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Mechanical and thermal analysis of raisin components[1]

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Abstract

Moisture content is known to change the mechanical properties of raisins. The progressive chemical removal of cell components was carried out to assess their contribution to the overall raisin properties. It was achieved by preparing an alcohol insoluble residue which was then sequentially extracted and its carbohydrate composition analysed. The removal of structure and geometry effects was undertaken by pressing uniform mouldings of the raisin and its insoluble components, which were conditioned over saturated salt solutions at room temperature. Dynamic mechanical thermal analysis (DMTA) of the mouldings indicated their decreasing stiffness with increasing temperature as well as the occurrence of the glass transition, which was complemented by Differential scanning calorimetry (DSC). The data from DSC and DMTA were interpreted in terms of contributions from the raisin cell-wall components and sugars and showed the glass transitions of the cell-wall polymers to be consistent with published results on grapes and wood. © 1997 Elsevier Science B.V.

Keywords: DSC; DMTA; Raisin; Cell wall; Glass transition

1. Introduction

Various properties of raisins have been studied, ranging from their dietary fibre content [1], characterisation of the pectic substances [2], their sorption isotherms [3,4] to their mechanical properties [5,6]. Lewicki and Wolf [7] used a compression–relaxation test described in [5], and various specific terms derived from it, to measure the effect of moisture content changes. Canellas et al. [6] considered the effect of storage time on raisins held at different temperatures. They measured changes in mechanical properties by the mass-normalised Warner–Bratzler force. Studies of the preparation of raisins from the native grape have been reviewed [8], but recently Sa and Sereno [9] have taken a biopolymer science approach and measured the moisture dependence of the glass transition of grapes by DSC. Biopolymeric materials have been increasingly studied over the past decade using DSC [10,11]. Other techniques such as DMTA have also been used and studies have included wood, proteins, starches, polysaccharides, sugars and various mixtures [12,13]. Excised plant tissue has also been studied in recent experiments at this laboratory [14]. The composition, structure and geometry of fruit and vegetable tissue complicates their mechanical analysis in terms of stress and strain units, which are necessary for modelling. One approach which has been useful in simpler process-fabricated structures has been to remove the structure and simplify the geometry by pressing test pieces of uniform geometry [15]. This approach had earlier been demonstrated for simple biopolymers [16]. However, in dealing with plant material, analysis of their composition is a compli-

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cated issue since extraction techniques may introduce artefacts through the labile nature of the components. Sequential cell-wall analysis has been developed in this laboratory [17,18] and in this study has been used to partition the various classes of cell-wall components.

This paper reports a study of the effect of moisture content on the mechanical properties of raisins and their components with the objective of identifying the basis of their moisture-dependent texture. Raisins were examined in whole and also when separated into skin and flesh. The progressive chemical removal of cell components was achieved by preparing an alcohol-insoluble residue which was then sequentially extracted using treatments developed in this laboratory. The progressive chemical removal of cell components enabled a study of the contribution of the insoluble residues to the mechanical properties of the whole raisin. Each material was equilibrated at different relative humidities, using saturated salt solutions at room temperature, to generate samples of different moisture contents. Differential scanning calorimetry (DSC) was carried out to classify transitions for equilibrated and sealed specimens. The removal of structure and geometry effects was undertaken by pressing uniform mouldings of the raisin and its excised fractions and the sequentially extracted insoluble components, which were then also conditioned to different moisture contents. Dynamic mechanical thermal analysis (DMTA) was used to obtain the stiffness of the test pieces as a function of temperature. The data from DSC and DMTA were interpreted in terms of contributions from the raisin components, and a comparison made with published results on grapes and wood.

2. Materials and methods

2.1. Materials

Sun-dried seedless raisins (cv Thompson) were obtained. Whole raisins were separated into their skin and flesh by using tweezers and a blade. Whole raisins, skin and flesh were frozen immediately in liquid N_2 and stored at −40°C until required. The average weights of whole raisin, skin and flesh were 0.48 g, 0.12 g and 0.36 g respectively.

2.2. Sample preparation

2.2.1. Preparation of alcohol-insoluble residue (AIR)

Whole raisins, skin and flesh were extracted for an AIR as described by Martin-Cabrejas et al. [17]. Samples were homogenised in a Waring blender with boiling ethanol (85% v/v final concentration) for 2 min and then homogenised with an Ystral homogeniser for 1 min before boiling for 5 min. The homogenate was filtered through 100 μm nylon mesh. The residue was re-extracted twice in boiling ethanol (85% v/v), and twice in boiling ethanol (100%). The final residue was washed three times with acetone and air-dried overnight.

2.2.2. Sequential extraction of AIR

The sequential extraction was carried out according to the method of Redgwell and Selvendran [18] (Fig. 1). AIR (65.4 g) from whole raisins was suspended in water for 2 h at 20°C. The water-insoluble residue (WIR) was extracted sequentially with 50 mM cyclohexane-*trans*-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetate (CDTA, Na salt) pH 6.5 for 6 h at 20°C (CDTA-1) and 2 h at 20°C (CDTA-2), then 50 mM Na_2CO_3 containing 20 mM $NaBH_4$ for 6 h at 1°C (Na_2CO_3-1) and 2 h at 20°C (Na_2CO_3-2); and then 0.5 M KOH containing 20 mM $NaBH_4$ to leave a KOH-insoluble residue (KOHIR). After each extraction the soluble components were filtered through glass fibre paper GF/C (Whatman), neutralised where required, dialysed exhaustively and freeze-dried. Small aliquots of residue (10%) from each step of the sequential extraction were also neutralised, dialysed exhaustively and lyophilised; these were then used to fabricate specimens for DMTA.

2.3. Compositional analysis

2.3.1. Sugar analysis from cell wall material

The neutral sugars were analysed following the method described by Selvendran et al. [19] using a Carlo Erba gas liquid chromatograph. The monosaccharides released by acid hydrolysis were reduced and analysed as alditol acetates. The separations were carried out on a 3 m × 2.2 mm column containing 3% OV-225 at 200°C in ≈45 min.

The uronic acids were determined colourimetrically, according to the method of Blumenkrantz and

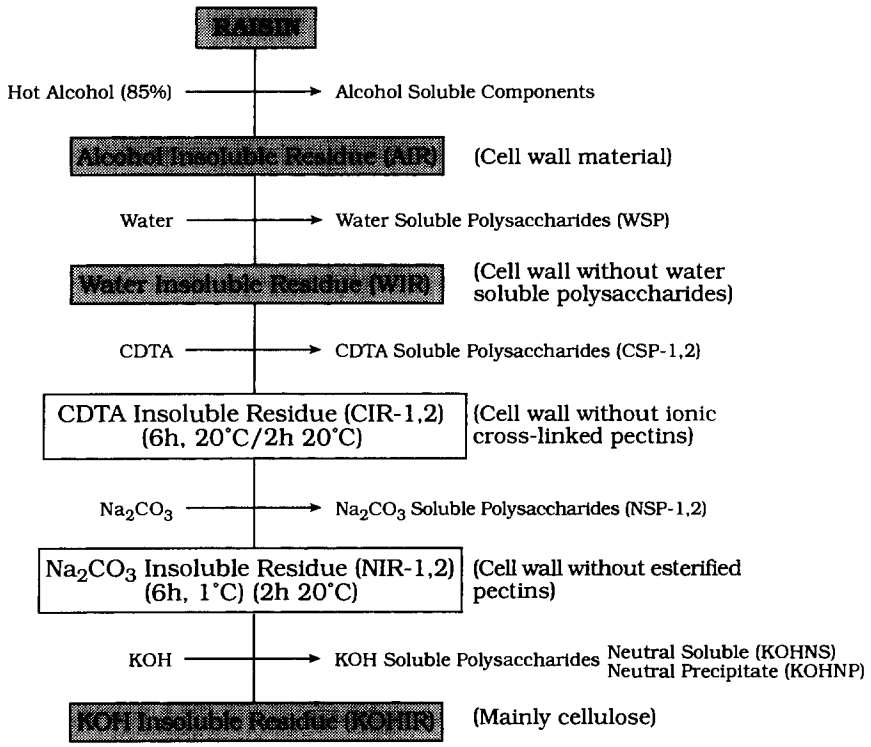

Fig. 1. Sequential extraction of raisin AIR.

Asboe-Hansen [20] modified by Selvendran et al. [19,21] using a Perkin-Elmer spectrometer.

2.3.2. Determination of moisture content

A vacuum oven was utilised to determine the moisture content of skin and flesh at 70°C as a function of time, as used by others for raisins [8,22]. This was shown to be the most effective temperature in the present work. Values were also obtained by Karl Fischer titration method [23], carried out using an AF7LC Coulometric Titrator Orion. The moisture content was calculated on wet weight basis % (wwb).

2.4. Conditioning at different relative humidities

Raisins (~1.8–4 g) were conditioned over saturated salt solutions at room temperature. Each test was carried out in duplicate. The following salts were used: P_2O_5 ($a_w = 0$), LiCl ($a_w = 0.113$), $MgCl_2 \cdot 6H_2O$ ($a_w = 0.328$), K_2CO_3 ($a_w = 0.432$), NaCl ($a_w = 0.753$), and KCl ($a_w = 0.843$) [24].

Moisture uptake was measured by weighing the samples before and during humidification until the equilibrium has been obtained.

2.5. Sample preparation by hot press for DMTA measurements

2.5.1. Hot press

The hot press was made up of a rectangular mould ring between two compaction dies, as described in detail elsewhere [15]. The temperature was controlled by a device comprising a heating and a cooling system. Each die was covered with an acetate sheet and ~1.5 g of the powder placed between the dies. A rectangular sheet, 28 mm long and 22 mm wide, was obtained and cut into strips. The samples were conditioned at different relative humidities and their water contents determined as described above.

2.5.2. Sample preparation

Raisins were cut in small pieces and dried in a hot box oven at 80°C for 17 or 19 h and reduced to powder

with a mortar and pestle. The same procedure was used to obtain powder from skin and flesh. The material was pressed as described earlier with a pressure of 35 kN at 100°C for 15 min.

Two different methods were tested in order to make samples of the AIR, WIR and KOHIR for DMTA. The powder was ground using a coffee grinder to reduce the particle size and used directly or when hydrated to 50–70% (wwb). The same pressing conditions as above were applied except that the temperature was 50°C, and the resulting sheet was cut and conditioned as described in the previous section.

2.6. Differential scanning calorimetry (DSC)

For this study, whole raisins were tested and when separated into skin and flesh. A powder was obtained and conditioned to different moisture contents as described in the previous paragraphs. DSC analyses were carried out using a Perkin–Elmer DSC 2 calorimeter. Each sample, ~5 mg, was accurately weighed and sealed hermetically in an aluminium pan. An empty pan was used as the reference. Samples were heated at a rate of 10°C min^{-1}, sensitivity 4.18 mJ (1 mcal) s^{-1}.

2.7. DMTA

The dynamic mechanical thermal analyzer (Polymer Laboratories) (DMTA) was used with the sample in the single cantilever bending mode at a frequency of 1 Hz and a strain of $\sqrt{2}$ corresponding to a nominal peak-to-peak displacement of 23 μm to measure stiffness. The heating rate was 2°C min^{-1}. The samples were typically ~28 mm long, 6 to 7 mm wide and 0.9 to 1.6 mm thick after conditioning to different moisture contents.

3. Results

3.1. Conditioning results and water-absorption isotherm

The moisture variation of each sample changed rapidly during the first 10 days, following which little changes were observed. The moisture contents for whole raisin, skin and flesh were 16.0, 15.9, and 17.2% (wwb), respectively, as measured by the Karl-Fischer method which was shown to provide good agreement with a vacuum oven treatment at 70°C. The water-absorption isotherm is shown in Fig. 2. The shape of this curve is reported to be characteristic of high sugar foods, such as raisin which contain ~70% sugars on wet basis [4]. At low water activity the moisture content was low. The high water content observed at high relative humidity was due to the dissolution of the sugars [4]. At zero water activity the moisture content was ~5% wwb, similar to a value of 8% reported by Lewicki and Wolf [7]. The moisture contents (wwb) of the residues were: AIR – 6%, WIR – 2%, and KOHIR – 2%.

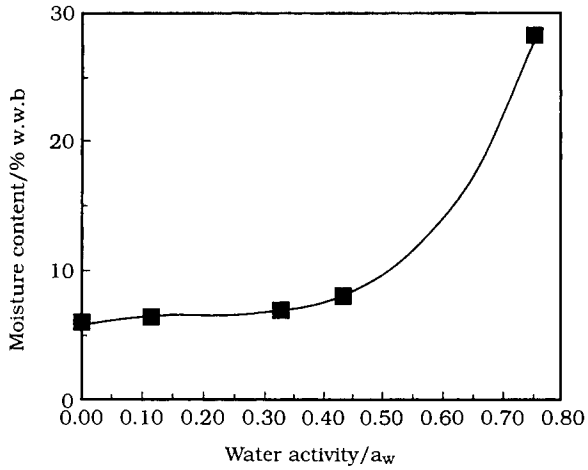

Fig. 2. Sorption isotherm of raisins.

3.2. AIR; carbohydrate composition

The yield of AIR (fresh weight) from whole raisins, skin and flesh was 6, 8, and 6%, respectively. The carbohydrate recovery of whole raisins, skin and flesh was 48, 28, and 45%, respectively; the remainder having comprised intracellular protein which will have co-precipitated with the AIR during extraction [17]. The carbohydrate compositions of whole, skin and flesh AIRs were similar; in addition to cellulosic glucose, they were rich in pectic polysaccharides as indicated by the levels of rhamnose, arabinose, galactose and uronic acid (UA). They also contained relatively low amounts of xylose and mannose.

Table 1
Sequential extraction of raisins AIR

Recovery (%)	Carbohydrate (mol%)								Total (μm/mg)
	Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA	
AIR (100)	2	0	7	4	3	5	36	43	477
WSP (3)	2	1	25	4	3	25	7	33	424
WIR (97)	2	1	9	6	3	4	31	45	494
CSP-1 (7)	2	1	4	1	0	3	1	91	853
CIR-1 (90)	3	1	10	7	3	5	43	29	442
CSP-2 (5)	3	1	7	1	0	3	2	84	170
CIR-2 (85)	2	1	9	7	3	4	40	33	472
NSP-1 (4)	3	1	14	1	0	5	1	76	546
NIR-1 (81)	2	1	9	8	4	5	49	23	442
NSP-2 (1)	4	1	18	1	0	7	3	67	398
NIR-2 (80)	1	1	8	8	4	4	49	24	442
KOHNS (5)	1	3	6	42	4	8	22	14	587
KOHNP (20)	4	0	25	4	2	6	10	50	126
KOHIR (55)	2	0	8	4	4	4	59	19	537

Rha – rhamnose; Fuc – fucose; Ara – arabinose; Xyl – xylose; Man – mannose; Gal – galactose; Glc – glucose; UA – uronic acid.
AIR – alcohol-insoluble residue; WSP – water-soluble polysaccharides; WIR – water-insoluble residue; CSP – CDTA-soluble polysaccharides; CIR – CDTA-insoluble residue; NSP – Na_2CO_3-soluble polysaccharides; NIR – Na_2CO_3-insoluble residue; KOHNS – KOH-soluble polysaccharides – neutral soluble; KOHNP – KOH-soluble polysaccharides – neutral precipitate; KOHIR – KOH-insoluble residue.

3.3. Sequential extraction of AIR

Cell-wall polymers were extracted sequentially from the whole raisin AIR using techniques which minimise polymer degradation [18]. Initial extraction in water solubilised polymers which were not cross-linked into the cell wall. Subsequently, CDTA released polymers cross-linked via Ca^{2+} only. The Na_2CO_3 treatments solubilised polymers by de-esterification and 0.5 M KOH extracted polymers which were probably retained in the cell wall by strong ester linkages [18].

The polymers extracted by water, CDTA and Na_2CO_3 were predominantly pectic in nature (Table 1). The water-soluble polymers contained higher levels of galactose and arabinose compared with the CDTA and Na_2CO_3-soluble polymers, indicating a higher level of branching. Most of the 0.5 M KOH-soluble polysaccharide precipitated on neutralisation (KOH-NP), and consisted of pectic polymers with a significant neutral component. In contrast, the polymers solubilised by 0.5 M KOH which remained soluble on neutralisation (KOH-NS), were rich in xylose, glucose and UA, indicating a mixture of xylan, xyloglucan and pectic polymers. Complexes of these polysaccharide species have been identified in cell walls of olive (*Olea europaea*; [25]). At each stage of extraction, the insoluble residue demonstrated a corresponding decrease in the sugars solubilised. The final residue was rich in cellulosic glucose, but also contained significant pectic material as indicated by the UA component.

3.4. Differential scanning calorimetry DSC

Results obtained for the whole raisins, skin and flesh conditioned to different moisture contents are shown in Fig. 3.

3.5. Hot press and DMTA

It was difficult to obtain reproducible DMTA scans from blocks of flesh or whole raisins, possibly because of the high sugar contents. Results from raisin skin blocks are shown in Fig. 4. The DMTA scans of the AIR, WIR and KOH residue samples fabricated with water added to the residues showed the bending modulus (E') to decrease with increasing temperature (Figs. 5–7). Data from tests on the samples fabricated directly from the residues were inhomogeneous and porous and gave lower moduli as expected.

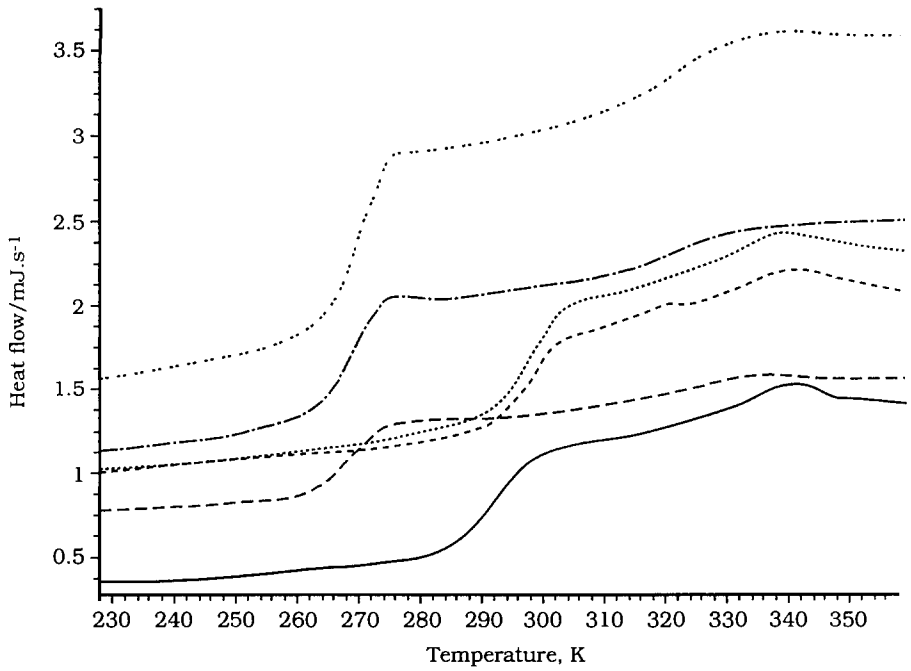

Fig. 3. DSC scans for raisins at moisture contents (in % wwb): whole (· · · ·) – 1.9 and (– · –) – 6.4; skin (– – –) – 1.6 and (— —) – 6.5; and flesh (———) – 2.8 and (- - - -) – 6.7.

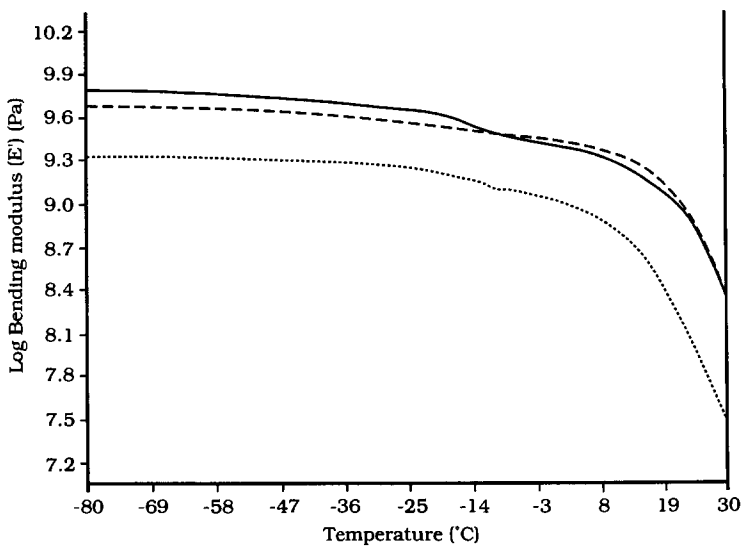

Fig. 4. DMTA E' of raisin skin block (– – –) – 3.7, (———) – 5.5, and (- - -) – 6.7% (wwb).

4. Discussion

Preliminary DSC scans on residues were featureless, indicating the dominance of the sugar component in the raisin DSC response. However, it was difficult to obtain reproducible DMTA scans from blocks of flesh or whole raisins, possibly because of the high sugar contents. Water has a plasticising effect on all systems

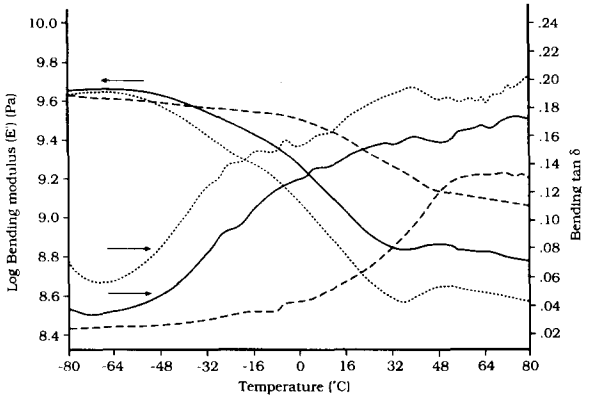

Fig. 5. DMTA E' and tan δ of AIR block at (– – –) – 5.5, (———) – 10.9, and (- - -) – 14.4% (wwb). Arrows indicate appropriate scale.

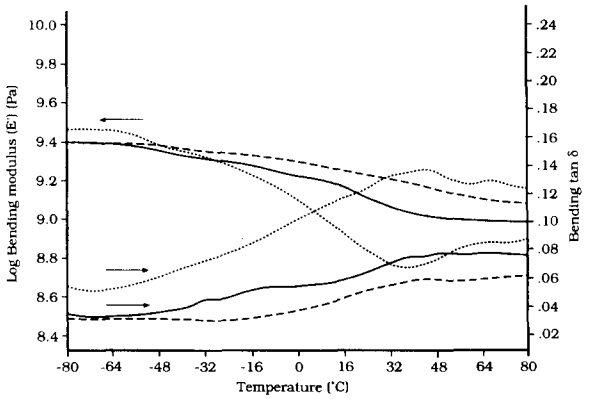

Fig. 6. DMTA E' and tan δ of WIR block at (– – –) – 3.0, (———) – 11.3, and (- - -) – 22.3% (wwb). Arrows indicate appropriate scale.

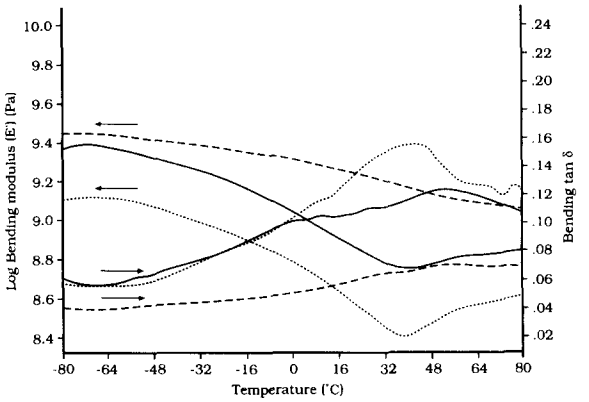

Fig. 7. DMTA E' and tan δ of KOHIR block at (– – –) – 1.6, (———) – 16.0, and (- - -) – 20.1% (wwb). Arrows indicate appropriate scale.

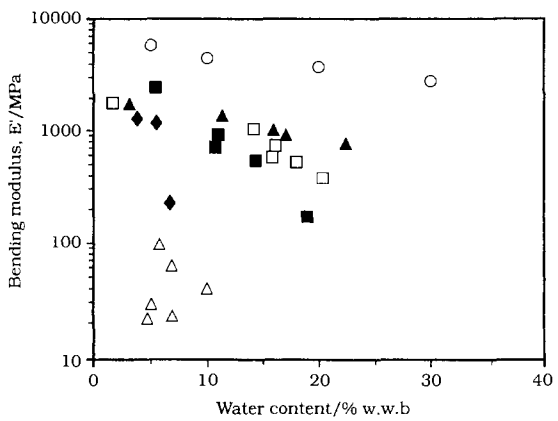

Fig. 8. E' at 20°C from DMTA measurements of: (△) – whole raisin, (◆) – raisin skin, (■) – AIR, (▲) – WIR, (□) – KOHIR, and (○) – wood [27] as a function of moisture content.

whether raisin or residue, consistent with previous observations on single components [13,16] and mixtures [15].

The modulus of the residues at low temperature is consistent with glassy values reported elsewhere [13,15,16]. Whereas the stiffness of raisins at 20°C decreased at a water content of 5–10% (wwb), the modulus of the residues, containing principally pectic polysaccharides and cellulose, decreased at higher water contents (Fig. 8). Sugar addition to starches [26] or cereal mixtures [15] has a similar effect. The removal of water-soluble non-crosslinked pectic polysaccharides between the AIR and the WIR accounted for a decrease in modulus, whereas the further removal of water-insoluble cross-linked pectins between the WIR and KOHIR had relatively little effect. The reasons for this are unclear but the lubricating effects of the water-soluble pectins may decrease the modulus. The modulus of wood is some five times higher than the WIR but showed similar dependence on moisture content.

All tan δ peaks were broad, indicating heterogeneity of the sample, although there was some evidence for two separate peaks as observed for wood [27] and amylopectin–gluten mixtures [28]. It is also interesting that Kalichevsky and Blanshard [29] noted the

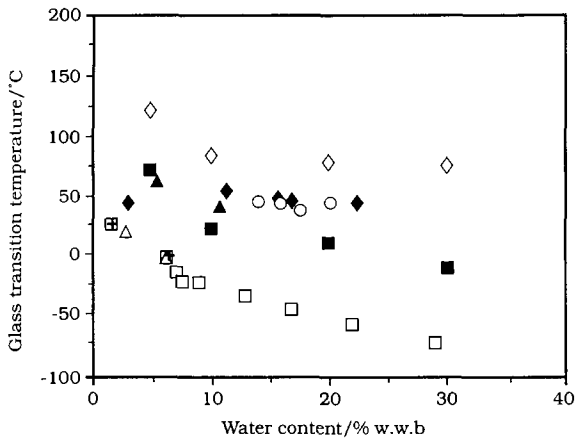

Fig. 9. T_g as a function of moisture content: (i) by DSC; whole raisin (△), raisin skin (◆), raisin flesh (+), grape (□) [9]; (ii) by DMTA: AIR (▲), WIR (◆), KOH (○), hemicellulose [27] (■), lignin [27] (◇).

difficulty in observing transitions by DSC for amylopectin–fructose mixtures for which the DMTA tan δ peak was broad. The DSC T_g data for raisins (Fig. 9) were consistent with results for grapes at higher moistures [9]. The T_g was higher for the residues and increased with the number of extractions. The difference between the raisin and the AIR was principally due to the sugar component, of order 70% of raisins [4], which plasticises the polymers as observed in other studies [13,15,26]. The T_g of wood components taken from [27] provide upper and lower bounds for the residue data of this study. Data for cellophane indicate a $T_g > 195$°C for moistures <0.5% [30].

5. Conclusions

The stiffness of raisin and cell-wall components decreased with increasing temperature and with increasing moisture content. The glass transition temperature, T_g, for cell-wall polymers was greater than that for raisin which, in turn, was comparable to that published for grape. The T_g of raisin and grape are dominated by their high sugar content. The results were consistent with plasticisation of raisin cell-wall polymers by sugar and water. The T_g of the KOH-insoluble residue from the raisin was comparable with that reported for wood. The T_g in cell-wall residues was broad as determined by DMTA and was difficult to detect by DSC. Conversely, the T_g was more easily measured for high sugar raisin material by DSC compared to DMTA.

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