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Differential scanning calorimetry of low-moisture apple products

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Abstract

Differential scanning calorimetry (DSC) was used to detect thermal phase transitions in low-moisture apple products, cell walls and related materials. Freeze-dried (FD) apple tissue equilibrated over P_2O_5 exhibited a T_g around 11°C, similar to that of FD apple juice and slightly higher than the predicted value for the sugar mixture in juice (7°C). Samples also showed an endothermic peak around 50–70°C. Cell wall (CW) material from apple prepared by five different methods and dried over P_2O_5 showed an endothermic peak (onset around 120°C and peak between 130–160°C) caused by water evaporation. No glass transition was detected in CW preparations for any water activity. The same behavior was observed for microcrystalline cellulose, apple pectin, pine wood and walnut leaves equilibrated over P_2O_5. Low-moisture CW exhibited a more hydrophobic behavior than apple tissue as revealed by adsorption isotherms.

Keywords: DSC; apple; cell walls; glass transition; sugars; water activity

1. Introduction

Plant tissues are structures whose physical behavior during processing would be better understood if the material properties of constituent solids and fluids were known. Most edible vegetable tissues consist of two relevant structures at the cellular level (Aguilera and Stanley, 1990): the protoplasm and the surrounding cell walls (CW). In living tissue the protoplasm can be viewed as an essentially incompressible and highly viscous fluid exerting hydrostatic internal pressure (normally 1–8 bars) against the cell walls. CW have the structure of a fiber-reinforced composite, chemically and mechanically dominated by cellulose, embedded within what was traditionally viewed as an 'amorphous' matrix (Nicklas, 1992).

Shrinkage of food pieces during air drying affects adversely the quality of dried products and in spite of its technological importance it is not well understood. This phenomenon is extensive in some fruits and vegetables affecting the rate of drying, and the physical and functional properties of the product. Shrinkage of plant tissue has been related to glass-rubber transitions of the protoplasm (Karathanos et al., 1993) but not to thermal transitions of CW. This appears to be derived from the observation that collapse during freeze-drying (FD) of concentrated amorphous sugar solutions is related to the glass transition (Levine and Slade, 1986; Flink, 1983; Tsourouflis et al., 1976; Bellows and King, 1973). FD induces minimal product shrinkage when the temperature of the dry matrix (T) is below a 'collapse' temperature (T_c) which is closely correlated but higher, than the glass transition temperature (T_g). T_c is quite low for citrus juices (-24 to -36.5°C) but higher for potato tissue (-1.5°C) (Bellows and King, 1973).

Although the sugar (and acid) solution represents 85%–90% of the total weight, CW accounting for only 1%–3% are responsible for the rigidity and solid-like behavior (Bourne, 1983). Phase transitions in low-moisture fruits and vegetables are dominated by a single T_g which almost coincides with that of the sugars present in the material at the same moisture content (Roos, 1995; Sa and Sereno, 1994; Karathanos et al., 1993). Practically, no other major thermal transitions were reported for dehydrated fruit products let alone for CW material. Lin et al. (1991) applying high-sensitivity DSC to moist CW preparations of soybean hypocotyls found one step-like transition in the range 50–60°C (moisture content not mentioned), reported to represent a T_g, but this result was not substantiated further.

There is considerable interest in studying thermal transitions in food polymers, particularly to test the hypothesis that there is a drastic decrease in mechanical (e.g., modulus) and viscoelastic (e.g., viscosity) properties and increased molecular mobility in the food matrix at temperatures above T_g (Slade and Levine, 1991; Roos, 1995). For instance, the T_g concept explains well structural changes

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during caking of amorphous powders (Aguilera et al., 1993). The matrix where cellulose fibers are embedded in CW is largely composed of polysaccharides and some protein, and was referred to by botanists as an 'amorphous' phase or matrix (Heredia et al., 1995). Hence, there is interest to see whether CW present discernible glass transitions that would assist in explaining shrinkage during drying. The objective of this study was to analyze thermal transitions of low-moisture apple products such as CW preparations, tissue, juice and related materials by DSC.

2. Materials and methods

2.1. Materials

Apples (variety Granny Smith) were grown in the Central Valley (Chile) and purchased at a local supermarket about 4 months after harvest. Ripe apples were peeled and cut into small pieces (core removed), frozen in liquid nitrogen and crushed with a mortar and pestle. Fresh apple had the following gross composition: 84.2% water, 1.8% insoluble solids and 14.0% soluble solids. Apple juice was pressed out from mashed fresh apple and separated by vacuum filtration. Commercial clarified apple juice was bought from Watts Foods (Santiago). Freeze-drying of samples was performed in a Labconco freeze-drier 4.5 (Labconco Corp., MO). Apple pectin (type NSS, Herbstreith, Pektin-Fabrik, Germany), microcrystalline cellulose (Avicel PH-101, FMC Corporation, PA) as well as pieces of pine wood *(Pinus radiata)* and walnut leaves were also examined in the DSC. Salts used in desiccators were all analytical grade.

2.2. Preparation of cell wall material

Several extraction methods based on the work of Selvendran (1975) were used to isolate CW material from 50 g ground apple tissue. Solvents used (analytical grade) were 80% aqueous ethanol (EtOH), sodium dodecyl sulphate (SDS), sodium deoxycholate (SDC), phenol-acetic acid-water (PAW) and deionized water. After extraction the residue corresponding to CW material was freeze-dried and stored over P_2O_5 until used (referred to as 'anhydrous' material).

2.3. Leaching with water

Extraction for 8 h in 500 mL of deionized water at room temperature and then re-extracted similarly twice. After a final wash the insoluble material was boiled for 1 h and filtered.

2.4. Extraction with water and ethanol.

Extraction overnight under agitation in 500 mL of deionized water. The residue was obtained after filtering through a screen, boiled in 500 mL deionized water and rinsed several times. It was then re-extracted in a similar way with EtOH and brought to boil. The solid material thus obtained was rinsed 3 times with deionized water and filtered.

2.5. Extraction with water and 1.5% SDS

Extraction six times for 8 h under agitation in 500 mL of deionized water. The residue obtained after filtering through a fine screen was re-extracted with a 1% SDS aqueous solution for 10 min at ambient temperature. The material thus obtained was rinsed 3 times with deionized water and filtered.

2.6. Extraction with water and 1% SDC

The method was similar to that used for 1.5% SDS.

2.7. Extraction with SDC/PAW

The procedure developed by Selvendran (1975) involving sequential treatment with 1% aqueous SDC and PAW was modified as follows: 50 g of crushed apple were extracted with 100 mL of a 1% aqueous SDC for 5 min. To this preparation 2 mL of antifoam agent and 2 mL of 3 mM Na metabisulphate solution were added and the suspension was macerated with glass beads under agitation for 20 h at a temperature of 1–5°C. The contents were centrifuged at 15 000 g for 10 min and the residue was rinsed with deionized water in a centrifuge tube. The wet pellet was re-extracted twice with 25 mL of PAW (2:1:1 w/v/v) each time, centrifuged (15 000 g), washed twice with water and ether, and centrifuged into a wet residue.

2.8. Differential scanning calorimetry

DSC studies were performed in a Perkin-Elmer DSC 7 calorimeter equipped with a thermal analysis station. The instrument was calibrated by standard procedures. To increase the weight of the sample placed in aluminum DSC pans (#0219–0062) to about 12–18 mg, an acrylic compression cell was made to shape the material into a small dense tablet. An empty aluminum pan was used as reference and runs were performed at least in duplicate. Equilibration of CW samples to different water activities (a_w) was performed at 20°C in desiccators containing saturated salts solutions (see Adsorption isotherms). Samples were heated at a rate of 10°C/min both in a first scan and in the re-scanning. CW and related material (except pectin) were scanned from room temperature (about 20°C) to 200°C since heating beyond 220°C induced browning of samples. Some samples were also scanned in perforated pans. FD apple tissue and juice were scanned between − 30 to 100°C to locate the T_g of sugars, and pectin from 0 to 180°C.

2.9. Adsorption isotherms

An adsorption isotherm at 25°C was done by exposing samples of FD apple tissue and CW material, previously dehydrated over P_2O_5, in desiccators of different relative humidities until they achieved constant weight (about 20 days). Saturated salt solutions were used to give relative humidities (shown in parenthesis) in the desiccators (Spiess and Wolf, 1987): LiCl (11%); CH_3COOK (23%); $MgCl_2$ (33%); K_2CO_3 (44%); $Mg(NO_3)_2$ (53%); $(NH_4)_2SO_4$ (79%) and $BaCl_2$ (90%). Moisture contents were determined gravimetrically from the weight gain of the sample.

3. Results and discussion

3.1. Cell wall material

Isolated CW of plant material are defined as the insoluble residue after extraction and washing the ground tissue with ethanol (Knee, 1985). Variations of this basic method have been used to prepare material for NMR and EPR studies of apple CW (Newman et al., 1994; Irwin et al., 1992). Specific extraction methods remove undesirable contaminants (cytoplasmic proteins, starch, nucleic acids, polyphenols, etc.) to varying extents. Methods adopted in this study are based on work of Selvendran (1975) who tried different aqueous solvents and procedures in an attempt to further purify CW of beans from cytoplasmic proteins and other contaminants while minimizing pectin solubilization. CW material extracted with SDC/PAW (overall yield from apple tissue around 2.0%–2.4%) was selected for further DSC experiments since this method provides water-insoluble, structural carbohydrates almost free of pectins (Lecas and Brioullet, 1994).

3.2. DSC of CW material

Cooling rates of formation of a glassy material as well as heating rates in DSC experiments affect the shape (e.g., step or step plus superimposed exo- or endotherm) and position of a T_g in the thermogram (Threlfall, 1995). Higher cooling rates give a higher T_g (Eisenberg, 1984). Thus, the scanning rate selected (10°C/min) was the same as for other studies attempting to find thermal transitions of biopolymers (Glasser et al., 1995; Appelqvist et al., 1993) and twice the value used by Sa and Sereno (1994) and Karathanos et al. (1993) in their studies with fruits and vegetables.

No major transitions were detected in thermograms below 100°C during first heating of the five anhydrous CW preparations (Fig. 1). The main thermal event registered in all cases was a wide endothermic peak centered between 124–136°C with onset at 118–122°C. A minimum sample weight of 2.2 mg was needed to detect this endothermic peak. After immediate cooling to 30°C and rescanning the endothermic peak disappeared.

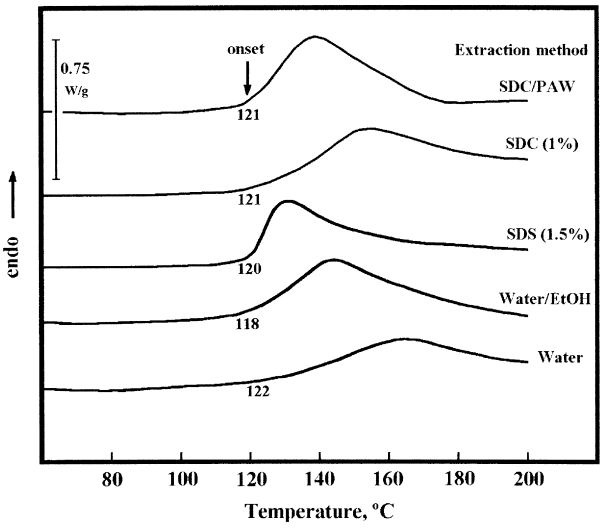

Fig. 1. DSC tracings of anhydrous apple cell walls prepared by different extraction methods. Arrow points at onset of endotherm.

Other authors have reported an endothermic peak above 100°C during DSC of biopolymers. Scandola et al. (1991) found a peak centered at approximately 130°C for dextran powder and attributed it to water evaporation. In the same study samples of amylose, dextran and pullulan exhibited a decrease in weight caused by water loss when assayed thermogravimetrically from room temperature to 150°C. DSC endothermic peaks at about 120–125°C ascribed to water evaporation were also reported for samples of wood (Hon and Xing, 1992).

We confirmed a weight loss by weighing the pans before and after some DSC runs as well as by running samples in perforated pans. Moisture release during heating of CW material equilibrated over P_2O_5 for 2 weeks suggests that samples were not truly 'anhydrous' and that some sorbed water was not completely removed in the desiccator. It is suggested that desiccators be evacuated to accomplish a faster and more complete removal of moisture (Roos, 1997). We recommend that methods such as oven drying and the Karl Fischer procedure be used to better determine residual moisture contents of samples after equilibration over P_2O_5. Onset of endothermic peak should be related to pressure build-up inside the pans because of water evaporation. The pressure at which the seams of pans started to leak can be estimated at 2.0 bar (0.2 MPa), which corresponds to the approximate vapor pressure of water at 120°C (initial temperature of peaks in Fig. 2). Using the ideal gas law and the volume of Al pans (40 μL) we calculated that at least 0.043 mg of water must be released to the vapor phase to exert that pressure.

No glass transition was found when CW samples were scanned up to 200°C under conditions of the DSC experiments. The size of the step change in specific heat (C_p) in the thermogram depends on the fraction of the amorphous phase present. Thus, if the material is semicrystalline and the

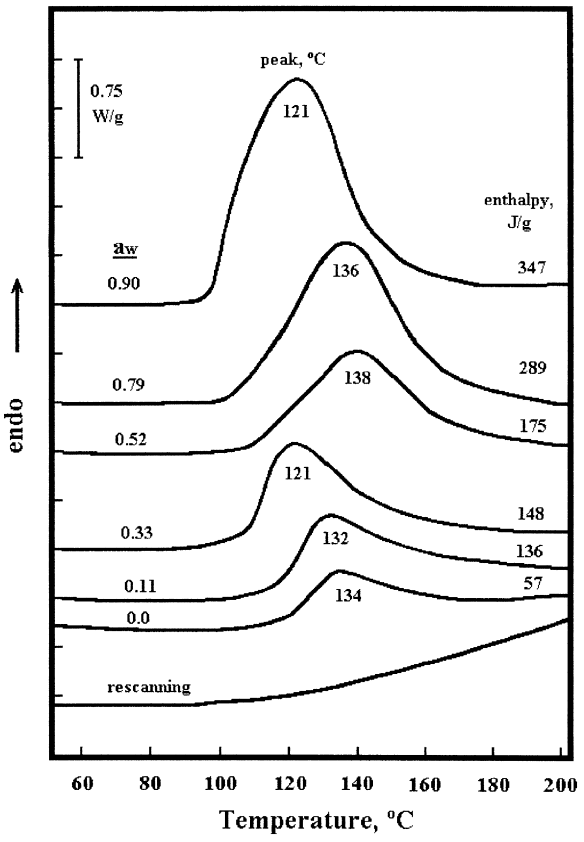

Fig. 2. DSC tracings of apple cell walls (SDC/PAW) as a function of water activity showing peak temperatures and enthalpy.

amorphous fraction is small the step will be small. DSC pans opened after heating (and reheating) contained a material showing some signs of browning. Gidley et al. (1993) have commented that a T_g is rarely observed for anhydrous polysaccharides because decomposition is supposed to happen below the putative T_g. In contrast, if a T_g was hidden under the endotherm it would have appeared as a step change on rescanning, which was not the case. Slade and Levine (1991) using data of Kelley et al. (1987) from DMTA experiments proposed an 'extrapolated T_g' for anhydrous lignin and hemicelluloses close to 200°C. Several authors have experienced difficulties in detecting T_g of vegetable tissue by DSC. Anglea et al. (1993) were not able to detect a T_g in fresh potato tissue but they found one in material which was exposed to osmotic dehydration in sucrose solutions (T_g midpoint -48 to -53°C). Sa and Sereno (1994) scanned non-annealed samples of grape, onion and strawberry from -120 to 100°C finding only glass transitions which decreased with increasing a_w in a manner similar to pure sugars (e.g., sucrose). Gidley et al. (1993) did not find a detectable T_g by DSC in the range 5–150°C for polysaccharides commonly associated with cell walls of algae and plants (e.g., alginate and pectin). Hence, detected and reported T_g's of fruits and vegetables are related to the sugars originally present or added by processing rather than to cell wall material.

3.3. Effect of water activity on DSC scans

CW material (extracted with SDC/PAW) equilibrated to different a_w did not exhibit any major thermal transitions during a first scanning in the DSC other than the endothermic peak related to water evaporation which was centered between 121 and 138°C (Fig. 2). The peak did not appear in thermograms after immediate rescanning meaning that steam was lost to the exterior and did not condense on the sample upon cooling. The enthalpy associated with the endothermic event changed from 347 to 57 J/g as a_w decreased from 0.90 to 0.00 (Table 1). A few values of enthalpies of endothermic peak obtained at the Nestle Research Center (CRN) with the same CW material and scanned in a Mettler DSC 820 are also listed in Table 1. The enthalpy and peak temperature were lower for samples run in punctured pans (data not shown).

It is known that the total heat of adsorption in low-moisture materials shows a maximum at the BET monolayer value (m_o). An average value of 3.49 J/mg can be assumed for the sum of the heat of vaporization and the heat of sorption $(\Delta H)_o$ at m_o for several polysaccharides (Karel, 1975). From enthalpy values of endothermic peak listed in Table 1 and the assumed $(\Delta H)_o$ the amounts of 'sorbed' water not removed by P_2O_5 but by evaporation in the DSC were calculated and are listed in Table 1. Evidently, calculated values of sorbed water for $a_w > (a_w)_o$ are underestimated since the total heat of sorption should decay to the latent heat of vaporization of pure water (2.18 J/mg at 130°C) as a_w increases above the monolayer value.

As shown in Fig. 2 the endothermic peak did not appear on immediate rescanning of the sample but a slow partial recovery was observed after 10 and 18 weeks of storage of scanned pans at room temperature (data not shown). This result can be interpreted as moisture from the environment being adsorbed back into CW material through faulty seams.

Appelqvist et al. (1993) reported an endothermic event between 45–80°C for a broad range of low-moisture

Table 1
Moisture content of cell wall material (SDC/PAW extracted) calculated from the enthalpy value of the endothermic peak.

a_w	Enthalpy J/g	g H_2O/ g sample
0.00	57	0.016
0.00 [a]	35	0.010
0.11	136	0.039
0.33	148	0.042
0.44 [a]	165	0.047
0.52	175	0.050
0.75 [a]	248	0.071
0.79	289	0.083
0.90	347	0.099

[a] Values correspond to DSC runs made with the same material at CRN (Switzerland).

(< 25% w/w water) polysaccharides which was not moisture-dependent, disappeared on rescanning but reappeared after storage and the peak enthalpy increased with moisture content. This peak was not related to water loss but they attributed this event to thermal disruption of the hydrogen-bonded network of water and polymer chains (Gidley et al., 1993). Similarly, Glasser et al. (1995) found a broad endotherm for cellulose acetate below 125°C, though the material was dried at 125°C for 5 days. The endotherm reappeared after storage at 30°C and this phenomenon was attributed to moisture sorption or physical aging. The moisture contents of CW material (< 20% w/w water) in our study were in the same range as those of Appelqvist et al. (1993).

3.4. DSC of apple products and related biomaterials

Fig. 3 shows thermograms of apple tissue, apple juice and related biomaterials after equilibration over P_2O_5. FD apple and FD apple juice showed the same T_g (11°C) which remained after immediate rescanning of the sample. Clarified commercial juice exhibited also a T_g but lower (1°C) than natural juice, probably caused by the presence of sugars formed during the enzymatic clarification process [e.g., rhamnose, a sugar in pectin has a T_g (anhydrous) = − 7°C; Roos (1995)]. Fructose, sucrose and glucose are the main sugars in apple juice in approximate proportions of 7:2:1 (Fuleki et al., 1992) and have T_g (anhydrous) of 5, 62 and 31°C, respectively (Roos, 1995). Using Fox's relation ($1/T_g = \Sigma w_i/T_{gi}$; Roos, 1995) it was possible to estimate a T_g of 7.1°C for the anhydrous mixture of sugars, which does not differ much from the value found for FD apple products (1–11°C) equilibrated over P_2O_5. FD apple and FD apple juices presented a small endothermic peak between 50 and 70°C which presumably corresponds to soluble polysaccharides as discussed before (Gidley et al., 1993).

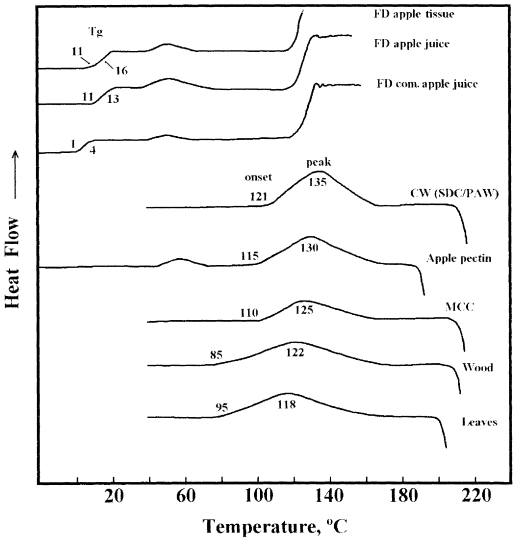

Fig. 3. DSC tracings of cell walls preparation, freeze-dried apple tissue and juice, apple pectin, microcrystalline cellulose, wood, and leaves in anhydrous state after equilibration in P_2O_5.

Samples of anhydrous microcrystalline cellulose (MCC) and a commercial apple pectin were run in the DSC for comparison. MCC may be considered as a good source of isolated cellulose microcrystals as it is prepared by acid attack to the amorphous regions of native alpha-cellulose followed by mechanical disintegration (Battista and Smith, 1962). Newman et al. (1994) found a high similarity between the NMR spectra of MCC and that of apple cell walls. MCC, pectin, wood and leaf tissue showed a broad endothermic peak with midpoints at 115–130°C but not a discernible T_g. The nature of this endothermic peak was similar to that detected for CW material, i.e., water vaporization. An endothermic peak (50–60°C) of a similar nature as the one reported by Appelqvist et al. (1993) was present for pectin.

3.5. Adsorption isotherms (AI)

Moisture sorption isotherms provide important information of the relationships between water content and its physicochemical state in foods. Materials studied showed substantial differences in water adsorption properties. While the AI of apple tissue presented a shape typical of many hygroscopic materials (sharp increase in moisture at $a_w > 0.5$) those of CW and MCC (from Spiess and Wolf, 1987) lie below the former as if they were more hydrophobic materials (Fig. 4). The AI of FD apple shows similar values as data for vacuum-dehydrated apple slices of Lazarides et al. (1995), grape (Sa and Sereno, 1994) and FD strawberries (Roos, 1993). AI curves of FD apple ran parallel but above the curves of amorphous fructose and sucrose, main sugar components in apple juice. Data for amorphous sugars was adapted from illustration 429 in Iglesias and Chirife (1982). The monolayer values from BET and GAB sorption-isotherm models (Roos, 1995) for CW were $m_o = 3.40$ and 2.37 g/100 g, respectively. Both values are lower than those reported for some fruits and vegetables (Roos, 1993).

3.6. Final comments

This study tried to assess whether glass transitions of apple CW material could be detected by conventional DSC techniques. No T_g's were recorded that would correspond to polymeric components of CW in the temperature range reported in the scientific literature for cellulose, wood and some food polysaccharides. Several possible explanations follow.

1. T_g can be difficult to identify by DSC even for synthetic polymers. As discussed by Vodovotz and Chinachoti (1996), DSC is insensitive to T_g when changes in specific heat are small and in multicomponent systems its detection may not be simple if many transitions occur in the

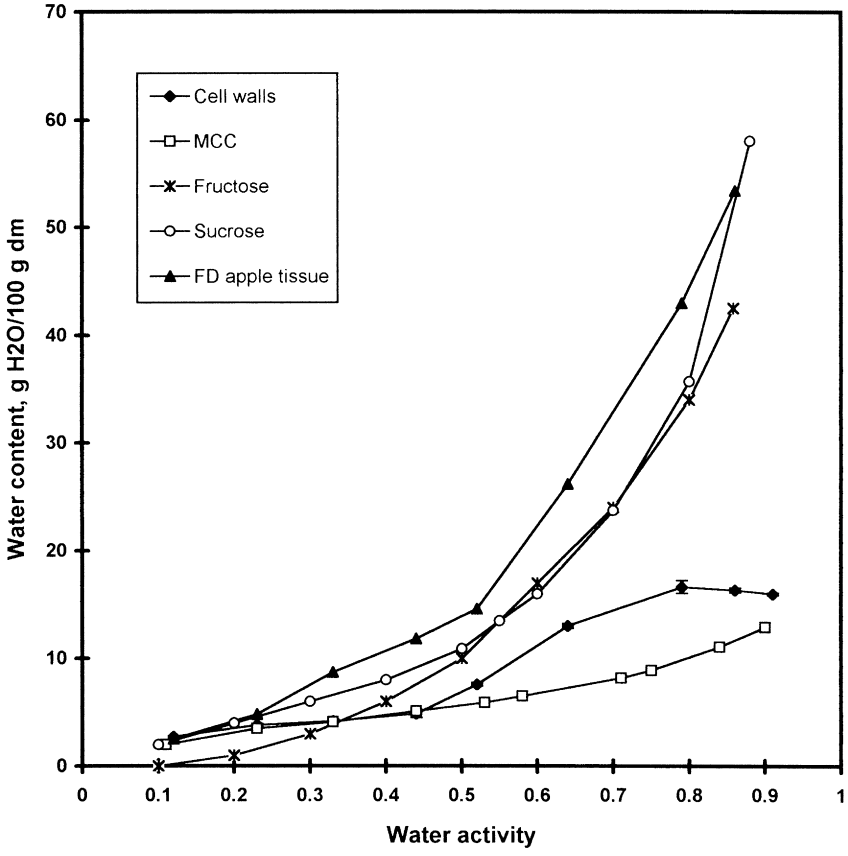

Fig. 4. Sorption isotherm of dehydrated apple and apple cell walls. Curves for amorphous fructose and sucrose from Iglesias and Chirife (1982) (Figure 429) and for microcrystalline cellulose from Spiess and Wolf (1987). Data at 25°C.

same temperature range. DMA (dynamic mechanical analysis) is a more appropriate technique for determining T_g as it is 1000 times more sensitive than DSC. Perez (1992) also recognizes the higher sensitivity of mechanical over thermal methods in the case of semi-crystalline materials.

2. Interpretation of data available in the literature on glass transitions of polymers related to cell walls must be made with full appreciation of their limitations. Salmen and Back (1977) proposed a relationship between the T_g of the amorphous cellulose and moisture derived from lattice theory. A glass transition in the vicinity of 100°C was identified for water-saturated lignin in wood by dynamic mechanical analysis (Salmen, 1984). Using DTA, Irvine (1984) detected a 'transition' for whole wood between 50 and 120°C which was assigned to lignin. The plasticizing effect of water on isolated lignin and hemicelluloses produced two plateau, one at 50°C and the other 'well below room temperature', respectively, though the latter was not observed. Two separate glass transitions (α_1 and α_2) were identified by Kelley et al. (1987) using DMTA for maple and spruce wood and assumed to correspond to amorphous lignin and hemicellulose, respectively. DSC runs (only at 25% moisture content) revealed an endothermic peak at about 50°C which disappeared on rescanning and reappeared after 24 h at a slightly higher temperature and with reduced intensity. A second transition with midpoint at -22°C appeared in the thermogram as an extended step change from -45 to 0°C. The authors concluded that thermal events in the DSC experiment ''...correspond to the α_1 and α_2 peaks in the DMTA spectrum and confirms two separate glass transitions arising from the amorphous components of wood''. In a separate work Lin and Lin (1989) reported that lignin is an amorphous thermoplastic polymer with T_g of about 160°C (supposedly anhydrous) which is profoundly affected by moisture and sulfite treatment (decreasing T_g to 70–90°C). Glasser et al. (1995) commented that cellulose fails to reveal distinctive first- or second-order thermal transitions during heating due to the abundant presence of hydrogen bonds.
3. What is the relevance of a T_g detected in an isolated and dehydrated material? Some researchers suggest that T_g is not a characteristic parameter but reflects the thermal and mechanical history of the sample (Hay, 1992). Materials studied after isolation and preparation may not be the same as the 'native' materials. For example, interactions between cellulose microfibrils and the matrix components (hemicelluloses and pectins) in vivo may be likened to a liquid crystal state (Carpita and Gibeaut,

1993) while there is evidence that some cell wall polysaccharides may exist as crystalline microfibrills (Millane and Hendrixson, 1994). It is conceivable that isolation and dehydration may induce an amorphous arrangement of otherwise crystalline polymeric structures that in vivo are immersed in a gel-like matrix.

4. Conclusions

After scanning and rescanning by DSC several samples of apple CW material under different a_w (as well as CW-like materials) no T_g was detected in the temperature range 30–200°C. Instead a single T_g almost equivalent to that of the mixture of soluble sugars present in apples was observed in FD apple tissue and juice. An endothermic peak above 120°C and associated with water vaporization was detected for low-moisture CW preparations and related materials.

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