 and 4.4% water (w.b.) (RH = 11%), respectively.

pattern (Figs. 5 and 6):- In the glassy state i.e., when $(T-Tg) \leq 0$ the ratio increased gradually. The increase became steeper at the end of the DSC measured glass-transition i.e., for $(T-Tg) = 0$. For lactose, this increase occurred at higher $(T-Tg)$ values, typically 10 °C. As the temperature approached the DSC measured crystallisation temperature range, the ratio decreased sharply. On further heating, for sucrose, the ratio remained fairly constant while for lactose it recovered to its maximum value once the crystallisation process was completed.

This behaviour was very reproducible (e.g., Fig. 7). While the shape of the intensity ratio plot seemed to be 'universal' in the sense that it was similar for both sugars at all seven moisture contents, the ratio values should only be used as relative rather than absolute values, as they varied between sugars, water content and even replicate measurements on similar samples. If FTIR is to be used to determine Tg, Tc, Tm, etc., the measurement should rely on sudden changes in spectral properties (e.g., absorbance ratios) rather than on absolute values of absorbances or absorbance ratios.

3.3. Hydrogen bonding

Of particular interest to this study, is the use of FTIR to monitor the change in hydrogen bonding when the sugar undergoes the various state/phase transitions described above. Hydroxy groups rarely exist in isolation and in carbohydrates O–H groups are usually involved in intra- and inter-molecular (with other carbohydrate molecules or with water) hydrogen bonding with other hydroxy groups.

Wolkers and coworkers[21] reported the use of the wavenumber shift of the O–H stretching band, typically centred between ~3200–3600 cm^{-1}, with temperature to measure the glass transition temperature of carbohydrates. Changes in the wavenumber are interpreted as being dominated by changes in hydrogen bonding.

Indeed, the stretching vibration of a hydroxy group involved in a hydrogen bond is expected to have a lower

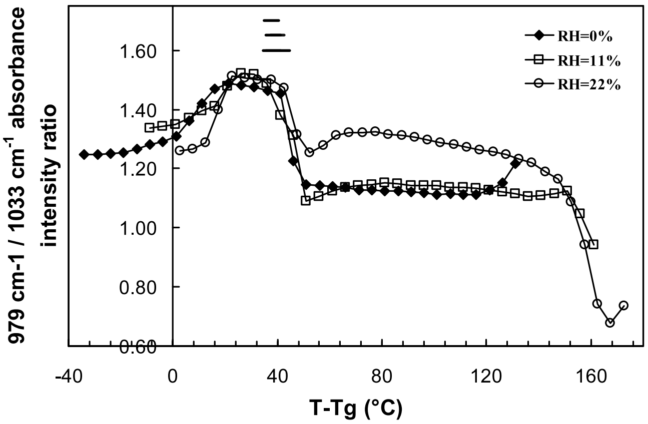


Fig. 5. Effect of temperature on the ratio of the absorbances at 979/1033 cm^{-1} in freeze-dried sucrose containing 0.5 (RH = 0%), 3.3 (RH = 11%) and 4.7% (RH = 22%) water (w.b.). The bars represent the DSC measured crystallisation ranges from top to bottom RH = 0, 11 and 22%.

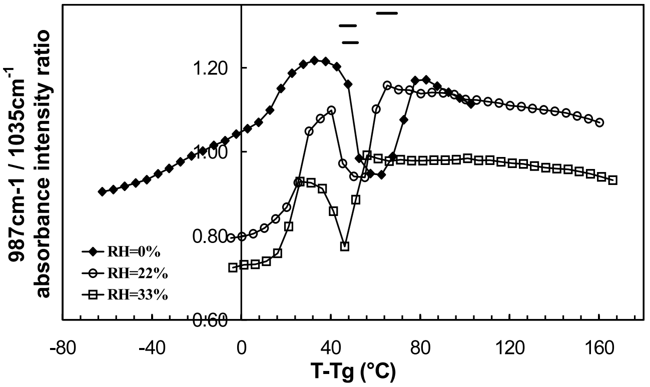


Fig. 6. Effect of temperature on the ratio of the absorbances at 987/1035 cm^{-1} in freeze-dried lactose containing 0.4 (RH = 0%), 5.7 (RH = 22%) and 6.3% (RH = 33%) water (w.b.). The bars represent the DSC measured crystallisation ranges from top to bottom RH = 0, 22 and 33%.

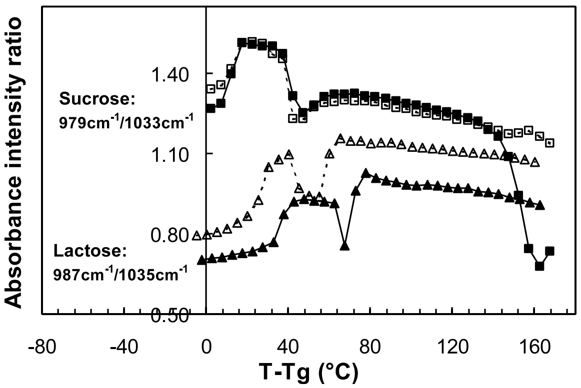


Fig. 7. Effect of temperature on the ratio of the absorbance described in Figs. 5 and 6 for freeze-dried sucrose and lactose hydrated at RH = 22% (20 °C). Duplicate analyses are displayed.

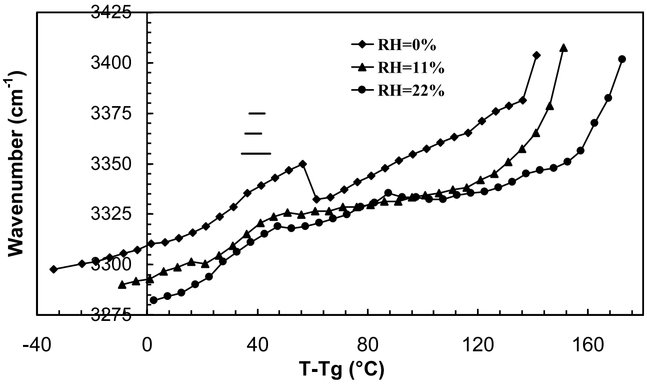


Fig. 9. Effect of temperature on the wavenumber of the O–H stretching band in freeze-dried sucrose containing 0.5 (RH = 0%), 3.3 (RH = 11%) and 4.7% (RH = 22%) water (w.b.). The bars represent the DSC measured crystallisation ranges from top to bottom RH = 0, 11 and 22%.

wavenumber than its non-hydrogen bonded counterpart[19] as it will have a lower bond force constant due to electron delocalisation in hydrogen bonded structures.

As the temperature increased, for both sugars and at all water contents, the band resulting from the O–H stretching vibration shifted to higher wavenumbers compatible with a weakening of hydrogen bonding (Fig. 8). In order to quantify this effect, the wavenumber for maximum O–H absorbance ($\nu_{\mathrm{OH}_{\max}}$) was identified for each spectrum and the results were plotted as a function of $(T-\mathrm{Tg})$ and examined in relation to the glass transition, crystallisation and melting (where achieved) for each sample (Figs. 9 and 10). For sucrose, $\nu_{\mathrm{OH}_{\max}}$ increased gradually (and linearly) up to a temperature approximately half way between the end of the DSC measured Tg [i.e., $(T-\mathrm{Tg})=0$] and the onset of crystallisation where the increase was steeper (Fig. 9). At the end of the crystallisation range, the change in the $\nu_{\mathrm{OH}_{\max}}$ was more gradual with even a decrease observed in the case of the sample containing 0.5% water. A similar pattern was observed for lactose as it crossed its glass–rubber boundary with no significant change of the slope of $\nu_{\mathrm{OH}_{\max}}$ versus $(T-\mathrm{Tg})$ until the crystallisation range was approached where a steep increase of $\nu_{\mathrm{OH}_{\max}}$ occurred. In contrast with sucrose, a very pronounced decrease in $\nu_{\mathrm{OH}_{\max}}$ occurred as a result of crystallisation for all lactose samples reflecting a major increase in hydrogen bond density and strength in crystalline lactose (Fig. 10). The expected increase in $\nu_{\mathrm{OH}_{\max}}$ as the temperature was increased post crystallisation was observed. As expected, increasing water content for a given $(T-\mathrm{Tg})$ led to a decrease of $\nu_{\mathrm{OH}_{\max}}$ as sugar–water hydrogen bonds occurred.

This significant difference in the behaviour of the O–H bond during the crystallisation suggests a more extensive involvement of H-bonds in crystalline lactose compared to sucrose.

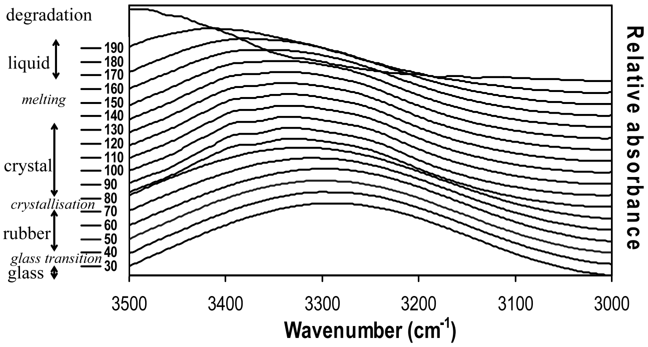


Fig. 8. Effect of temperature on the mid-infrared spectrum (3500–3000 cm^{-1}) of freeze-dried sucrose containing 3.3% water (w.b.) (RH = 11%). Spectra acquired between 30 (bottom) and 200 °C (top) in steps of 5 °C. For clarity, the spectra were stacked and only half of the available data (10 °C steps) is displayed. The spectra are examined in the context of the DSC measured transitions (left).

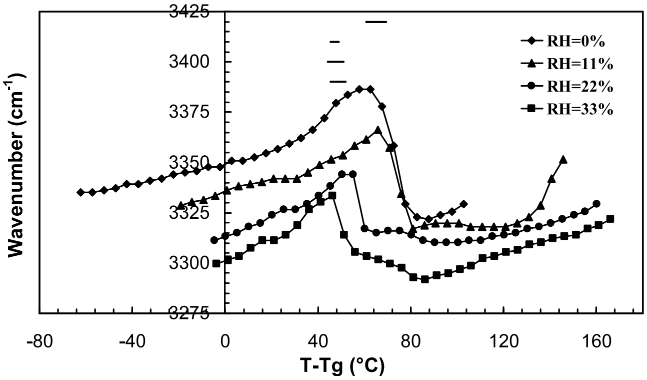


Fig. 10. Effect of temperature on the wavenumber of the O–H stretching band in freeze-dried lactose containing 0.4 (RH = 0%), 4.4 (RH = 11%), 5.7 (RH = 22%) and 6.3% (RH = 33%) water (w.b.). The bars represent the DSC measured crystallisation ranges from top to bottom RH = 0, 11, 22 and 33%.

This is compatible with the significantly higher crystallisation enthalpy for β lactose compared to sucrose. For example, a crystallisation enthalpy (measured at a heating rate of 10 °C/min) value of −84 J/g was measured for freeze-dried (~ 1.5% water wet basis) sucrose compared to 102 J/g for β lactose. Also the difference between the heat of dissolution of the crystalline and amorphous sucrose (~ 61 J/g), β lactose (~ 67 J/g) (no data on amorphous α lactose was found and thus the heat of dissolution for amorphous α and β lactose were assumed to be the same) and α lactose (~ 112 J/g) are in agreement with a more extensively hydrogen bonded crystalline structure for lactose compared to sucrose.[22]

Furthermore, the molecular structure proposed for sucrose in the crystalline state using neutron-diffraction data involves two intra- and five inter-molecular H-bonds[23] while that of β lactose (anhydrous) proposed by Hirotsu and Shimada[24] using X-ray diffraction studies involved a total of eight hydrogen bonds (one intra- and seven inter-molecular) and that of α lactose (monohydrate) involves a total of 10 hydrogen bonds (one intra- and nine inter-molecular both with other lactose molecules and the trapped water molecules within the crystal lattice).[25] The higher number of H-bonds present within the lactose crystals could explain the dramatic decrease in $\nu_{\mathrm{OH}_{\max}}$ that occurred as a result of crystallisation (Fig. 11), which was not observed on such a scale for the sucrose samples. It is believed that lactose crystallised in the β form for the samples studied except at the highest moisture content where the α monohydrate form could have formed.

The fact that no step change in hydrogen bond characteristics was observed at Tg suggests that a 'threshold' of hydrogen bonding strength must be achieved to yield the significant slowing down of molecular mobility responsible for the transition from rubber to glass. These results are compatible with computer simulations of the rubber–glass transition of glucose–water[26] where the average residence time of water was found to decrease by a factor of less than 3 when major temperature changes were imposed: from 40 °C above Tg (5.75 ps) to 40 °C below Tg (2.00 ps). Also these authors found that glucose–glucose intermolecular hydrogen bonds led to the glucose molecules exhibiting a state of near full connectivity and thus behaving like a polymer. The extent of connectivity did not vary significantly between the glassy (Tg−40) and the rubbery (Tg+40) states. In the light of this, the measurement of the Tg directly from $\nu_{\mathrm{OH}_{\max}}$[21] is questionable.

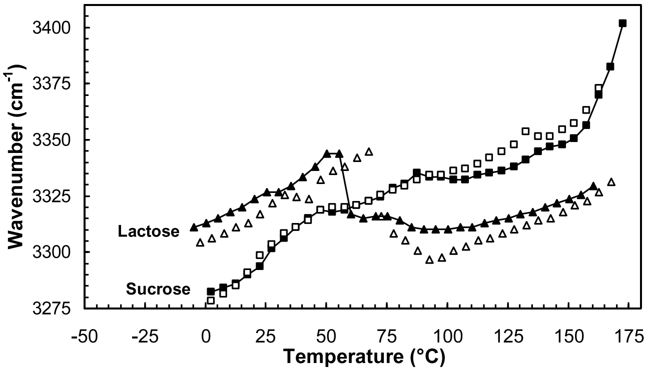


Fig. 11. Effect of temperature on the wavenumber of the O–H stretching band in freeze-dried sucrose and lactose hydrated at RH = 22% (20 °C). Duplicate analyses are displayed.

The changes in the hydrogen bond strength paralleled to a large extent the expected density changes of the materials as they changed from the rubbery state to a crystalline solid where a major change in specific volume would be expected (Fig. 1) compared to a lesser difference between the glassy and the early rubbery states. The density change at the glass transition is typically less than 1% over the temperature range Tg−10–Tg+10 K [6] while the difference between the density of crystalline sucrose (1.58 g/cm^3)[27] and anhydrous glassy sucrose at 25 °C, i.e., at Tg−47 K (1.47 g/cm^3)[28] is more than 9% and therefore the change of density on crystallisation from the rubbery state will be even greater (Fig. 1).

4. Conclusion

The molecular 'fingerprint' of the glass–rubber transition, crystallisation and melting of sucrose and lactose were characterised by mid-infrared spectroscopy. The 1200–800 cm^{-1} region, which is dominated by C–O and C–C stretching vibration, was sensitive to the physical (amorphous/crystalline, glassy/rubbery) state of the sugars and could be used to monitor these transitions. In this regard, the use of FTIR could be advantageous over other more routinely used techniques such as DSC, DMTA or DETA as the FTIR spectrum contains information on chemical identity allowing the study of mixed systems and the identification of physical and chemical processes as demonstrated for the study of the Maillard reaction by Turner and coworkers[29] and Sivasundaram and coworkers.[30] Another powerful method capable of providing chemical identification in mixed systems is ^{13}C NMR. While the assignment of the ^{13}C NMR spectrum of carbohydrates is much easier than FTIR, the technique lacks sensitivity (^{13}C natural abundance) and often hours of data acquisition per spectrum are required making real-time studies not always feasible (depending on the time scale of the process studied).

Another strength of FTIR is its ability to monitor hydrogen bonding. This was used to probe the change in hydrogen bonding through the various transitions. The results suggested that no step change in hydrogen bond characteristics occurs at Tg. A pronounced increase in hydrogen bond strength accompanied the crystallisation of lactose and, to a much lesser extent, sucrose. This could explain the difference in the crystalline heat of dissolution reported for these two disaccharides.

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